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**PROCEEDINGS:
FLUE GAS DESULFURIZATION
SYMPOSIUM - 1973**



Office of Research and Development
National Environmental Research Center
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

PROCEEDINGS: FLUE GAS DESULFURIZATION SYMPOSIUM - 1973

May 14-17, 1973
Jung Hotel
New Orleans, Louisiana

E. L. Plyler, Chairman
M. A. Maxwell, Vice Chairman
Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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PREFACE

A Flue Gas Desulfurization Symposium was held May 14-17, 1973, in the Jung Hotel, New Orleans, Louisiana, under the sponsorship of the Environmental Protection Agency, Office of Research and Development, Control Systems Laboratory. The primary purpose of the symposium was to present the current status of "throwaway" and "regenerable" flue gas desulfurization processes as applied to controlling SO_x emissions from full-scale facilities.

The symposium included sessions on technology and application of first generation processes such as lime/limestone scrubbing, magnesia scrubbing, catalytic oxidation and sodium sulfite scrubbing as well as a session on second generation or advanced processes. In addition, a panel discussion was held concerning the disposal and uses of by-products from flue gas desulfurization processes.

Over 430 representatives of government and industry were in attendance during the 4-day symposium.

These proceedings have been reviewed by the Environmental Protection Agency and approved for publication. Except for minor editing for consistency of presentation, the contents of this report are as received from the authors. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. All papers presented (as well as transcriptions of the panel discussions and the symposium summary) are included in these proceedings.

Copies of this report are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations -- as supplies permit -- from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

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HEALTH RATIONALE
FOR STRICT CONTROL OF SULFUR OXIDE EMISSIONS

by

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Man has been subject to air pollution since his primordial ancestor lit the first fire. It was not, however, until people became crowded together in cities that pollution was more than a family problem from the hearth. Today with the phenomenal growth of both the population and use of power in the technologically advanced countries, pollution has reached such magnitude that it threatens the health and well being of the population on a global scale.

Even though there had been occasional speculation and complaints about the health effects of air pollution since the days of Edward I, it was not until the occurrence of certain air pollution episodes in the Valley of the Meuse, in London and in Donora, Pennsylvania that people finally came to realize that it was a threat to human health. These episodes made it obvious that under certain conditions air pollution could kill.

Despite the drama of the episodes, the greatest impact of air pollutants on human health results from day to day exposure under unexceptional conditions.

Environmental pollutants can effect the health of individuals or communities over a broad range of biological responses as shown in Figure 1. At any point in time more severe effects such as death will be manifested in relatively small proportions of the population. Mortality studies have shown that elevated levels of SO_2 contribute to approximately 1 percent of excess deaths.

Illness from sulfur oxides may be either short-lived (acute) or relatively permanent and irreversible (chronic).

Bronchitis is an example of a long-term or chronic effect. Investigators in Japan, Britain, and the United States have demonstrated excess bronchitis morbidity in areas with moderately elevated SO_2 exposure. A significant and consistent excess bronchitis morbidity occurred over an exposure range of 100 to 350 $\mu\text{g}/\text{m}^3$ SO_2 with associated total suspended particulate levels of 66 to 365 $\mu\text{g}/\text{m}^3$. The following slides show results from several studies conducted by the Environmental Protection Agency in different areas of the United States.

Table 1 demonstrates that nonsmokers as well as smokers from high exposure communities of four areas consistently reported more chronic bronchitis than their smoking counterparts in low exposure neighborhoods.

As shown in the last row of Table 2, the contribution of air pollution towards the prevalence of chronic bronchitis is one-fifth to equal that of cigarette smoking among males in the four areas.

A remarkably consistent excess of acute respiratory disease ranging from 14 to 64 percent was found in children exposed to SO_2 levels of 50 to 275 $\mu\text{g}/\text{m}^3$. These findings pertained largely to children who had lived in the polluted areas for three years or longer suggesting a chronic alteration in their defense mechanisms.

Figure 2 shows excess croup frequency among children from high pollution neighborhoods in the Salt Lake Basin who had lived in that neighborhood for three or more years. Similar findings in children in Idaho-Montana are presented in Figure 3. Aggravation of symptoms

in diseased subjects such as asthmatics and cardiopulmonary subjects have been repeatedly demonstrated at daily SO_2 levels well below the indicated threshold for excess mortality. However, some studies have demonstrated illness aggravation to be most strongly related to suspended sulfates. Figure 4 reveals that at the same total suspended particulate level, asthma attack rates were higher on days with high sulfate concentrations. These data are from a study conducted by EPA in the Salt Lake Basin.

As shown in Figure 5, when symptom aggravation in heart and lung patients in New York were computed against exposure within a defined temperature, daily levels of suspended sulfates more so than SO_2 or total suspended particulates were closely associated with these attacks of illness. The threshold for the adverse effect occurred at sulfate concentrations of $9.2 \mu\text{g}/\text{m}^3$, a level below the average daily sulfate concentrations of most northeastern cities.

These findings confirm results from animal studies in which metallic sulfates were shown to exert adverse biological effects at concentrations below those of SO_2 . These results are physiologically coherent since SO_2 alone tends to be absorbed high in the respiratory tract while sulfates can be delivered deep into the lung. It is important for environmental scientists to determine the relationship between SO_2 and suspended sulfates. Although SO_2 serves as a precursor to the formation of sulfates, the relationship is nonlinear; there is reason to believe that SO_2 reacts in a complex manner with particulate matter. Certain

metal particles, water vapor and oxidizing chemicals in the atmosphere may promote the formation of more potent respiratory irritant sulfate aerosols.

The section of the biological response spectrum entitled "functional changes preceding disease" can be exemplified by pulmonary function tests. A diminution in the pulmonary function test indicates some resistance in air flow to the lungs and serves as a sentinel that a disease process may ensue. Studies have shown lung function of school children living in areas of moderate SO_2 and TSP pollution was impaired compared with children living in low exposure communities. In a study conducted in Japan, lung function of school children responded rapidly to seasonal changes in air pollution. Function became worse in polluted seasons and during less polluted months returned to levels of children in low exposure areas. These data suggest that the lung function may be reversible and improved air quality will enhance lung function in children.

Experimental laboratory studies on humans and on lower animals exposed to artificially produced SO_2 and suspended sulfates have shown subtle physiologic changes, the significance of which is still obscure. Russian investigators have demonstrated neurobehavioral effects of sulfur oxides including changes in the electroencephalogram. Histopathological studies in animals showed marked histopathological changes in nasal epithelium at concentrations of SO_2 which had no direct effect deeper in the lungs.

There are no existing data on the relationship between sulfur oxides and pollutant burdens.

Table 3 summarizes the levels of SO_2 and suspended sulfates associated with biological responses over the entire spectrum. As shown in the table, adverse health consequences ranging from functional changes preceding disease to death itself have been associated with SO_2 exposures in the range of 80 to 120 $\mu\text{g}/\text{m}^3$ for one or more days. Even in communities where national primary standards for SO_2 have been achieved, daily sulfate levels in the range of 7 to 14 $\mu\text{g}/\text{m}^3$ have been associated with aggravation of symptoms in particularly vulnerable population groups such as asthmatics and cardiopulmonary subjects. Although pressure is currently being exerted to relax our existing national air pollution standards because of the energy crisis, we must bear in mind that such action could be costly in terms of safeguarding the nation's health. We must pursue a prudent course whereby the energy needs of the country are met in a manner which poses a minimum threat to the public health.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Human Studies Laboratory of the U. S. Environmental Protection Agency for providing from their research much of the data used in the figures and tables.

Table 1. RATIOS OF CHRONIC RESPIRATORY DISEASE AREA PREVALENCE RATIOS
(MALES) BY GEOGRAPHIC AREA AND BY CATEGORIES
OF AIR POLLUTION AND SMOKING

Exposure	CRD prevalence ratios (males)			
	Utah	Idaho-Montana	New York	Chicago
Low				
Nonsmoker	1.0 (3.0) ^a	1.0 (1.25)	1.0 (4.6)	1.0 (4.0)
Smoker	6.5	13.6	3.0	3.8
High				
Nonsmoker	2.3	2.8	3.4	1.3
Smoker	8.9	14.7	4.7	4.5

^aBase period prevalence rate per 100 people in parentheses.

Table 2. RATIOS OF CHRONIC RESPIRATORY DISEASE AREA PREVALENCE RATIOS
(MALES) BY POLLUTION AND SMOKING SOURCES OF RISK

Exposure	CRD relative prevalence (males)			
	Utah	Idaho-Montana	New York	Chicago
Pollution ^a	2.27	2.78	3.45	1.33
Smoking ^b	6.53	13.64	3.02	3.80
<u>Pollution</u> <u>Smoking</u>	$\frac{1}{3}$	$\frac{1}{5}$	$\frac{1}{1}$	$\frac{1}{3}$

^aNonsmokers of high exposure/nonsmokers of low exposure area.

^bSmokers of low exposure area/nonsmokers of same area.

Table 3. EFFECTS OF SULFUR OXIDES ON HEALTH
BY LEVEL OF RESPONSE

Level of response	SO ₂ , μg/m ³ (ppm)	Sulfates, μg/m ³
Death	500-1000 (0.20-0.40) ^a	No data
Illness (acute and chronic)	80-275 (0.03-0.11) ^a	7-14 ^a
Functional changes preceding disease	90-120 (0.035-0.45) ^b	9-11 ^a
Changes of uncertain significance	500-1000 (0.20-0.40) ^c	250 ^c
Pollutant burdens	No data	No data

^a24 hour average.

^bAnnual average.

^cExperimental studies with artificial SO₂ or other sulfur oxides.

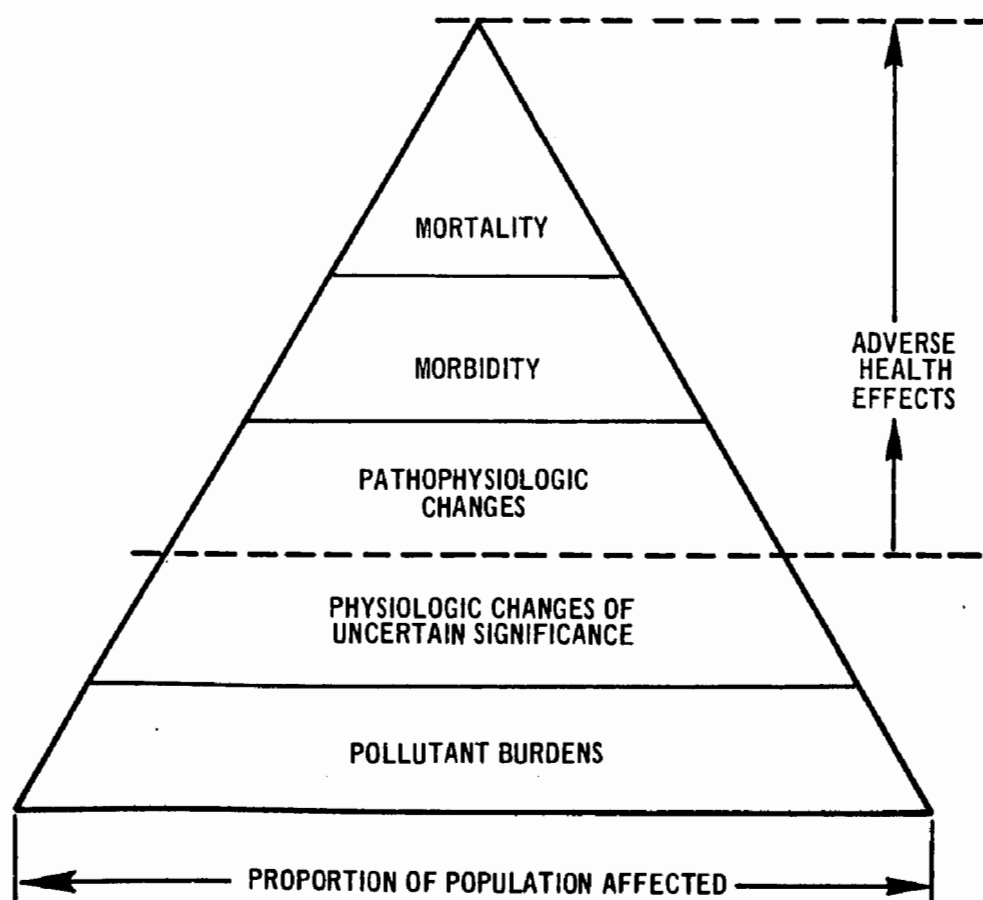


Figure 1. Spectrum of biological response to pollutant exposure.¹

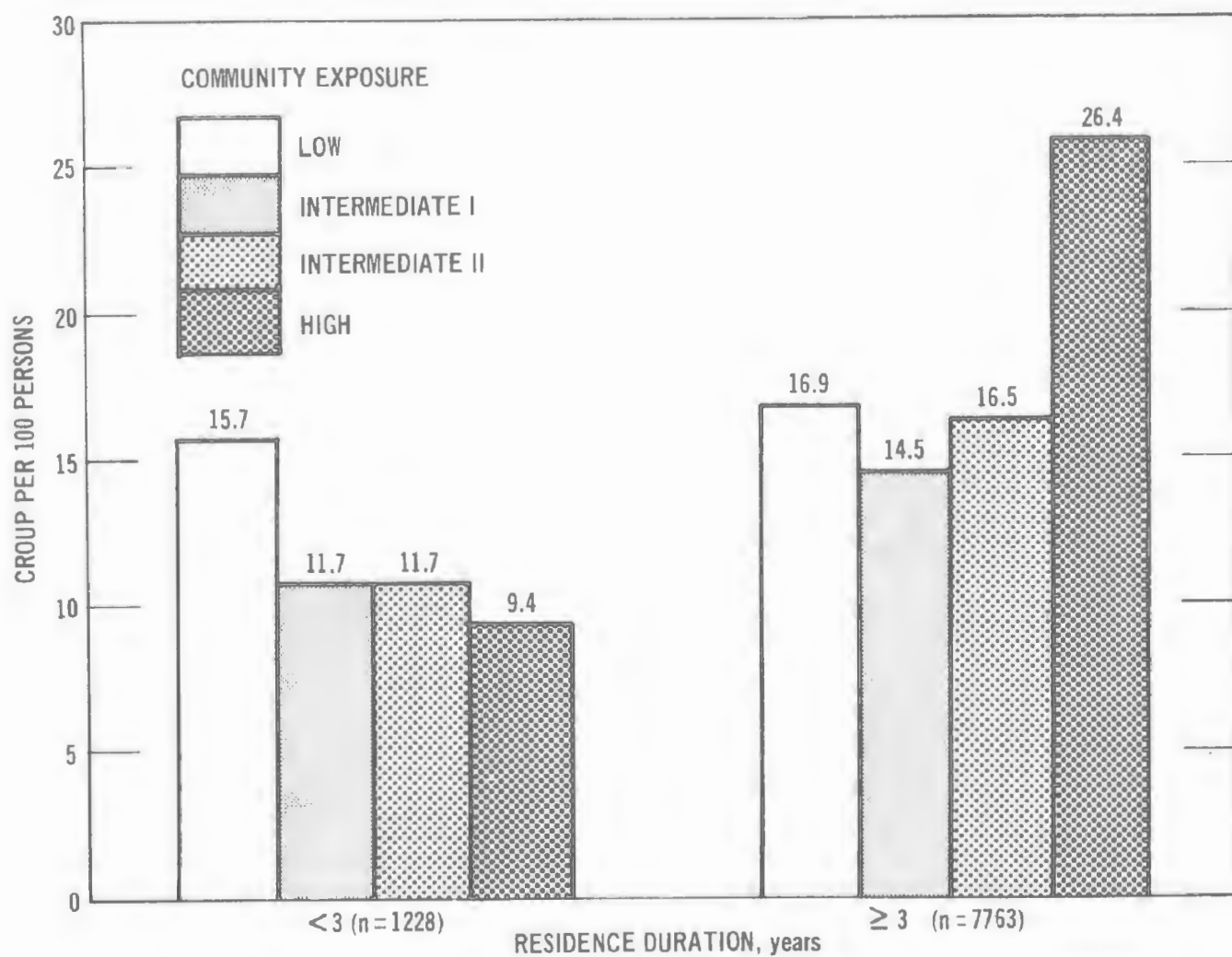


Figure 2. Salt Lake Basin: incidence rates for croup in children by residence duration and sulfur oxides exposure.²

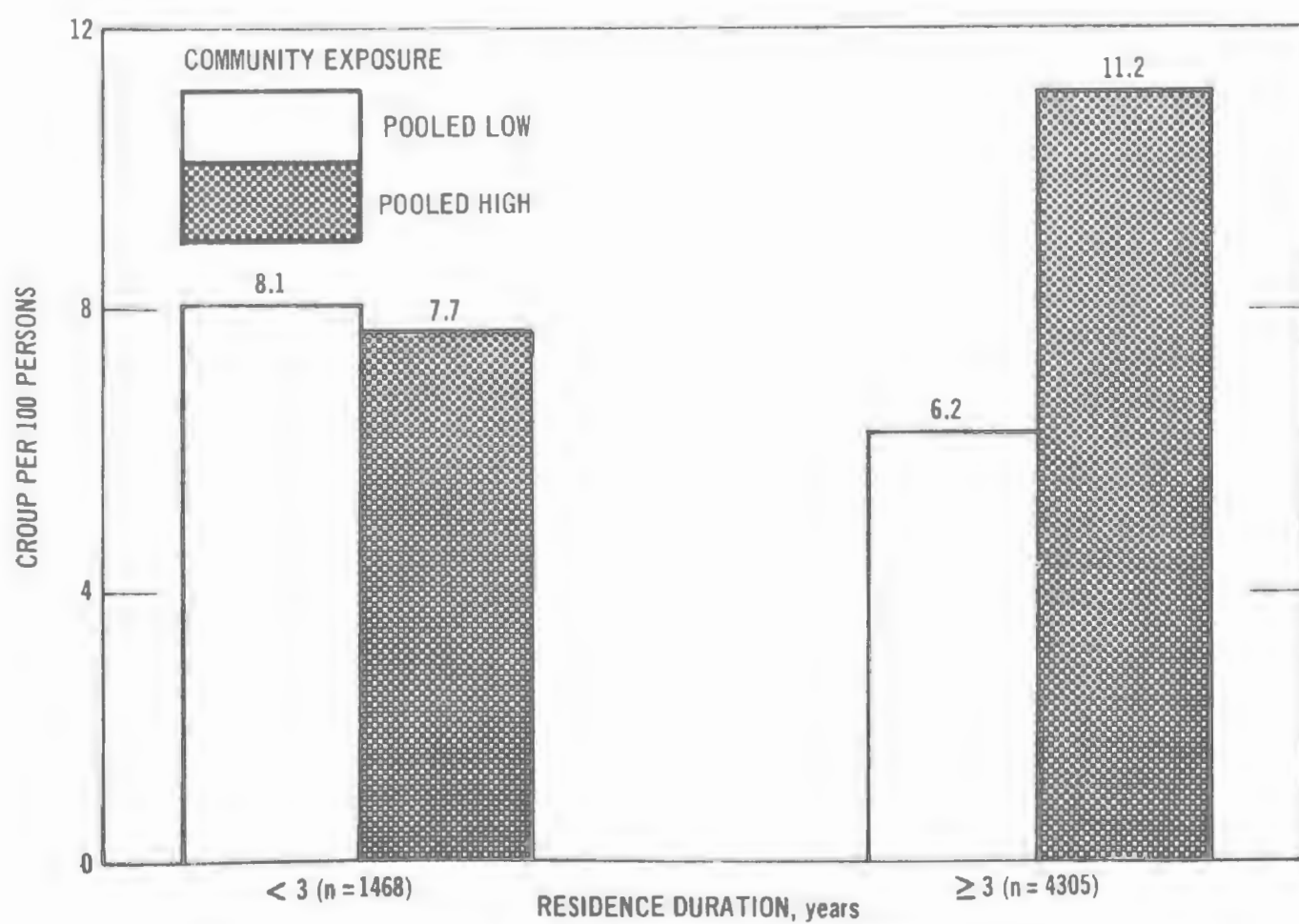


Figure 3. Idaho-Montana: Incidence rates for croup in children by residence duration and sulfur oxides exposure.²

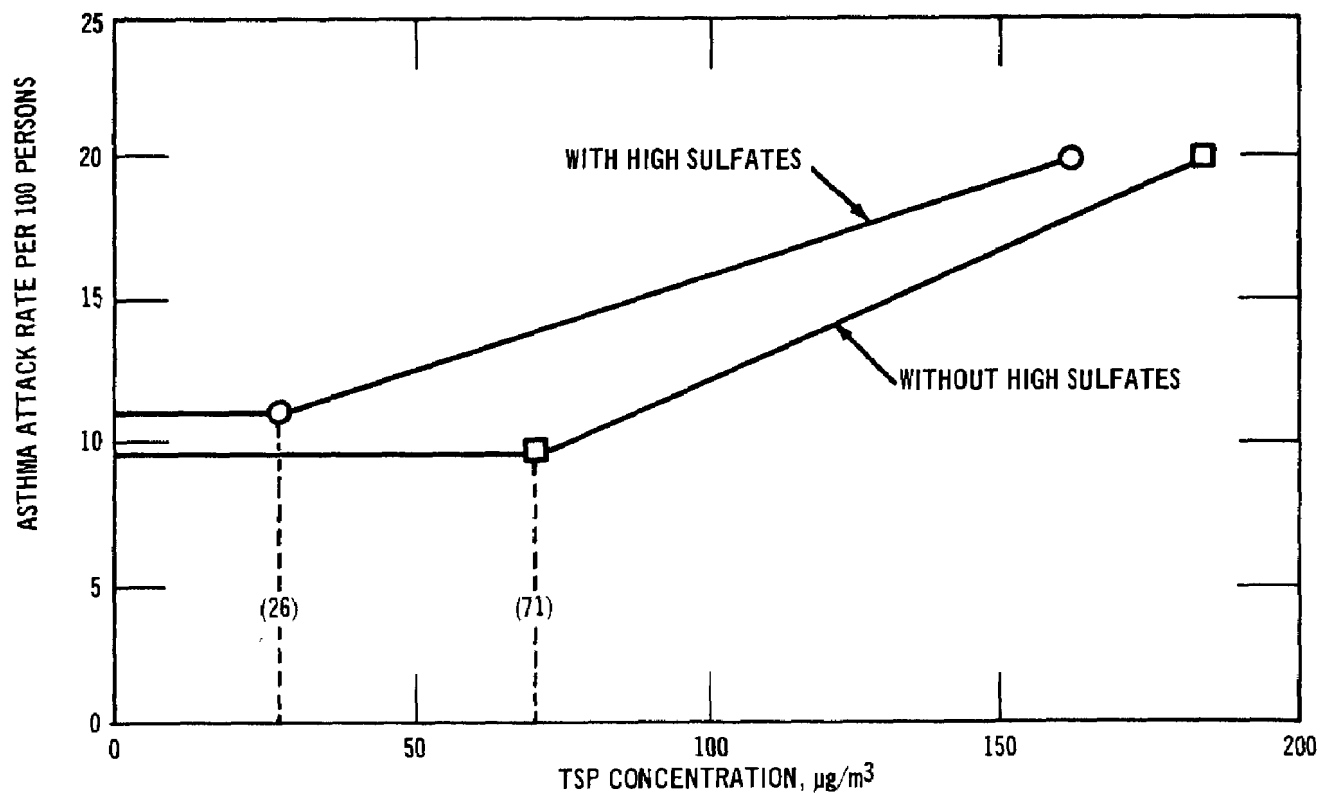


Figure 4. Salt Lake Basin: asthma attack rates by total suspended particulate level and by category of sulfate content.² (Minimum temperature $\geq 51^\circ\text{F}$.)

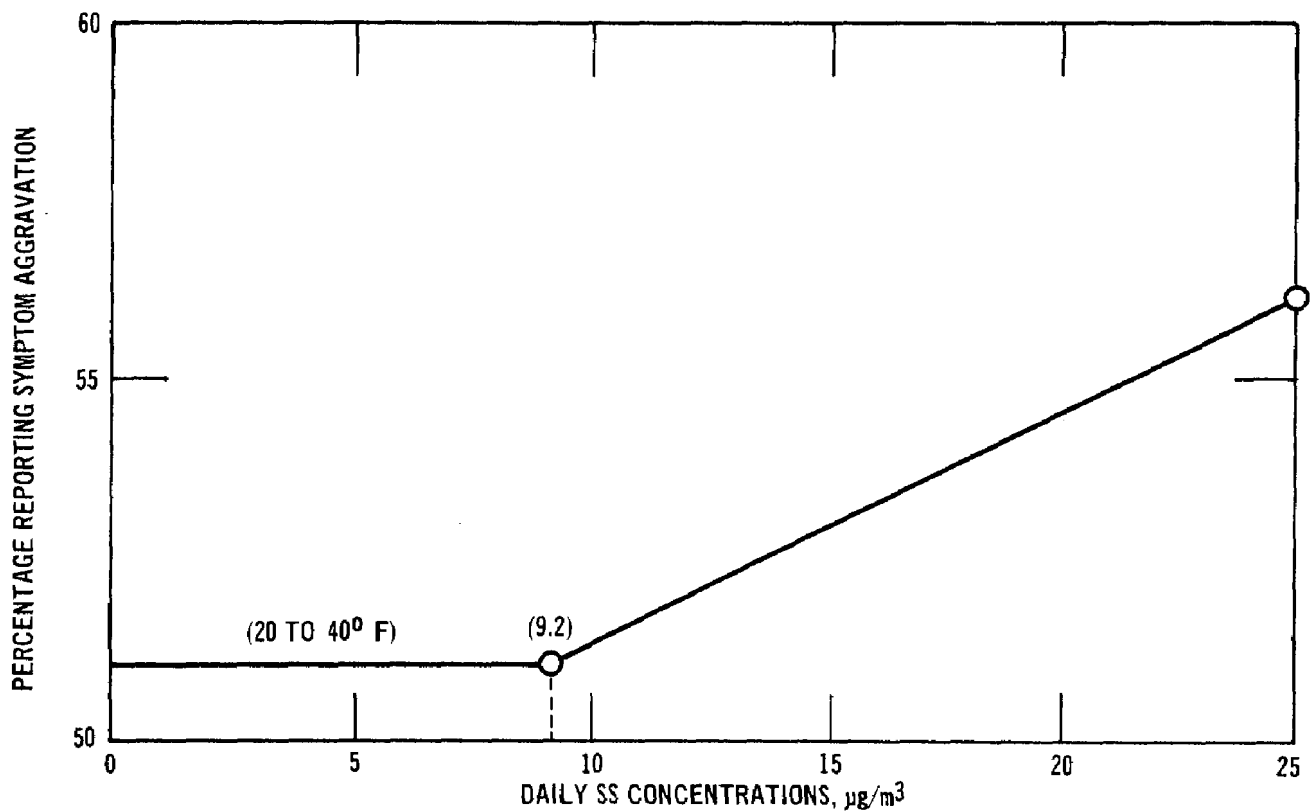


Figure 5. New York: Percentage of cardiopulmonary subjects reporting symptom aggravation by daily suspended sulfate (SS) concentrations.²

TECHNOLOGICAL ALTERNATIVES
TO FLUE GAS DESULFURIZATION

by

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TECHNOLOGICAL ALTERNATIVES
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Introduction

The single most important factor today in controlling air pollution from stationary industrial sources is the reduction in emissions of sulfur oxides. The omnipresent sulfur in domestic coals and in both domestic and imported oils poses a serious challenge to the efforts of Federal, state, and local environmental agencies to significantly diminish the release of over 30 million tons of sulfur oxides into the atmosphere each year.

Natural gas is, of course, the cleanest fuel but it is already in short supply and, even with accelerated domestic development and importation of LNG, demand will undoubtedly outstrip supply. Also new supplies are likely to be bid away from industrial and utility uses for residential and commercial uses. Domestic oil production has leveled out and it is expected that much of our future oil needs will be met by imports of foreign, mostly Mid-Eastern, oils. But these oils generally contain sulfur in concentrations which will, in many cases, preclude use of the residuum without some measure of hydrodesulfurization.

Desulfurization of imported oil certainly represents one strategy for meeting the need for low sulfur fuels. But such a solution would spawn a set of new problems. There are the fundamental problems of national and economic security arising from reliance on large imports of a vital fuel. Since new refineries equipped for desulfurization of residual fuel would be required, siting and environmental problems of supertanker ports and refineries emerge. If such facilities are located offshore, there is further aggravation of the balance-of-payments problem. However, importation of crude oil for desulfurization in this country and of desulfurized residual fuel will be important in meeting our clean fuel needs. The technology for

desulfurization of oil is reasonably well established so it will not be covered in this analysis of technological options.

Coal, our most abundant fossil fuel resource, presents the serious environmental challenge. As the traditional fuel used in utility and industrial power plants in large sections of the nation, particularly in the industrial Midwest, coal is the source of a significant fraction of the sulfur oxides emitted in those areas. Nearly all of the coal in the Central coal region has sulfur content exceeding 3 percent and much of the coal in the Appalachian coal region has sulfur content in the 2 to 3 percent range. In the eastern half of the country, only Central Appalachia* has significant deposits of low sulfur coal. And, unfortunately, the terrain in this area is very mountainous so the all-too-common ravages of surface mining--landslides, slumps, massive erosion, and acid mine drainage--are even more severe.

Most of the coals in the vast sub-bituminous and lignite fields of the West have lower sulfur content but their use to solve air pollution problems in the Midwest appears to be limited to the western fringe of the industrial region (Minneapolis, Chicago, Kansas City) because of the high cost of transportation from Montana and Wyoming. Although Western coals are already being used locally, limited water availability and problems with re-establishing vegetation on mined lands are potential constraints.

Technology which removes the sulfur from the coal before combustion or from the gases during or after combustion is therefore essential if air quality is to be improved and if coal production is not to be displaced by a flood of imported oil. Maintenance of a viable coal industry is also essential if part of our clean fuel needs are to be met in the 1980's with synthetic fuels produced from coal.

*Southern West Virginia, western Virginia, eastern Kentucky, and northeastern Tennessee

One technology for reducing sulfur oxide emissions from coal-burning plants is the subject of this symposium--flue gas desulfurization or stack gas cleaning. The past year has seen both significant progress in the development of commercial stack gas control systems and a rising chorus of concerns about the application of such systems. Questions about the reliability, costs, and associated environmental effects of stack gas control systems have generated a more fundamental question: Because of the current and potential problems with stack gas cleaning devices, and the promise of precombustion coal treatment processes, shouldn't application of sulfur oxide abatement technologies be delayed until the new coal cleaning processes become available? Even if the premises to this question are conceded, the answer is not a simple yes or no; rather the answer may be both no, in the near-term, and yes, in the intermediate-term.

This paper will attempt to place into perspective the current status of stack gas cleaning systems relative to the status of coal cleaning processes. It will review the status of the coal precombustion cleaning processes, estimates of their costs, and forecasts of their application. The focus will be on liquefaction and gasification processes which will convert high sulfur coals into usable clean fuels in either liquid or gaseous form.

Status of Coal Liquefaction Processes

One approach to precombustion cleaning of coal is to liquefy the coal and to remove the ash and sulfur from the liquid phase. There has been considerable experimental work over the past decade to produce a synthetic crude oil which, in turn, could be used in the manufacture of gasoline. Conversion of coal to a liquid fuel requires the addition of hydrogen, but considerably less hydrogen is required to produce a power plant fuel than is required to produce feedstock for a gasoline plant. In fact, a liquid product is not required for power plant application, although a liquid phase is required for the hydrogenation and separation of ash and sulfur.

Solvent Refined Coal

One of the most advanced process for producing an ashless, low-sulfur power plant fuel is known as solvent refining [1,2,3]. In this process, pulverized coal is first

mixed with a heavy aromatic solvent (derived from coal) and then passed through a reactor under a hydrogen atmosphere at about 1000 psi and 800°F. Small quantities of hydrocarbon gases, hydrogen sulfide, and light liquids are formed along with a heavy organic material called Solvent Refined Coal (SRC). The gases are separated and treated; the solution is filtered to remove the ash and some undissolved coal; the solvent is recovered through flash evaporation. A schematic diagram of the SRC process is shown in Figure 1.

The SRC is a black pitch-like substance with a melting point of about 350°F containing about 0.1 percent ash. Its heating value is about 16,000 Btu's per pound regardless of the quality of the coal feedstock. Most of the inorganic sulfur is removed in this process and as high as 60-75 percent of the organic sulfur. For instance, it appears possible to convert Illinois coal with 3.5 percent sulfur to SRC with 0.6 percent sulfur. With the higher heat content, SRC with 0.6 percent sulfur would release about 0.4 pounds of sulfur per million Btu.

A 50 ton/day pilot plant is now being constructed near Tacoma, Washington by Pittsburgh and Midway Coal Mining Company, one of the developers of the SRC process [4,5,6,]. This project is being sponsored by the Office of Coal Research. Scheduled for completion in early 1974, this plant should provide the engineering data necessary to build a commercial plant. A smaller pilot plant, 6 ton/day, is being constructed under the sponsorship of the Southern Company and the Edison Electric Institute and is scheduled for completion in late 1973. This plant, which will use a solvent refining process developed by Consolidated Coal Company, will be built near Wilsonville, Alabama [4,5].

H-Coal Process

The H-Coal process, developed by Hydrocarbon Research, Inc. (HRI), introduces a coal slurry into a ebullating bed reactor where, in the presence of a catalyst (cobalt molybdate), hydrogenation occurs [2,3,5]. The upward flow of the feed--which consists of crushed coal mixed with recycle oil and hydrogen--maintains the catalyst in a state of rapid motion and permits the continuous passage of unconverted coal and ash from the reactor. The H-Coal reactor operates at 2700 psi and 850°F. The problems of introducing feed into the pressurized reactor vessel and separating the unconverted coal and ash from the synthetic

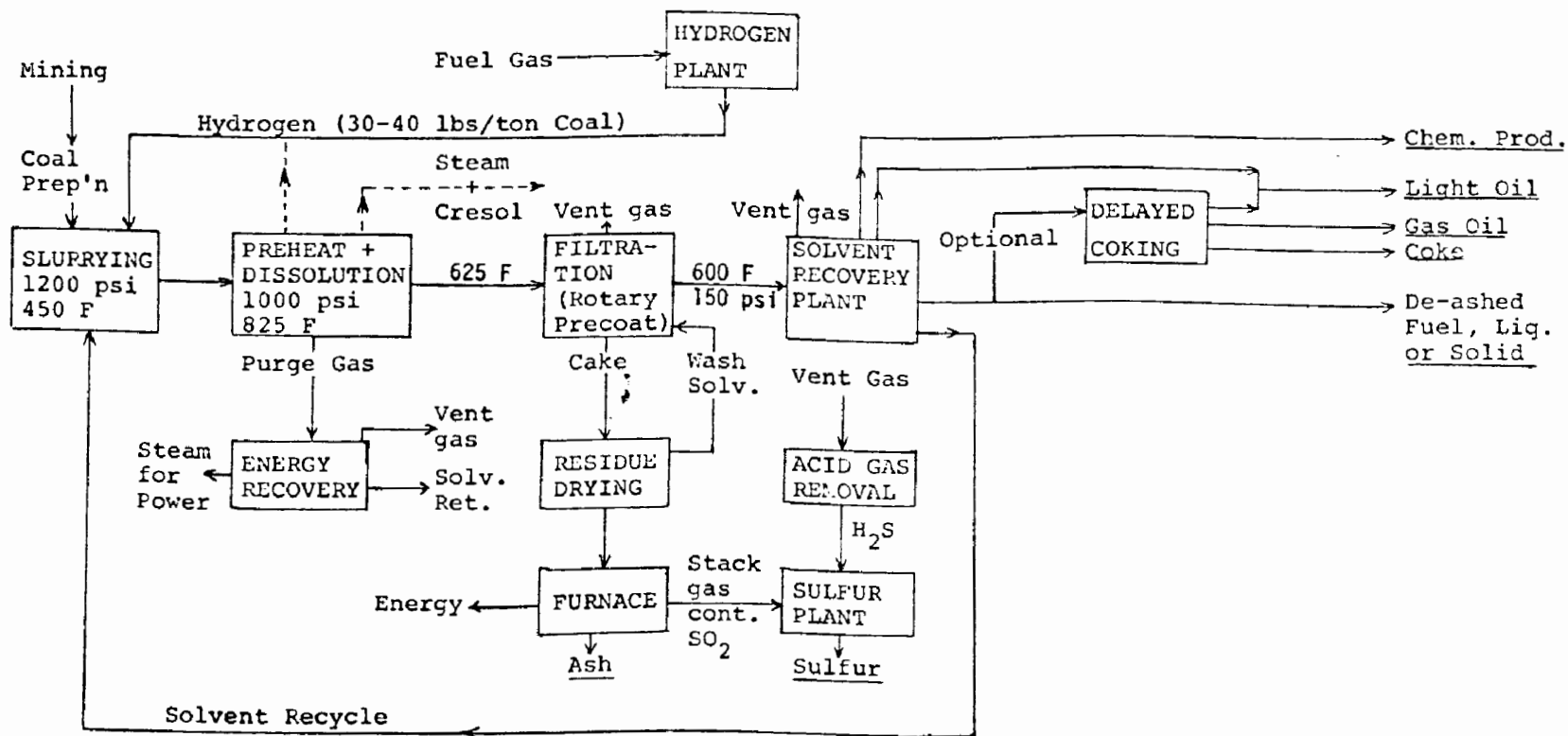


FIGURE 1. Solvent Refined Coal (SRC) Process

oil await final solution. HRI has stated that the processing conditions can be varied to obtain 1.5 to 1.0 percent sulfur without solids removal, 0.5 percent sulfur with ash removal and increased conversion severity, and 0.25 percent sulfur with secondary coal conversion [3]. The H-Coal process has been tested in a 2.5 ton/day pilot plant with high conversion and good catalyst recovery and without serious difficulties [1,5]. HRI has stated interest in building a 250 ton/day demonstration plant, but the financing for such a plant has not been secured [5]. A schematic diagram is shown in Figure 2.

COED Process

Another process which produces a liquid product from coal is the COED (Coal Oil Energy Development) process [2,3,4]. Developed by Food Machinery Corporation (FMC) under sponsorship of the Office of Coal Research, this multiproduct process uses fluidized-bed pyrolysis. A synthetic crude oil, a gas stream, and a char product are produced. Powdered coal is subjected to increased temperatures in four successive beds. Volatile liquid products are withdrawn at every stage and not subjected to the higher temperature where further cracking would occur. The liquid fuels yield is lower than for coal hydrogenation. Further, the sulfur content of the product char may be too high to meet air quality standards in many areas, without further desulfurization. The COED process can be modified somewhat to yield different product mixes, i.e., the hydrogen-rich gas stream can be used to convert more of the char to fuel oil. Pilot plant experience has indicated yield of about 1.2 barrels of fuel oil and 9000 standard cubic feet of gas per ton of coal. FMC has been operating a 36 ton/day pilot plant near Princeton, New Jersey, for several years to obtain process information on various types of coal [4]. No plans have been announced for a scale-up to a demonstration plant.

Coal Hydrodesulfurization

Another promising coal liquefaction process being developed by the Bureau of Mines (BOM) promotes hydrodesulfurization of the coal slurry by turbulent flow with hydrogen through a fixed bed of catalyst [1,3,7,8]. The coal, suspended in coal - derived product oil, is pumped with hydrogen through a packed bed of pelletized cobalt molybdate alumina. Turbulent flow through the bed prevents plugging (as the coal passes through its sticky phase prior to becoming liquid), keeps the catalyst surface clean for

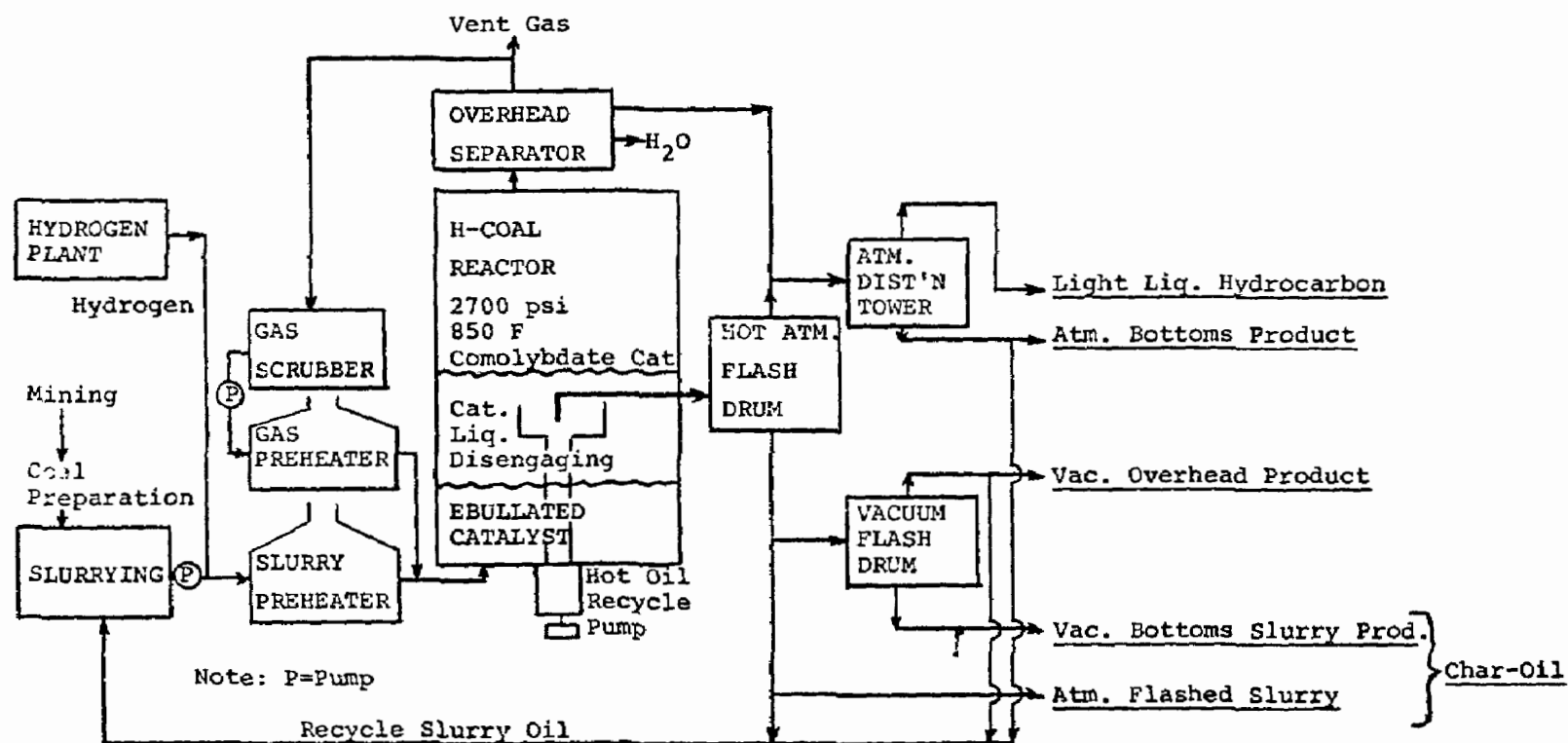


FIGURE 2. H-Coal Process

good contact, and promotes transport of the hydrogen into the slurry. The reactor operates at 2000 psi and 850°F. The goal of this design is to do just enough hydrogenation to remove the sulfur with the liquefaction of the coal essentially being a side effect, therefore use of expensive hydrogen is minimized. Sulfur is removed as H₂S which can be easily converted in elemental sulfur. Experiments have been conducted with a 0.1 ton/day reactor on 5 different coals. For example, a Kentucky coal having 4.6 percent sulfur and 16.0 percent ash was converted into a synthetic fuel oil having only 0.19 percent sulfur and 1 percent ash. BOM is now scaling up the size of the operation and is designing a 5 ton/day pilot plant.

Status of Coal Gasification Processes

One promising approach to precombustion cleaning of coal is gasification. Because of growing shortages in natural gas supply, interest is running very high in gasification processes which can produce a pipeline quality gas, i.e., a synthetic gas composed primarily of methane with heat content approaching 1000 Btu per standard cubic feet. More recently, interest in producing a low-Btu content gas as a clean-burning fuel for power plants has risen sharply. Because high-Btu synthetic gas would be too expensive, e.g., \$1.00-1.50 per million Btu, for power plant use, this review will concentrate on the direct use of low-Btu synthetic gas in power plants. However, in order to assess the status of the several gasification technologies, it will be necessary to review high-Btu gasification research.

For the sake of simplicity, coal gasification to low-Btu gas can be divided into two categories: present generation gasifiers (PGG) and advanced gasifiers (AG). Present generation gasifiers include coal gasification processes--Lurgi, Koppers-Totzek and Wellman Galusha--that are now commercially available. In this country, industrial interest is focused on the Lurgi process. Plans for construction of full-scale commercial coal gasification plants for production of pipeline quality gas have been announced by two companies. In addition, one utility has initiated construction of a combined-cycle (gas turbine-steam turbine) demonstration plant using a Lurgi gasifier to produce the gas.

As mentioned above, research on the production of pipeline quality gas from coal has been receiving considerable governmental and industrial support. A number of advanced gasification processes are under development and a cooperative government-industry effort, comprised primarily of the Interior Department and the American Gas Association, is currently evaluating four processes. Pilot plants are in operation for two of the processes and under construction for another two.

With utility interest in low-Btu gas for combined-cycle plants growing, several study efforts have been initiated to evaluate the possibility of modifying the advanced gasifiers now under development to produce low-Btu gas. Since low-Btu gas is produced in the initial stages of all of the advanced gasifiers (prior to methanation of the hydrogen and carbon monoxide), the proposed modifications appear to have merit.

Present Generation Gasifiers (PGG)

Coal gasification processes involve reacting coal, steam, and oxygen under heat and pressure in a specially designed reactor to form a synthesis gas of hydrogen, carbon monoxide, carbon dioxide, sulfur compounds and varying amounts of methane [1,2,3,9,10].

The Koppers-Totzek and Wellman Galusha processes operate at atmospheric pressure, produce no methane directly, and require a rather high oxygen consumption [1,4]. The Lurgi gasifier is the only high pressure gasifier (ca.300-450 psi) commercially available [1,10].

The Lurgi Gasification Process. In the Lurgi process, the synthesis reaction takes place in a water-jacketed vessel [2,11]. The crushed coal (with the fines briquetted with process tar) is fed through a coal lock chamber downward into the gasifier. Steam and oxygen are introduced at the bottom of the gasifier, heated by the high temperature ash at the bottom, and flow upward through the reaction zone. The crude gas and unreacted steam are quenched upon leaving the gasifier to cool and remove dust, tars, ammonia, and phenols. A cross-sectional view of the Lurgi gasifier is shown in Figure 3.

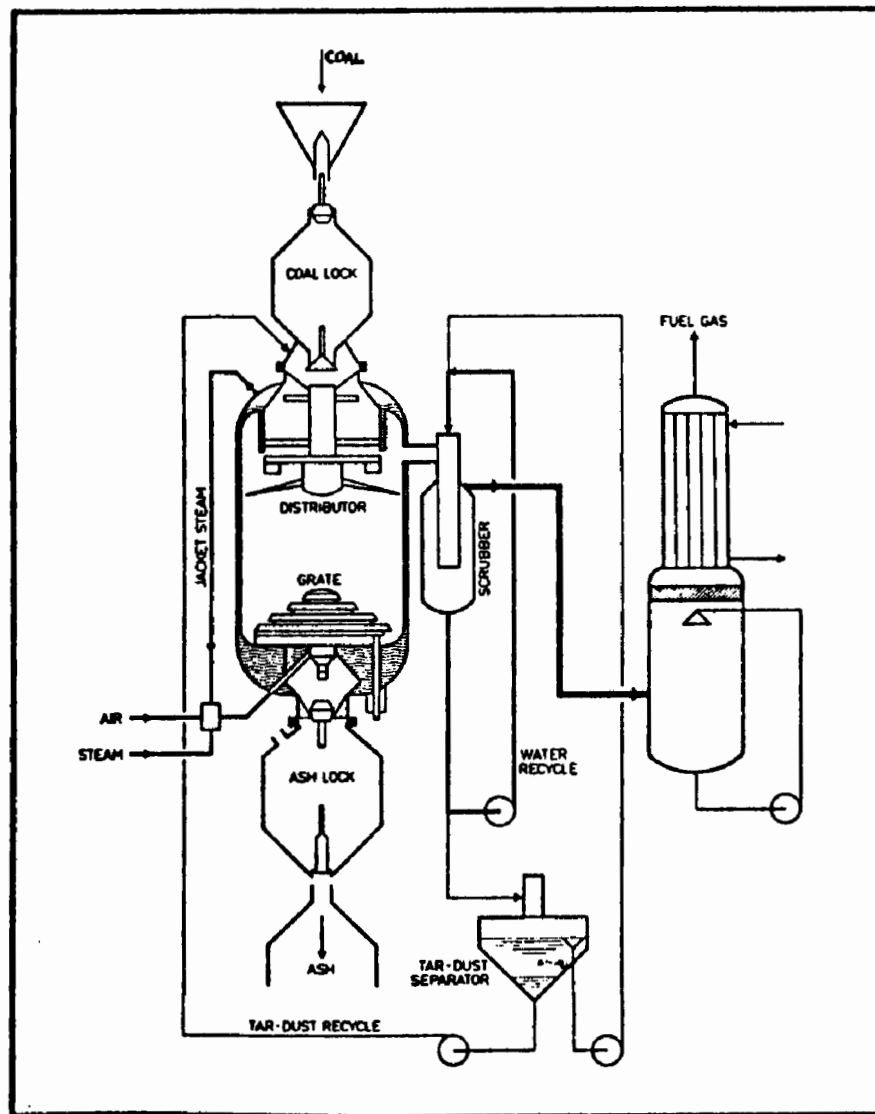


FIGURE 3. Lurgi Gasification Process

For the production of pipeline quality gas, relatively pure (>98 percent) oxygen must be supplied to the gasifier, since any nitrogen dilutes the pipeline gas [11]. The crude gas leaving the gasifier at 700 to 900°F will, in this case, have a heat content, above 400 Btu per cubic foot. For pipeline quality gas, the crude gas is subjected, in turn, to a catalytic shift conversion process to establish the H₂-to-CO ratio required for the subsequent methanation step, a physical absorption process to remove sulfur compounds and carbon dioxide, and a methane synthesis process which catalytically combines carbon monoxide and hydrogen to form methane and water. The resulting gas, when compressed and dried, has a heat content of 950 to 970 Btu per cubic foot [11].

On the other hand, for the production of low-Btu gas, air may be fed to the gasifier, yielding a gas with a heat content of less than 200 Btu per cubic foot [1,2,10,12,13]. Before using in either a conventional gas-fired boiler or in a combined-cycle power plant, the sulfur compounds (largely H₂S with some COS) must be removed. Although there are a variety of available gas cleaning processes (Lurgi's proprietary Rectisol process which uses low temperature methanol, Stretford process, potassium carbonate scrubbing, etc.), all require cooling the gas to 100 to 200°F [1,2,13]. This requirement reduces the overall thermodynamic efficiency of the gasification-power plant system. This represents a serious fuel and cost penalty in the design of a combined-cycle plant.

At the present state of technology, sulfur compounds must be removed from the gas before it is introduced into the gas turbine because of the sensitivity of the turbine blades to sulfur exposure. However, the loss of efficiency in cooling and reheating the gas for scrubbing significantly degrades the attractive theoretical efficiency of the combined-cycle. Research on processes to remove the sulfur compounds in a high temperature environment is underway. Development of a high temperature gas cleaning process is probably essential for widespread application of both PGG and AG systems.

Commercial Applications of Lurgi Gasifiers. Abroad, the Lurgi gasifiers have found commercial use in India, Australia, West Germany, South Africa, USSR, and UK [9,11]. Recently, Lurgi gasifiers have been installed to provide synthetic gas for a 165 MWe combined-cycle power plant in Luenen, Germany [5,10].

Two full-scale commercial coal gasification plants have recently been announced [11,14]. Both are to be located near Burnham, New Mexico, and are to use strip-mined coal from the Navaho Indian Reservation. One will use 8.5 and the other 9.7 million tons per year of coal. Each plant will employ approximately 30 Lurgi gasifiers to produce 250 million cubic feet of 970 Btu per cubic foot gas. One plant is planned by El Paso Natural Gas and the other by the combination of Transwestern Coal Gasification Company, Pacific Coal Gasification Company, and Western Gasification Company. The plants are scheduled to go on line in the 1976-1978 period.

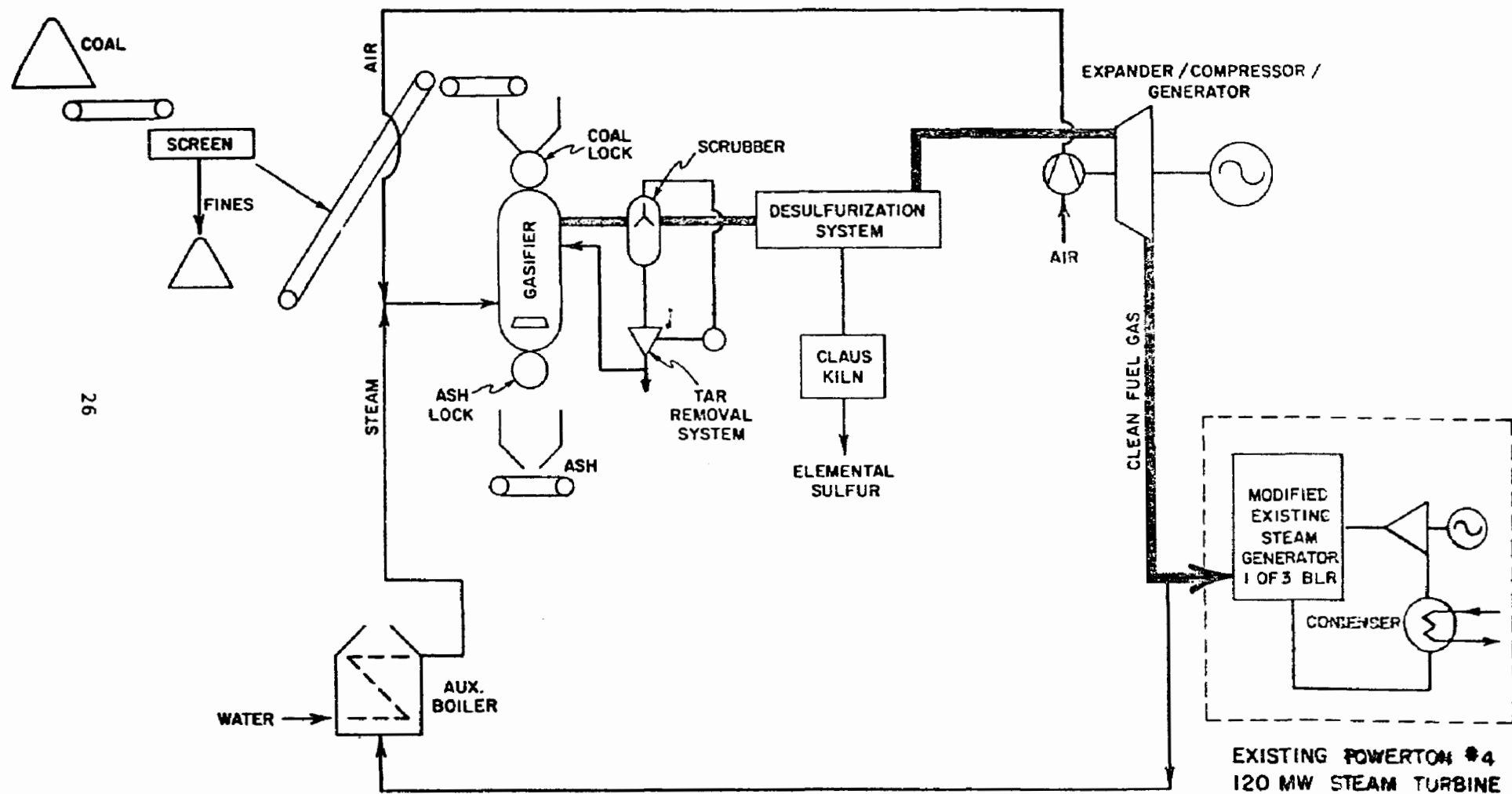
Commonwealth Edison is assessing the feasibility of using Lurgi technology to gasify Illinois coal for direct firing or in a combined cycle at its Powerton Station [4,12]. Called the "Clean Power Fuel Demonstration Plant," this project seeks to demonstrate Lurgi technology with American coals for power plant operation. A schematic of the gasification plant for the Powerton Station is shown in Figure 4. The project, sponsored in part by the Edison Electric Institute, will involve 3 Lurgi gasifiers and is slated to be in operation in late 1975.

Advanced Gasifiers (AG)

As indicated above, a number of advanced gasifiers are under development. Four of the processes are now at the pilot plant stage while a number of other promising systems are still in the experimental stage. Because of the possibility that some of these advanced gasifiers can be adapted for production of low-Btu utility gas, they will be briefly reviewed below.

Advanced Gasifier Pilot Plant Studies. The AG processes which are at the pilot plant stage are indicated in Table 1, along with the developmental and sponsoring agencies and the pilot plant status [1,2,3,4,9].

FIGURE 4. Commonwealth Edison's Clean Power Fuel Demonstration Plant



All of the four employ fluidized bed reactors with the synthesis gas glowing through a coal bed. All processes use the shift reaction, purification, and methanation steps described above for production of pipeline quality gas with the Lurgi gasifiers. Schematic diagrams of the four pilot plant projects are presented in Figure 5.

TABLE 1

Summary of Advanced Coal Gasification Processes
in Pilot Plant Stage

<u>Process</u>	<u>Development Agency</u>	<u>Sponsoring Agency</u>	<u>Pilot Plant Status</u>
1. HYGAS (Electrothermal)	IGT	OCR-AGA	In Operation
2. CSG (CO ₂ Acceptor)	Consol	OCR-AGA	In Operation
3. BI-GAS	BCR	OCR-AGA	Under Construction
4. Synthane	BOM	BOM	Under Construction

IGT: Institute for Gas Technology

BCR: Bituminous Coal Research

Consol: Consolidated Coal Company

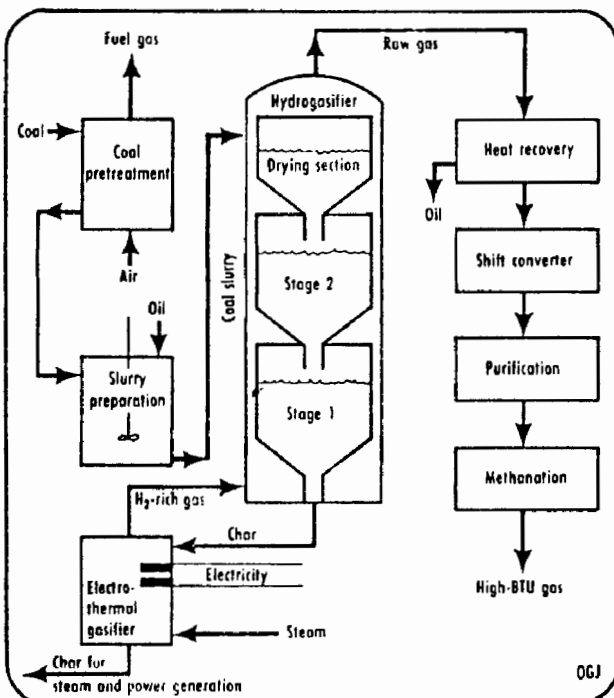
BOM: Bureau of Mines, Department of Interior

OCR: Office of Coal Research, Department of Interior

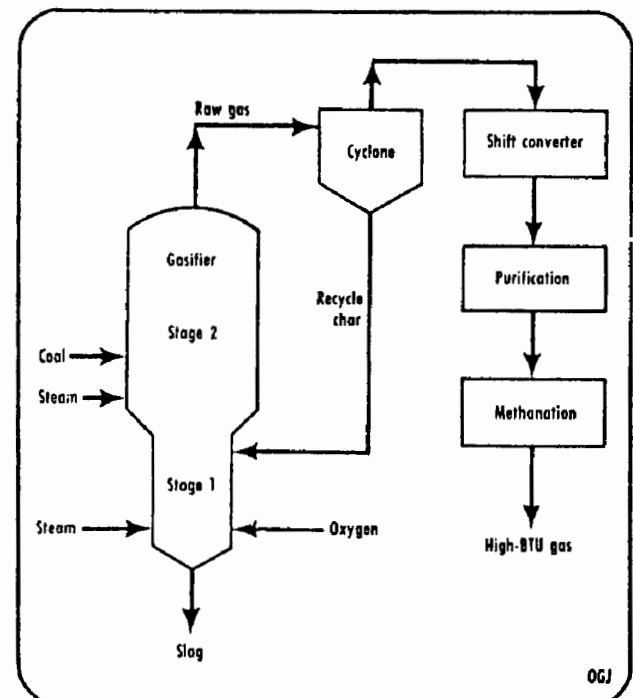
AGA: American Gas Association

Methane is produced in the AG by (a) devolatilization of the coal and (b) reaction of freshly devolatilized coal with H₂ and CO present in synthesis gas and steam introduced into the reactor [2]. The four AG systems now in the pilot plant stage have a number of similarities but basically differ on the mode of production and composition of the synthesis gas supplied to the reaction of H₂ and CO with freshly devolatilized coal.

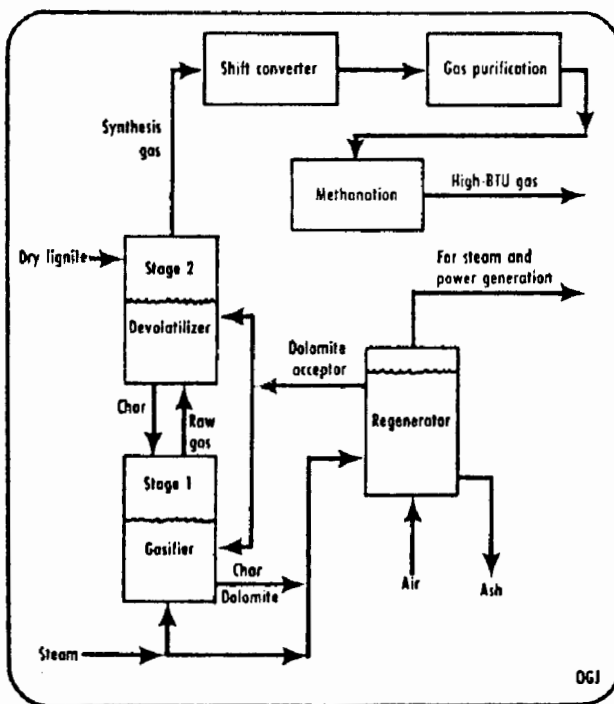
Hygas-electrothermal process



Bigas process



Carbon dioxide acceptor process



Synthane process

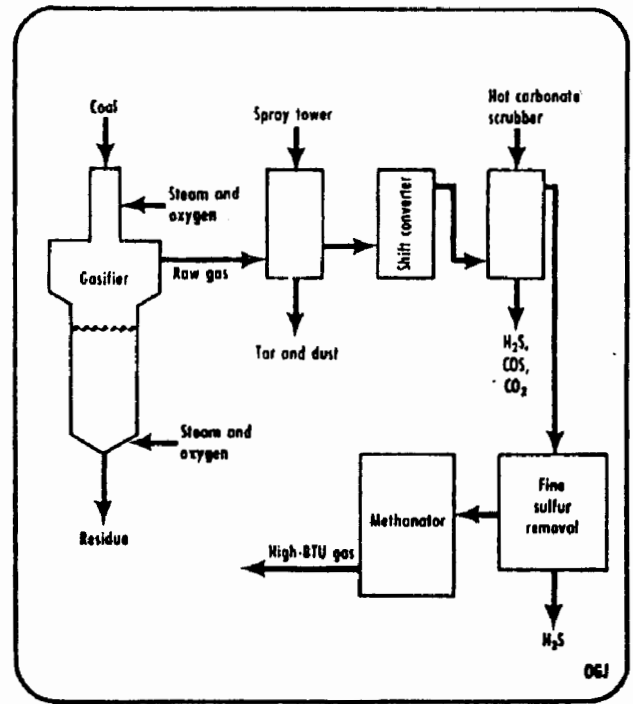


FIGURE 5. Schematic Diagrams of Advanced Gasification Pilot Plants

Three of the processes--HYGAS, BI-GAS, and Synthane--are fairly similar, in that ground coal is reacted with steam and oxygen to produce a synthesis gas [1,2]. If the coal is of the caking variety, it is typically pretreated with oxygen to render it noncaking. The coal is then introduced into the reactor vessel which operates around 1000 psi, the higher pressure shifting the equilibrium mixture to higher concentrations of methane.

In the HYGAS-Electrothermal process, the hydrogen-rich synthesis gas is produced by electrically-heated gasification of char. In the BI-GAS process, oxygen is fed to a high-temperature stage with recycled char and steam to provide energy for production of the synthesis gas. Similarly, in the Synthane process, synthesis gas is produced by oxygen and steam reaction with char.

The CO₂-Acceptor process uses quite a different method for supplying heat to the gasifier to generate the synthesis gas. Process heat is carried to the reactor by calcined dolomite (MgO·CaO) which releases both sensible and chemical energy as it absorbs CO₂. The calcined dolomite is regenerated with char in a separate fluidized-bed reactor. This allows elimination of the electrothermal gasifier or oxygen plant but reduces the gasification temperature so that only the most reactive coals such as lignites can be used and increases the complexity of the system.

Other Advanced Gasification Processes. In addition to the four processes just described, there are a number of other processes for which data has been obtained in experimental units [1,2,9]. The Institute of Gas Technology is developing two other process, both of which use the same gasifier as employed in the Hygas-Electrothermal process. In the HYGAS-Oxygen process (similar to the Texaco process), oxygen is supplied to a separate char gasifier, the synthesis gas from which is purified by the removal of CO₂, the addition of steam, and catalytic shifting before being fed into the hydrogasifier. In IGT's Steam-Iron process, synthesis gas produced in an air-blown char gasifier is used to reduce iron ore Fe₃O₄ to Fe + FeO. The latter is used to decompose steam to hydrogen, reforming Fe₃O₄ which is recycled. The steam is fed to a hydrogasifier.

The Bureau of Mines is developing a second gasification process called the Hydrane process which offers the unique possibility of directly converting raw coal to methane by reacting the coal with hydrogen [1,15]. While the economic advantages of such an approach are well known, the tendency of most American coals to agglomerate has led to a pretreatment stage in which the coal feed stream is partially oxidized. Such pretreatment also reduces the coal's reactivity for methane production, thus requiring the indirect steps of steam-oxygen gasification, water-gas shift reaction, and methanation. In the Hydrane process, almost all (up to 95 percent) of the methane is produced by direct hydro-gasification of raw coal in a "falling dilute phase" reactor [15]. The remainder of the pipeline methane is produced by methanation of carbon monoxide which constitutes 3 to 4 percent of the synthetic gas. The hydrogen for the hydro-gasification is produced by gasification of the residual char. The Hydrane process has been tested at bench-scale in a 3-inch diameter reactor. The process offers the promise of both high thermal conversion efficiency and low gas production costs.

Two other processes, both of which gasify coal with steam and oxygen in molten baths, deserve mention. The Kellogg process uses a molten sodium carbonate bath and the ATGAS process uses a molten iron bath with a limestone flux [1,2,4,16]. In the Kellogg process, the sodium carbonate strongly catalyzes the steam-coal reaction, permitting complete gasification at temperatures low enough to allow methane production in the gasifier [1,2,16]. The gasification temperatures can be lowered from 1900°F to 1700°F. The molten carbonate also supplies heat to the reaction, disperses the coal and steam uniformly throughout the reactor, permitting the direct gasification of agglomerating coal, and reacts with the sulfur to release H₂S in the product gas.

In the ATGAS process, the coal is dissolved in the molten iron bath, releasing organic and inorganic sulfur constituents [1,4]. Because of the high affinity of sulfur for iron, iron sulfides are formed which migrate to a slag floating on the molten iron bath. The iron sulfides react with the limestone flux, releasing the iron and fixing the sulfur as calcium sulfate which must be discarded. The carbon which is dissolved in the molten iron is reacted with steam and air to produce a sulfur-free synthesis gas of CO, H₂, and nitrogen oxides. Little methane is produced directly

so the indirect steps of shift reaction and methanation are required to increase the heat content of the gas. It may be possible to use the synthesis gas directly in a combined cycle plant. The process operates at atmospheric pressures and agglomerating coals can be gasified without devolatilization. Outstanding problems with this process include lance construction materials, refractory lining, and control of particulate emissions. Experimental design data has been obtained on a gasifier of about 2MWe capacity [4].

Adaptation of AG Processes for Low-Btu Gas Production.

The possibility of adapting AG processes for the production of low-Btu utility gas is being investigated in a number of laboratories. Early efforts have already verified the potential for such adaptation as well as have identified some of the unresolved problems [13,17]. Because of the loss of efficiency associated with cooling the synthesis gas for sulfur removal (as described above), probably the major unresolved problem is the yet undeveloped technology for hot cleanup of tar, dust, and sulfur from the synthesis gas.

It should be noted that, while the Office of Coal Research has been given the responsibility for developing low-Btu gasification processes as well as those for pipeline gas, the trend in both OCR and industry funding is not supportive of adaptation of the largely developed AG processes. Rather, OCR and industry appear to be pursuing new AG processes specifically designed for low-Btu gasification.

Design of New AG Processes for Low-Btu Gas Production.

Within the past two years, several new AG systems have been proposed for production of low-Btu utility gas production. The major difference between these designs and adaptation of existing high-Btu systems is that the new designs are optimized for production of low-Btu gas. Although several efforts are underway, probably the most advanced is the team effort headed by Westinghouse and partially funded by OCR. The team also includes Public Service Indiana, Amax Coal Company, and Bechtel [18,19]. This effort would be oriented toward developing a total combined-cycle system using a fluidized combustor to produce a low-Btu (150 to 200 Btu per cubic foot) fuel gas. Lime would be added to the devolatilization stage where it reacts with the sulfur, producing calcium sulfide particles. The synthesis gas emerging from the reactor still has to be cleaned of particulates but the gas is relatively free of sulfur compounds. The cleaned hot gas can then be combusted to drive first a gas turbine and

then give up the remainder of its heat to steam boiler.

Plans call for a pilot plant to be constructed in the Pittsburgh area by mid-1974 to be followed by a commercial plant to be constructed at a public service Indiana plant near Terre Haute by late 1977.

Other industry teams are also working with the Office of Coal Research to define design characteristics for low-Btu AG and combined cycle systems [4]. One team is composed of Combustion Engineering and Consolidated Edison. Another team is made up of Pittsburgh and Midway, Foster-Wheeler, and Pratt and Whitney.

Outstanding problems for all of these processes include advanced gasifier design, hot gas clean-up, and advanced turbine materials technology.

There are a number of other coal gasification processes in various stages of R&D which have not been mentioned in this review. Also the classification of the processes reviewed has been somewhat arbitrary, e.g., the ATGAS process could have placed in the last category considered since it appears to have greater potential for production of utility fuel than for pipeline gas. The omissions and commissions reflect only the need for brevity and the judgment of the author.

Status of Advanced Combustors

There is another class of emerging technology which should be mentioned because it bridges the gap between conventional coal-fired boilers and coal gasification process. This technology involves the combustion of coal in the presence of a sulfur acceptor such as limestone. Because of the necessity to continuously remove the ash and the reacted and unreacted limestone, it is necessary to use a moving or fluidized-bed combustor. The first generation combustors operate at atmospheric pressure. In addition to reducing sulfur emissions, such combustors may, because of lower flame temperatures than in pulverized coal boiler, reduce nitrogen oxide formation and may offer cost savings.

One systems which should be mentioned is that developed by Pope, Evans, and Robbins [2]. This fluidized-bed boiler has operated successfully in the pilot plant stage and is ready for scaling to a demonstration plant. The Office

of Coal Research has recently granted Pope, Evans, and Robbins a contract for the design, construction and operation of a 30 MWe fluidized-bed boiler. In England, the National Coal Board is developing an atmospheric, fluidized-bed combustor. Partial funding for these projects has been provided by the Environmental Protection Agency and the Office of Coal Research.

These systems do involve changes in boiler design and manufacture and boiler operation which, although much less extensive than with coal gasification, have represented a barrier to acceptance by manufacturers and utilities. The general opinion seems to be that, if significant departures from conventional boiler design are to be made, then it is logical to go the extra step to gasification with potential for much improved thermal efficiency and decreased environmental problems or to liquefaction with potential for decreased environmental problems. Similar reasoning seems to apply in the case of stack gas cleaning which is viewed by many utility managers as a troublesome, short-lived solution.

Comparison of Alternative Technologies

The alternative technologies described above embody different physical processes which are introduced into the utility fuel cycle in different ways, e.g., liquefaction may produce a new fuel to substitute directly for coal while gasification may require an integrated gasifier-gas turbine-steam boiler system. Further, the various technologies are at considerably different stages in the R&D process. In a number of cases, engineering studies of systems incorporating the technologies have not been conducted. These factors make it quite difficult to compare the alternative technologies on a common basis. Insofar as possible, the technologies will be compared on the basis of (1) applicability for power plant use; (2) capital and operating costs; and (3) associated environmental factors. Because of the limited utility interest in advanced combustors, the comparison will be limited to coal liquefaction, present generation gasifiers, and advanced gasifiers.

Applicability for Power Plant Use.

The major difference between the coal liquefaction and gasification processes for utility boilers is that liquefied coal products have high energy content (16,000 Btu per pound) and are in a physical form convenient for both transportation and storage

while the low heat content and physical form of low-Btu gas from coal is such that it can be neither transported (by pipeline) nor stored.

Coal Liquefaction. In terms of physical suitability, liquefied coal products (LCP's) could, with minor boiler modifications, be used in nearly all utility and industrial boilers. For instance, SRC could be used in either the pelletized solid form or, if heated, could be handled as a viscous fuel oil. Coal liquefaction would probably be accomplished at a large centralized, possibly mine-mouth, plant and could probably thereby achieve economies of scale. The ash and sulfur disposal problems at the processing plant could be quite significant and may severely limit the number of potential plant sites. The sulfur would probably be converted to elemental sulfur which could be more easily stored than many sulfur compounds.

LCP's, largely ash-free, still contain some sulfur. SRC with 0.6 to 0.7 percent sulfur could be used in nearly all areas of the country under the New Source Performance Standards and in most areas under standards established by State Implementation Plans or by state and local regulations. But the sulfur content in SRC just slips under the requirements in many areas and is too high in some such as New Jersey and New York. If allowable sulfur concentrations are reduced in the future, SRC would probably not be adequate. By comparison, the sulfur emissions with SRC are as much as twice those apparently achievable with stack gas cleaning. Other LCP processes, such as the Bureau of Mines turbulent catalytic hydrodesulfurization, have demonstrated the ability to reduce the sulfur content by one-half or even two-thirds below that achievable with SRC. Supposedly such low concentrations can be achieved with H-Coal although the matter is somewhat confused at this point [5].

Other factors which may affect the applicability of LCP's are supply and cost. Much of the particulate and sulfur emissions in urban and industrial areas comes from industrial rather than utility boilers. Many of these boilers, because of space limitations and highly unfavorable economics, cannot be retrofitted with SGC or gasification systems. LCP's represent, therefore, the only technological alternative to low sulfur oil or natural gas. As LCP's become commercially available, in limited supply at first, industrial boilers may pay the premium price for the clean fuel [18]. At the same time, utilities may elect to use LCP's for their older,

less efficient, lower load capacity boilers which cannot be retrofitted with SGC systems and, under regulatory and market pressures, retrofit their newer boilers with SGC units or use low sulfur coal. LCP's may provide the option for utilities to continue to use their older and smaller units with reduced air pollution to meet peak loads--this could be extremely important if siting problems, new plant startup difficulties, and regulatory delays persist.

Present Generation Gasifiers. If the synthesis gas is only to be combusted in a modified conventional boiler, then PGG systems can be used with both new and existing plants. However, to offset the increased cost of the Lurgi (or other) gasifiers, a combined-cycle must be used to increase the thermal efficiency. Commonwealth Edison plans to install a gas turbine as part of the gasification demonstration project at its existing Powerton Station. It appears then that the application of PGG system will be restricted essentially to new plants. There may be some limited application of PGG systems for conventional boilers until hot sulfur and ash clean-up processes and improved turbine blades are developed but PGG systems will generally be applied on new systems.

Advanced Gasifiers. For the reasons just given, AG systems will be applied only to new power plants. All AG systems, either as adaptations of high-Btu content gasifiers or as new designs involve the integration of a gasifier with a combined-cycle unit.

Comparative Costs of Alternative Technologies

A most important comparison, and the one most fraught with uncertainties, is that of costs, both capital and operating. Cost analyses of emerging technologies are hazardous enough, but estimates of capital and operating costs for processes only at the level of bench-top experiments approach speculation. Also because of recent cost escalations it is very important to compare costs calculated in the same period and preferably as recently as possible. Cost analyses as recent as 1970 and 1971 may be quite out-of-date. Some recent cost data will be presented to indicate, at least, relative economic attractiveness.

One recent comparison based on conservative assumptions casts an equally jaundiced eye at all technological alternatives [5]. This sobering comparison prepared by Chem Systems Inc. should bracket the maximum costs that may be anticipated. These costs estimates are given in Table 2.

Table 2

Cost Comparison of Technological Alternatives
for Sulfur Control

Technological Alternative	Total Annualized Energy Costs, ^{1/} ¢/10 ⁶ Btu	Total Capital Investment Costs, ^{2/} \$/KWe
Stack Gas Scrubbing*	80-85	104
Low-Btu Gas	90-95	132
Liquefied Coal Product	85-90	(?)

¹Interior coal priced at \$7/ton (or 30¢/10⁶ Btu) and a load factor of 0.70

²Includes contingency of 15% of capital expenses.

*The costs of stack gas scrubbing quoted by Chem Systems were based on an analysis by the Federal Power Commission. The system analyzed was a 1000 MWe boiler using high sulfur Interior coal. The system economics were penalized by inclusion of an electrostatic precipitator, coal storage and preparation facilities and ash, dust, slag systems--the entire waste disposal system--with the wet lime/limestone scrubber, giving \$70.5 per KWe. \$17 million was included for utilities and \$13.5 million was included for contingency, yielding \$103.5 per KWe for total investment. The individual costs were broken down as follows:

Coal	30¢ /10 ⁶ Btu
Operating Costs	14¢ /10 ⁶ Btu
Waste Disposal	11¢ /10 ⁶ Btu
Capital Charges	<u>31¢</u> /10 ⁶ Btu
	86¢ /10 ⁶ Btu

Chem System indicates that the "relatively high estimated costs may have been unfavorably influenced by Commonwealth Edison's recent experience on the Will County stack gas unit"[5].

The estimates of low-Btu gas costs were developed by the Federal Power Commission Coal Gasification Task Force for a 1000 MWe plant using a combined cycle. The onsite process costs were \$71.8 per KWe and the total plant investment including contingency was \$132 per KWe. The total energy costs (in terms of gas) were 92¢ per million Btu.

The economics of LCP's are somewhat more complicated in that the cost of the product is quite sensitive to size of plant. To illustrate the trends for SRC, the cost of SRC as a function of coal feed to the plant is shown in Figure 6. For a plant producing 7,700 tons of SRC per day* required to fuel a 1000 MWe generator, the energy cost (in terms of SRC) were 88¢ per million Btu. As envisioned, one LCP plant, probably located at the mine-mouth, would produce enough fuel for several power plants. It is suggested that central plants processing 40,000 to 50,000 of coal per day may eventually be developed.

There are a number of other cost estimates for the various technologies, however, it is indeed fortuitous when the costs have been computed on a common basis. Three recent publications gave cost estimates of electrical power production from low-Btu gas, although not in directly comparable terms. Lurgi indicates that, for a 330 MWe plant using 30¢ per million Btu coal, the energy production costs would be about 10 mills per Kw-hr and the capital costs would be about \$200 per KWe [19]. IGT has estimated that, for a 1000 MWe plant using 24¢ per million Btu coal, the capital costs would be \$200 per KWe and, assuming a 90 percent load factor, the total energy production costs would be 6.9 mills per Kw-hr [20]. Finally, ATC has estimated that, for a 1000 MWe plant using 30¢ per million Btu coal, the capital investment is \$163 per KWe and, assuming a 90 percent load factor, the energy costs would be 6.8 mills Kw-hr [21].

As mentioned above, cost analyses of LCP plants are considerably more difficult because the effect of plant size on the economics. Several recent publications have estimated the costs of SRC and H-Coal, although again the costs are not on a comparable basis. On the basis of an analysis on a SRC plant processing 10,000 tons of coal per day, Pittsburgh and Midway suggests that, as a rule of

*In the Pittsburgh and Midway SRC process, this output would require 13,300 tons of Interior coal.

S.R.C. SELLING PRICE
\$/MM BTU

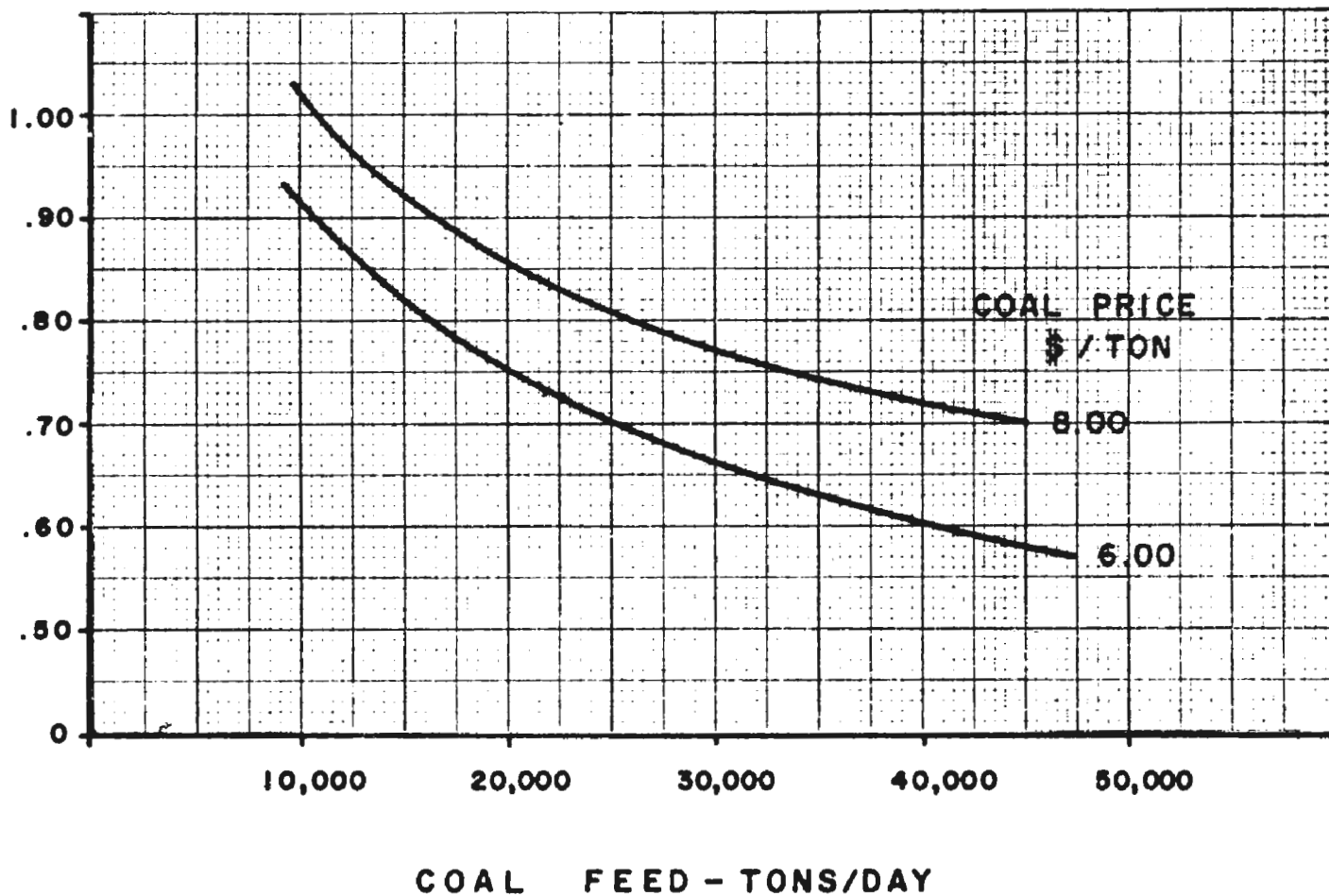


FIGURE 6. SRC Economics as a Function of Plant Capacity and Coal Price

thumb, SRC will sell at a price equal to the cost of raw coal plus 35¢ per million Btu [6]. For 30¢ per million Btu coal, this gives an energy cost of only 65¢ per million Btu, considerably below the adjusted Chem Systems estimates. Analysis by Chem Systems indicated for an SRC processing 44,000 tons of 35¢ per million Btu coal per day would yield a fuel oil (produced by blending enough of the lighter hydrocarbons formed in the SRC process with the SRC to make 127,000 barrels per day of a pumpable product) which costs about 70¢ per million Btu. The total plant investment would be \$209 million which, reflected in incremental capital costs to electrical plants, would be about \$63 per KWe [5]. For the H-Coal process, two feed coals--both priced at 35¢ per million Btu--were analyzed. Processing Illinois seam coal with 3.4 percent sulfur at the rate of 29,000 tons per day resulted in an energy cost of 83.5¢ per million Btu while a Pittsburgh seam coal with 4.2 percent sulfur at 25,000 tons per day resulted in 88.8¢ per million Btu. Both plants would produce about 70,000 barrels per day of a pipeline product. The incremental capital investments for the two plants would be \$78 per KWe and \$90 per KWe, respectively. It should be noted, however, that the interest rates used for the LCP plants are those for normal refinery financing, rather than utility financing, as usually used for stack gas scrubbing and for low-Btu gas production.

Although not really germane to these comparisons, an excellent common base cost comparison for pipeline coal gasification was recently published [22]. To the extent that some of the PGG and AG processes may be adapted for low-Btu gas production, this is an informative comparison. The economics of five processes are compared in Table 3. The study also computed costs for coal at 35¢ per million Btu and for 9 and 15 percent gross return on rate base. This study did not directly take into account the differences between lignite and bituminous coals, although some of the processes are operable only with specific grades of coal, i.e., the CSG process must use lignite.

Associated Environmental Factors

While it is too early to characterize all of the environmental effects associated with the alternative technologies, it is possible to describe them in general and to give a limited amount of specific information. Most of the environmental factors, except for those associated with mining, are most easily discussed by considering each technology generically.

Table 3

Comparison of Pipeline Gasification Process Costs [22]

Process	Total Capital Investment, ^{1/} \$10 ⁶	20-year Average Gas Selling Price, ^{2/} ¢ / 10 ⁶ Btu
CSG (CO ₂ -Acceptor)	112	73.5
BI-GAS	179	88.9
HYGAS (Electrothermal).	165	89.3
Kellogg Molten Salt	167	87.4
Lurgi	297	119.6

¹ Plant capacity 250 million cubic foot per day; 20-year plant life; 7.5 percent interest; taxes and insurance at 3% of total fixed investment

² Coal price 25¢ per million Btu; 12 percent gross return on rate base; load factor 95 percent; by-product credit: sulfur \$5 per ton, ammonia \$20 per ton, phenol \$80 per ton, char \$0.15 per million Btu.

Probably the major environmental abuse, one for which we have not discovered a technological fix, is that due to strip mining for coal extraction. If we increasingly rely on strip mining for more of our coal production and do encounter increased need for coal to feed coal liquefaction and gasification plants, much improved surface mining regulation and enforcement and real innovation in mining and reclamation technology will be required. Because of the losses associated with the conversion techniques, the land disturbed by mining will correspondingly increase unless offsetting improvements are made in the power generation cycles (such as combined-cycles).

Coal Liquefaction. The land impacts are those associated with clearing and preparing the site for the plant, including coal storage, handling and preparation facilities, ash and sulfur disposal facilities, product storage facilities, and transportation facilities. If the plant is located at the mine-mouth, coal transportation would be minimized but LCP's would have to be transported by train or pipeline to the power plant. For many LCP plants, siting of both the plant and the transportation corridor may be a significant problem. Disposal of the ash, and possibly of the sulfur, may represent another serious problem area. If the plant is located at the mine-mouth, then disposal in the mined area might be feasible, otherwise the solid wastes generated in a large LCP plant would represent a massive landfill operation. A plant processing 40,000 tons of coal per day would generate 5,000 tons of ash (dry weight) per day using Eastern and Interior coals and up to 10,000 tons per day using Western coals.

The air and water impacts of coal liquefaction plants are not well characterized at this point. Most of the sulfur removed from the coal is converted to H_2S and then converted to elemental sulfur by various processes. Light hydrocarbons are generated in the liquefaction processes and some of these will be vented to the atmosphere. Emission standards for these and for H_2S (not converted to sulfur) will have to be established for these large sources. A major variation in the air emissions may depend on whether the char or other mineral residue is fired for process heat or sold for combustion elsewhere. Particulates and sulfur oxides from such combustion will be difficult sources to control. Water clean-up does not appear to represent a major problem, at least at this time.

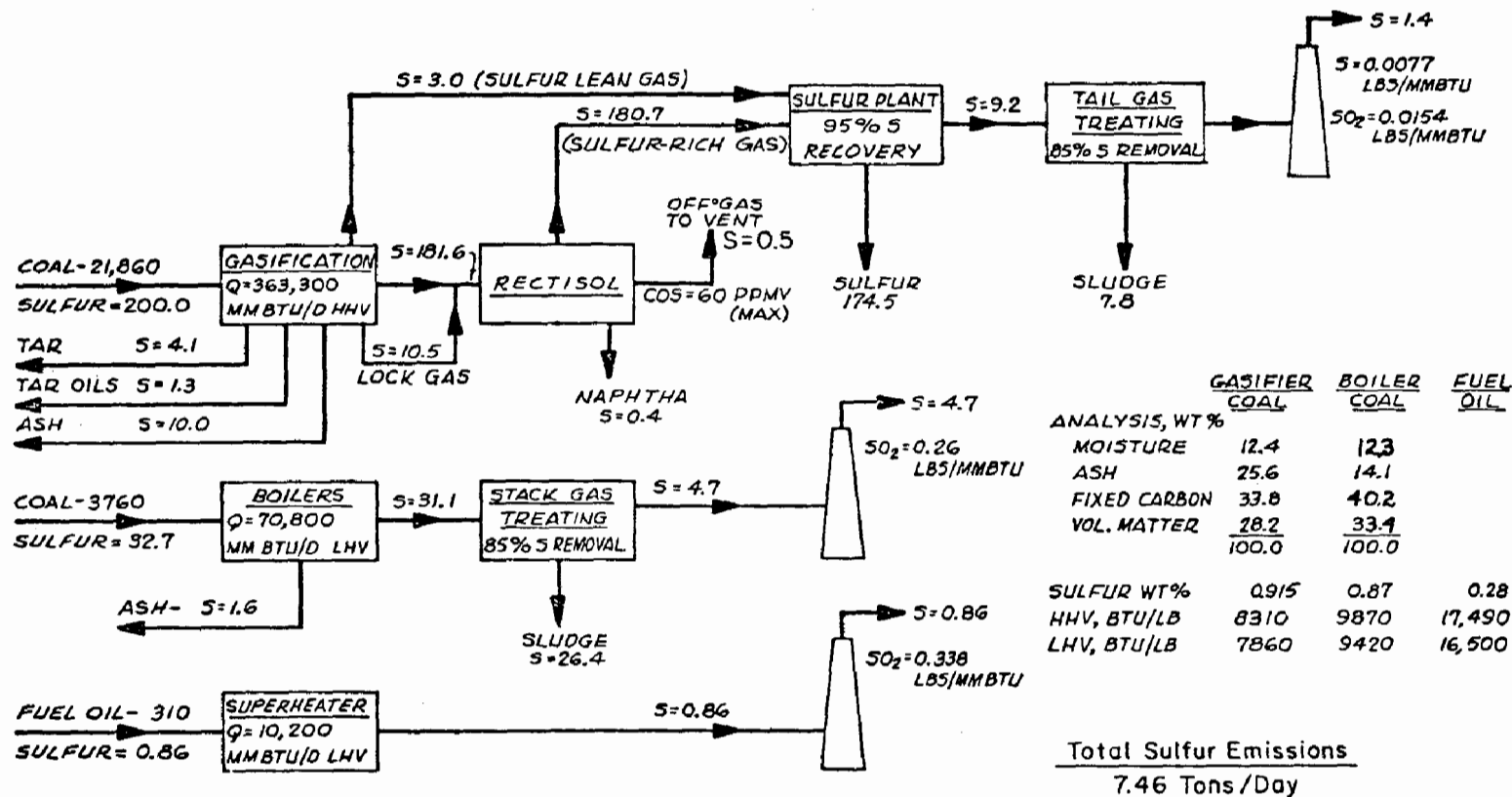
From an environmental point of view, LCP plants do hold considerable promise for shifting much of the environmental burden from the dispersed power plants to a centralized location. This is quite attractive to the utilities. Emissions to air and water may be more effectively controlled at a larger central plant, however, this has not yet been demonstrated. The concentration factor will undoubtedly exacerbate other impacts such as those on land.

Coal Gasification. The environmental impacts of gasification plants are better known, primarily because environmental assessments have been completed for both commercial high-Btu gasification plant proposals. The Federal Power Commission's Natural Gas Survey [1] estimated the following potential pollutants would be generated in a 250 million cubic foot per day plant, assuming use of Interior coal with 3.7 percent sulfur and 10 percent ash:

	<u>Tons per day</u>
Sulfur (Mainly as hydrogen sulphide)	300-400
Ammonia	100-150
Phenols	10-70
Benzene	50-30
Oil and Tars	trace to 400
Ash (based on coal with 10% ash)	1500

Control processes are known for many of these potential pollutants and are being incorporated into the engineering design of gasification plants.

As an example of the type of control planned for a high-Btu gasification plant, the sulfur balance diagram for the proposed Transwestern gasification plant is shown in Figure 7. The plant will use 25,600 tons per day of low sulfur coal for the gasifiers and process heat boilers. The sulfur input is 233 tons per day and only 7.5 tons are to be emitted, over 60 percent of which are from the coal-fired boiler. The maximum 24-hour average SO_x concentration expected is about 0.03 ppm. Concentrations of NO_x , H_2S , COS , and particulates are a fraction of the allowable New Mexico standards [11].



NOTE:
ALL QUANTITIES ARE IN SHORT TONS PER
DAY EXCEPT SHOWN OTHERWISE.

FIGURE 7. Sulfur Process Diagram for Transwestern Coal Gasification Plant

Water impacts of coal gasification plants of two types: pollution potential and consumption. For instance, in the Transwestern proposal, all the gas liquor streams are treated to remove the phenols, ammonia, and H_2S and all waste water streams treated to remove suspended oils and solids and residual organics. Water consumption, minimized in the Transwestern proposal by recycling, is 5100 gallons per minute (or 8,260 acre-ft per year). Twenty percent of this is consumed directly in the gasifier and 50 percent is evaporated in cooling towers and settling ponds. Without recycle, the consumption could have been 8,000 to 10,000 gallons per minute. In water-scarce areas, such water consumption for both PGG and AG systems may become an important factor.

Forecasts of Application

Forecasting application of emerging technologies is a difficult matter. However, because of their relevance to policy development for air pollution control, even rough forecasts are infinitely better than none at all. This section will review the major features of several recent forecasts of the application of technological options for clean fuel.

CEQ Forecast

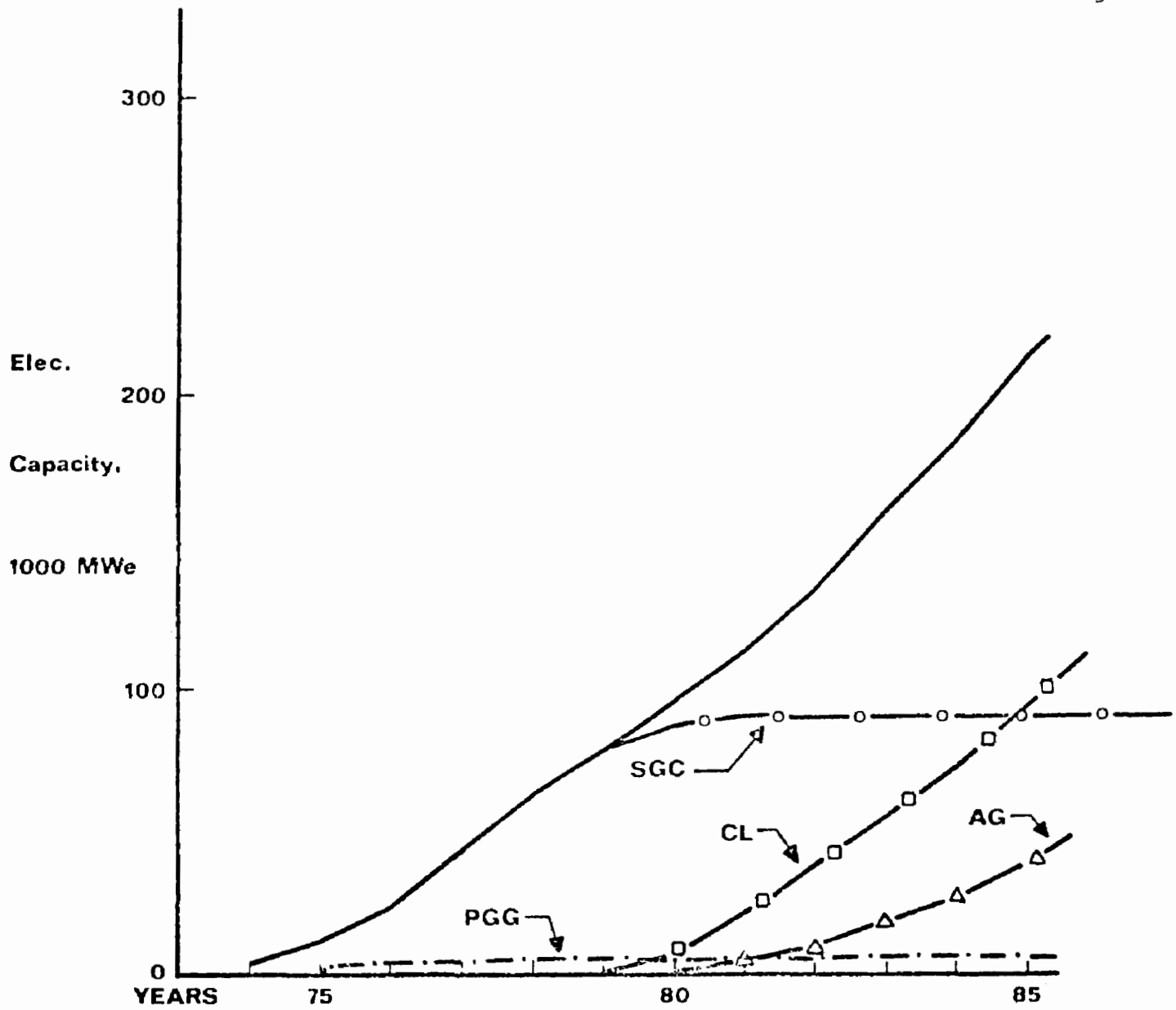
A forecast of the application of all of the major technological alternatives for the use of high sulfur coals for steam-electric plants has been developed by the Council on Environmental Quality [18]. This forecast includes four options: stack gas cleaning (SGC), present generation gasifiers (PGG), advanced gasifier (AG), and coal liquefaction (CL). The predictions assume that the forecasts for SGC installations in the "realistic" scenario of the SOCTAP report are valid from 1974 to 1977. In the period 1978 to 1980, it is assumed that only new coal-fired plants are equipped with SGC technology; beyond 1980 it is assumed that no plants are outfitted with SGC systems. These conservative assumptions would mean that 84,000 MWe, of which 61,000 MWe represent new plants, would have SGC devices by the end of 1980. Limited application of PGG processes would begin in 1975 and application of AG system would begin in 1980. Application of CL plants would begin in 1979 and would expand rapidly. The allocation of these processes to fuel new or existing plants are predicated on many factors which have been discussed above. The results of these assumptions are presented in Table 4 and are shown graphically in Figure 8.

TABLE 4.

PROJECTIONS OF UTILIZATION OF CLEAN FUEL OPTIONS
WITH LIMITED APPLICATION OF SGC SYSTEMS

Tech- nology	Type of Install.	Coal-Fired Steam Electric Capacity with Clean Fuel Technological Options,										MWe	
		74	75	76	77	78	79	80	81	82	83	84	85
SGC	new	900	3,800	8,200	12,000	12,000	12,000	12,000					
	retro	1,600	3,600	5,600	12,000								
PGG	new		1,000	1,000	1,000	1,000							
	retro												
AG	new							1,000	2,000	4,000	8,000	12,000	12,000
	retro												
CL	new								10,000	12,000	10,000	10,000	10,000
	retro						1,000	5,000	8,000	8,000	8,000	10,000	10,000
Annual Capacity Addition, MWe		2,500	8,400	14,800	25,000	13,000	13,000	18,000	17,000	24,000	26,000	32,000	32,000
Cumulative Capacity, MWe		2,500	11,000	26,000	51,000	64,000	77,000	95,000	112,000	136,000	162,000	194,000	226,000
Coal Usable, 10 ⁶ tons		6.4	28	66	129	162	195	240	283	344	410	491	572
Total Steam-Electric Coal Use, 10 ⁶ tons			384					460					613 93%
Percentage with Control			7.3%					52%					

FIGURE 8. CEQ Projections of Utilization
of Clean Fuel Alternative Technologies



This forecast shows dramatically that the only viable technological alternative for reducing sulfur oxide emissions until the early 1980's is stack gas cleaning. Even with rapid expansion in LCP availability, the first priority for use of LCP's will be for existing plants. Competition from industrial boilers also could limit availability of LCP's. In this forecast, equal amounts of coal cleaning would be achieved by SGC and CL in 1985, since AG and CL supply all clean fuel needs after 1980.

Hittman Forecast

The application of stack gas cleaning and solvent refined coal for power plants has been forecast by Hittman Associates [4]. Hittman emphasized only coal liquefaction because, in their opinion, SRC is the most advanced clean fuel option and has the greatest likelihood of success. Hittman assumed three cases: Base, Higher SGC, and Sooner SRC. In the Base case, it is assumed that commercial application of SGC begins in 1976 and the maximum supply capability is limited to installation on 20,000 MWe per year. SRC is commercially available in 1981 and is also supply limited for the first decade. The Higher SGC case differs from the Base case only in that the maximum supply capability is assumed to be 40,000 MWe per year. The Sooner SRC case differs from the Base case only in that SRC is commercially available in 1979. The projected application of SGC and SRC technologies for these three cases is shown in Figure 9. Some features of this forecasts are well-illustrated in Figure 9. SGC application is supply constrained until the 1983-1986 period; after then SGC application is demand constrained. SRC application is supply constrained and since, from the utilities' point of view, is the desirable approach to coal cleaning, SRC substitutes directly for SGC to the extent possible. Utilization of SGC continues, in this forecast, not only after 1980 but even after the 1983-1986 period. This application continues, although only on new plants, because Hittman feels that SGC will offer the least expensive alternative in many cases. The effect of the technological alternatives in the three cases on the reduction of sulfur oxide emissions is shown in Figure 10.

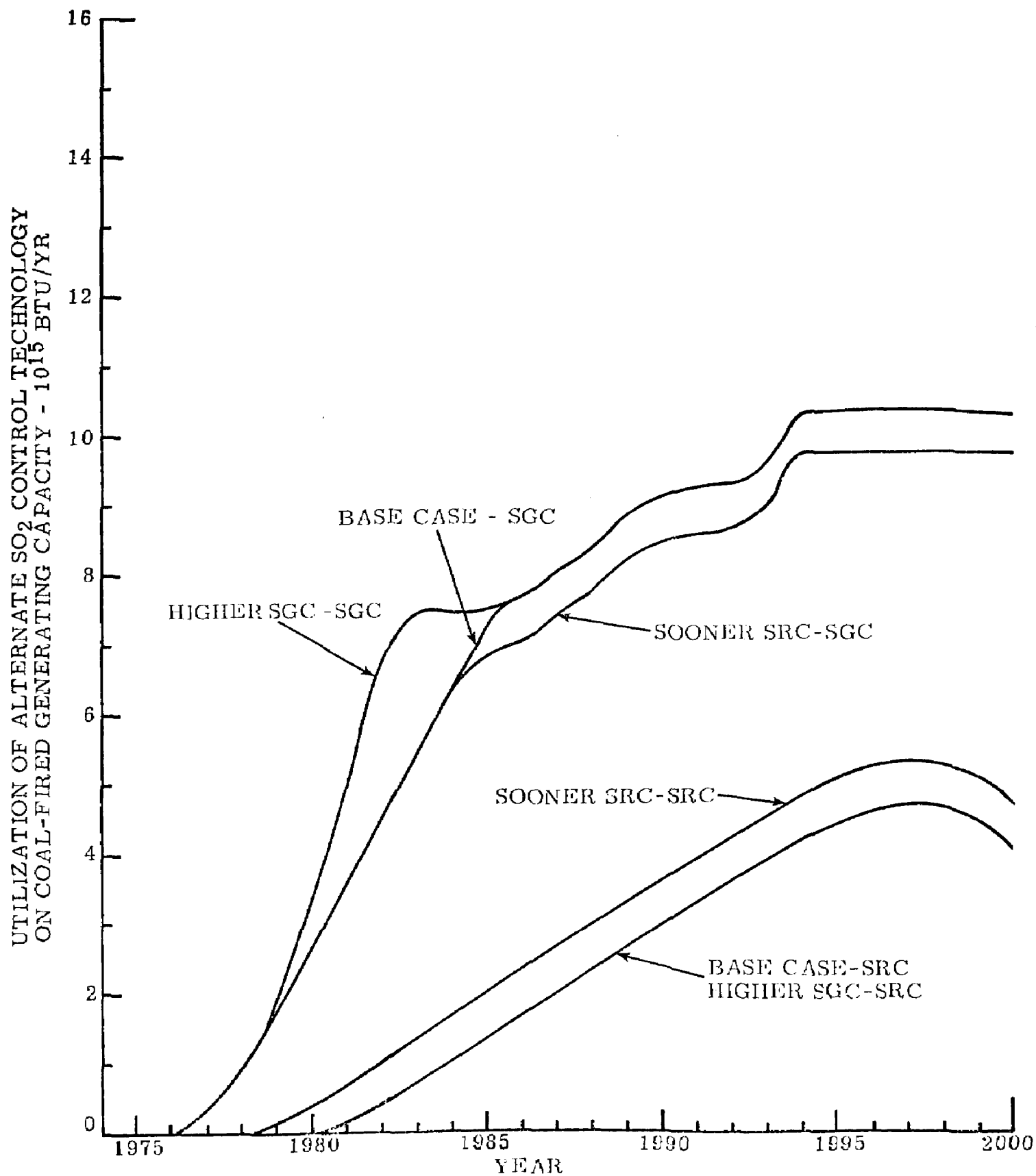


FIGURE 9. Hittman Projections of Utilization of Clean Fuel Alternative Technologies

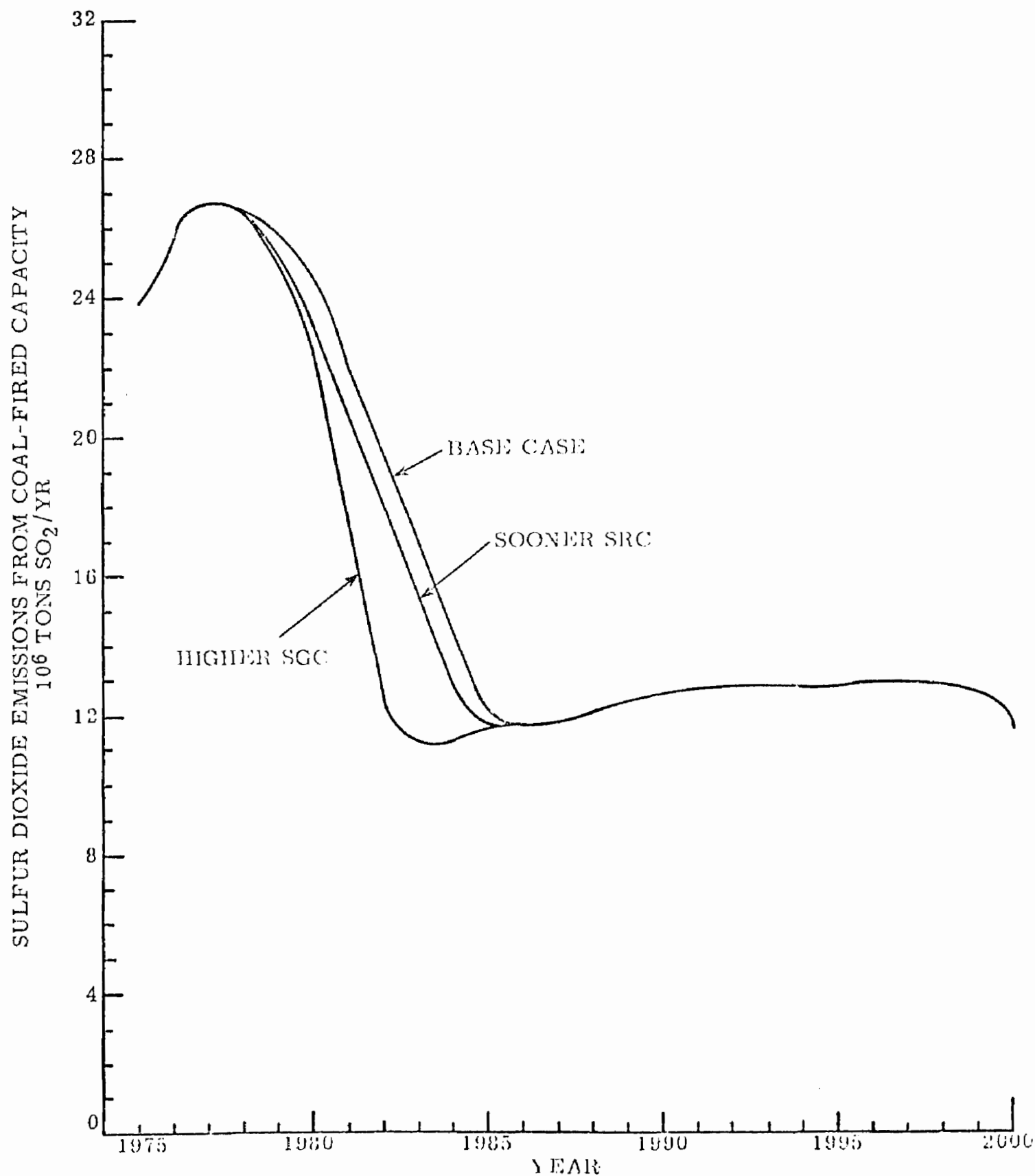


FIGURE 10. Reduction in Sulfur Oxide Emissions Associated with Hittman Projections

MITRE Forecast

Application of SGC and SRC processes as well as synthetic crude oil production and gasification were also projected by MITRE [23]. While the projection given in Figure 11 covers total coal utilization, the SGC and SRC components would probably be used mostly by the electric utilities. MITRE projects an optimistic expansion of coal utilization which triples over the next 15 years. Interestingly, MITRE assumes that 250 million tons of coal could be burned in 1980 with SGC which is roughly 100,000 MWe. The MITRE projection for SRC and synthetic crude production accounts for 150 million tons of coal which is much larger than that projected by any other source.

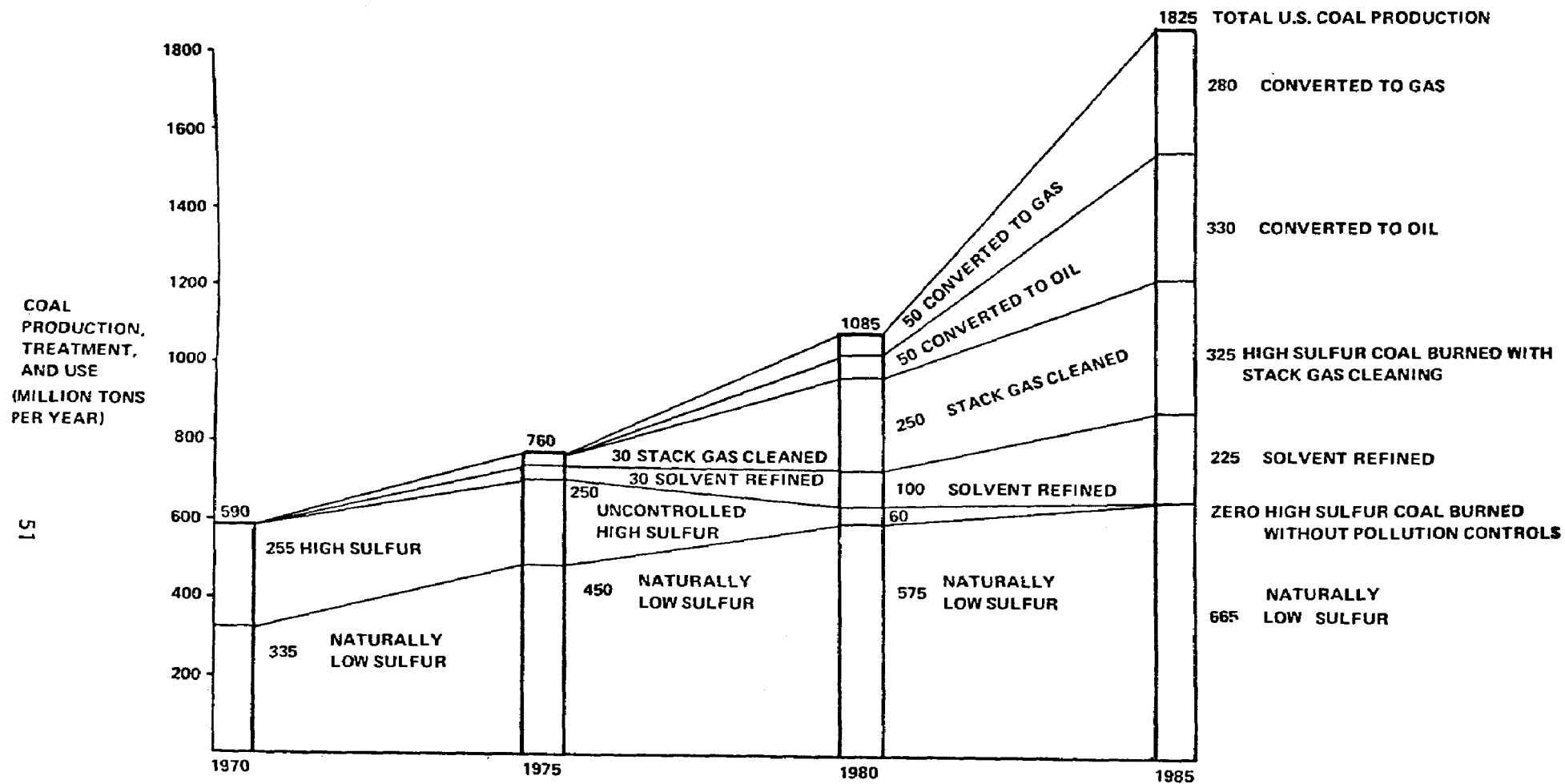
Chem Systems Projections

Chem Systems has made predictions when the CL and PGG/AG systems might become available [5]. Chem Systems believes that CL processes will become available by 1978 with construction and initial operation of both SRC and H-Coal plants. Chem Systems predicts that PGG plants will become commercial in the U.S. by 1976-1977 and application will start before the end of the decade. AG power cycles will be 3-4 years behind the PGG systems. Chem Systems suggests the following scenario for PGG system application:

- | | |
|------|---|
| 1976 | Commonwealth Edison 3-gasifier system successfully in operation. |
| 1978 | Installation of gasifiers on two 300-500 MW retrofit generators |
| 1980 | Gasifier systems in operation on three new 1000 MW generators and on five additional 300-500 MW retrofit installations. |

For this optimistic scenario, Chem Systems predicts a total of 5000-6000 MW of generator capacity on low Btu coal gas by 1980. Thus, low Btu gas could account for 2-3% of installed coal-burning generator capacity by 1980, or more significantly 4-5% of installed coal-burning utility generators feeding high sulfur Interior coals. These predictions agree reasonably well with the application of PGG and AG systems forecast by CEQ.

FIGURE 11. MITRE Projection of U.S. Coal Production and Utilization



[SOURCE: MITRE ANALYSIS]

Summary

In summary, this review of coal liquefaction, gasification, and advanced combustion processes indicates that technological alternatives to stack gas cleaning are just beginning to enter the pilot plant stage. Years of development remain before any of these technologies will see widespread commercial application. Low-Btu gas production for utility boilers using Lurgi gasifiers and solvent refining of coal appear to be the first technologies that will be applied. Two coal liquefaction processes--H-Coal and COED--and high-Btu gas production appear to lag somewhat behind the PGG and SRC technologies. Many other CL and AG processes with promising characteristics are only at the bench-top experimental stage.

All of the processes are expensive and it appears that electric power production costs will increase significantly as these new technologies are introduced. Although it is nearly impossible to generalize, it appears that stack gas cleaning will be significantly less expensive than the technological alternatives for many new and at least some existing power plants. The relative economics of the various technologies, of course, must be evaluated for the conditions of a given plant. Among the various alternatives, SRC appears to provide the least expensive fuel which should meet air quality standards in most areas. SRC may also enjoy economics of scale not available to PGG, AG and some CL processes. If, and there are a number of if's, AG combined-cycle systems can be successfully developed, they may compete with CL processes.

Environmentally, CL processes take the burden off the utilities to control air emissions and manage solid wastes and shift it to the processing plant. But the same ash and sulfur has to be disposed of at the processing plant. PGG and AG processes remove the sulfur from the synthetic gas stream and may, if hot clean-up processes are developed, do this without loss of thermal efficiency. But disposal of the ash and sulfur remains at the power plant. Air and water emissions from CL, PGG, and AG processes are not well characterized yet but it appears that some new problems may arise through the chemical processing of coal. Developmental work on advanced clean-up processes remains underway.

Concluding with the forecasts of application, a common element in all the forecasts is the 5 to 8 year lag between the commercial availability of SGC and that of the alternative clean fuel technologies. To the degree that sulfur oxide emissions must be controlled to meet primary air quality standards, it is quite clear that SGC is now and will continue to be for some years the only viable alternative to fuel switching. A delay in the application of SGC to plants requiring control until another technological alternative is available places too much burden on the air quality and too much reliance on yet-unproved technologies which, if successfully developed, many cost significantly more.

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STATUS OF FLUE GAS DESULFURIZATION TECHNOLOGY

by

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THE STATUS OF DESULFURIZATION TECHNOLOGY

Implicit in our efforts to assess the status of sulfur oxide control technology is the assumption that there is either a well-defined measure of the problem that the technology is designed to address or that there is a well-defined market for the technology, or both. This paper deals largely with the factors that must be considered in the development of a yardstick for measuring the status of sulfur oxide control technology.

In this conference, several papers will be given which will specifically address the technical, economic and regulatory factors relating to specific SO_2 control processes. It is the purpose of this paper to help provide a yardstick against which you can better judge for yourself the status of each process and the overall status of the technology.

To help put the sulfur oxide problem in perspective in the United States, let us first compare the mass emissions of the five principal pollutants. This is done in Figure 1. Using 1970 mass emission data, the pie-chart on the left shows the total mass emission of the five major ambient air quality pollutants: SO_x , NO_x , Particulate, Hydrocarbons, and Carbon Monoxide. For comparison, the pie-chart on the right replots the 1970 mass emission data but excludes emissions from transportation sources. The chart on the right, therefore, shows the distribution of these five pollutants which are emitted from stationary and some natural sources. Comparing the mass emissions, we see that stationary sources in the United States account for most of the sulfur

oxide and particulate emissions. They account for roughly half of the nitrogen oxide and hydrocarbons and about 1/5 of the carbon monoxide.

Mass emissions, however, do not provide an adequate index of the impact of a source on the ambient air quality. Other major factors influencing the impact of pollutants on ambient air quality include:

1. The geographical point of discharge
2. The height of the source above the receptors
3. Topography surrounding the discharge point
4. Proximity of source to other sources
5. Other factors affecting distribution such as
 - a. Wind Direction
 - b. Wind Speed
 - c. Ambient Temperature

To provide a measure of the relative impact of sources on ambient air quality, we have developed and applied a dispersion model which takes into account most of the factors mentioned above. This model assumes a rectangular dispersion of pollutants downstream from the source and considers the relative location of sources, height of discharge, wind direction and velocity. Using the model, it is possible to predict the ambient exposure of a receptor in the impacted area.

Using this model, we have calculated the average impact of various kinds of emitting sources. Figure 2 shows the relationship between the mass emissions and their impact on ambient air quality. In this figure we have classified sources into four major categories:

PP--Power Plants

IC--Industrial Combustion

IP--Industrial Processes

AS-Area Sources

Measured in terms of tons of pollutants emitted, the fossil fuel fired power plant accounts for over 50 percent of SO₂ emissions, industrial combustion accounts for 24 percent of the SO₂ emissions, 10 percent are from industrial processes (such as sulfuric acid plants, pulp and paper plants, refineries and smelters) and 12 percent from area sources (residential and commercial).

When the factors affecting ambient air quality other than mass emissions are applied (location, height, proximity to other sources, etc.), the impact of the sources are as reflected in the bar-graph on the right of Figure 2. Industrial combustion is seen to be by far the most important single source accounting for about 40 percent of the ambient air quality impact. Power plants and area sources each account for about 25 percent of the ambient air quality impact while industrial processes continues to be the smallest impactor accounting for only about 14 percent.

The data depicted in Figure 2 are a composite of 8 U. S. industrial cities. The data represent calculated annual averages which have been verified against measured annual averages. The verification or correlation with measured annual averages is quite good.

Combustion Sources

Since combustion sources represent the principal source of sulfur dioxide impacting ambient air quality, it is useful to look more

closely at this problem. Industrial combustion sources are characterized by being a large number of individual sources. They span a relatively large size range and relatively large range of different types of combustion from small gas burning systems to large residual oil and coal burning units. In general, they are further characterized as being too small to permit the economic use of desulfurization processes developed for larger power plants.

One obvious possible solution to this segment of the problem is to use low sulfur fuel thereby obviating the sulfur oxide emissions.

Figure 3 shows the relationship between the demand for fossil fuels by the utility industry in the United States over the next 16 years. Also shown is the source of supply of clean fuels supplemented by flue gas cleaning control technology required to achieve Ambient Air Quality Standards.

The principal observations that can be made from this figure are as follows:

1. Naturally occurring low sulfur fuel located in areas where it can be reasonably and economically used is inadequate.
2. Cleaned fuels will not make a significant impact on the supply pattern until the latter half of this decade.

If these projections are correct, they lead to several important conclusions. First, clean fuels is not the answer--at least not for the next 10 years. Second, the shifting of the limited supply of low sulfur fuels from utilities to industrial combustion will help in certain cases, but it is not likely to be a broadly applicable solution.

A key factor limiting the fuel switching approach will be the present ownership and the existence of extant contract arrangements surrounding these low sulfur fuels. Much of the low sulfur coals are captive to industrial processes and will probably not be dedicated to electric power generation. Many utilities have long-term contracts for low sulfur fuel and will understandably not be willing to give up their solution to the air pollution problem to make their low sulfur fuels available to other fuel users. Third, flue gas cleaning will play a principal role in the near future control of sulfur oxides. Flue gas cleaning will undoubtedly be the work-horse of the industry for at least the next ten years.

What Level of Control is Needed

So far, we have considered the average pollution problem--the average source category and the average solution. By considering only the average pollution levels in industrial cities, we can conclude that average reductions in pollutants of 10, 30, or 50 percent can result in meeting Ambient Air Quality Standards.

How meaningful, however, are the averages? For the individual source that must control its emissions to meet regulations, is it possible to control to the average level of reduction needed by the geographical area in which the source is located and meet his emission control obligations? Let's consider this question further.

In order to get an estimate of the level of control that a given individual source would have to achieve, the dispersion model described above was again exercised. The objective was to estimate the control capability that a specific control system would have to be able to achieve when installed on a single source to permit that source to meet applicable regulations. This, after all, is the real question that must be answered by the regulatory agency, the polluter and the research and development community charged with developing control technology to meet the regulatory goals.

Three cities, New York, Philadelphia, and the Niagara Frontier were selected largely because of the availability of data. In each city, the ten most seriously impacted receptor points based on ambient air quality annual averages were used.

For simplicity, the assumption was made that the contributions of electric power generating plants would be eliminated (that is 100 percent control of power plants could be achieved--this permits the most conservative control estimate for other sources). The level of control that would be required by other impacting sources to achieve ambient air quality standards were then calculated. In each case, it was found that greater than 90 percent control would be required for many of principal contributing sources. The calculations did not take into consideration further industrial growth in the areas studied.

While it might be argued that these three cities are not representative of all U. S. industrial cities, it seems almost certain that similar situations will be found in most other industrial cities

in which the impact of one or more sources will be such as to contribute to "hot spots" within that area.

The results of this study serve to establish a reliable estimate of the control capability required of control processes and equipment to deal with specific source problems. As a limit, flue gas desulfurization processes and other methods of control must be capable of at least 90 percent removal.

This is not to say that all processes must be capable of 90 percent SO₂ control. In many cases, lower levels of control will be adequate to meet standards. In marginal cases, processes such as the dry limestone injection process which appears to be capable of only 25 percent SO₂ control may be adequate to permit compliance. Each case must be evaluated in terms of its own unique needs and economics.

Summary

What is the status of sulfur oxide control technology? Many factors enter into the answer. This paper deals with a few of these factors that relate to the current definition of the problem and the current perspective of the need for flue gas desulfurization. In summary, these are as follows:

1. Low sulfur fuel will be a major tool in achieving ambient air quality standards over the next few years.
2. Low sulfur fuel, however, falls far short of being a sufficient solution for SO₂ control.

3. Fuel substitution can and will be used to a limited extent.
Major problems exist of a proprietary, legal and logistical nature that will preclude our approaching the full theoretical potential of fuel substitution.
4. Fuel cleaning technology is at least ten years away from making a major impact on the increased availability of clean fuel.
5. Flue gas cleaning technology is the principal tool available to the Nation for SO_2 control for at least the next 10 years.
6. Industrial combustion is the No. 1 problem source of SO_2 in the United States needing solution.
7. Considerable effort must be made to extend the application of processes which have been designed for utility application to industrial combustion control. In addition, increased attention must be directed toward developing processes uniquely applicable to small industrial combustion, industrial processes and area sources.

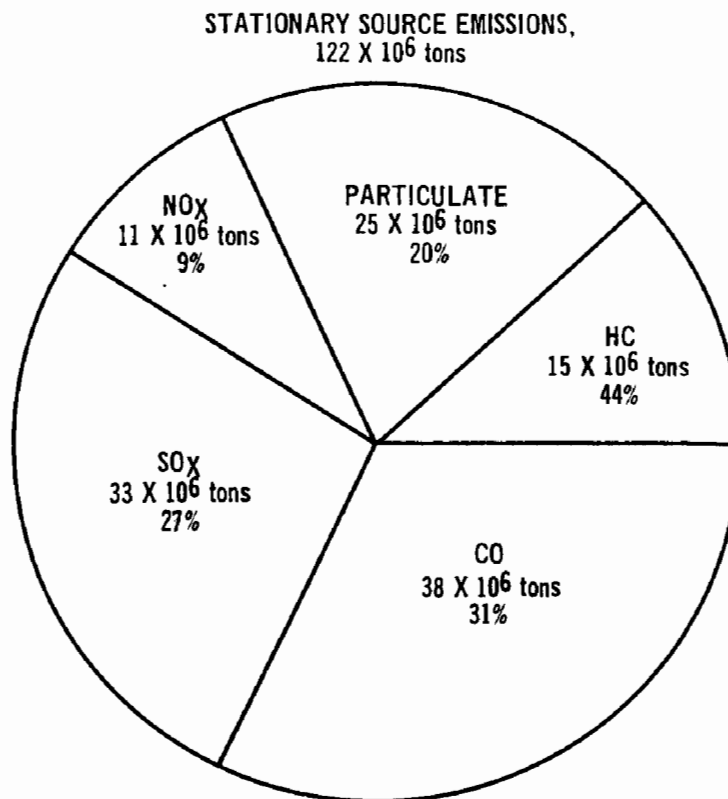
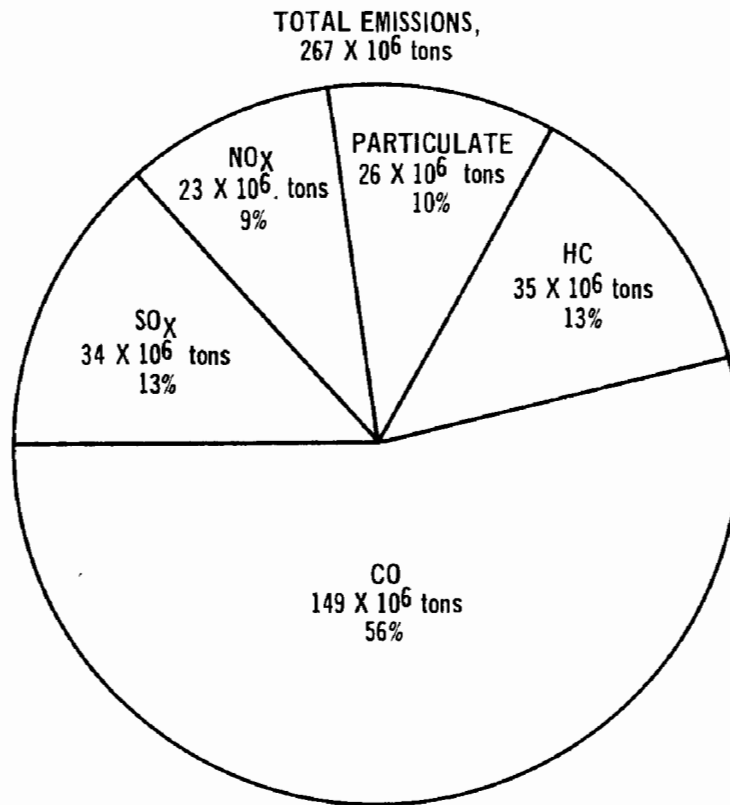


Figure 1. Emission relationships, 1970.

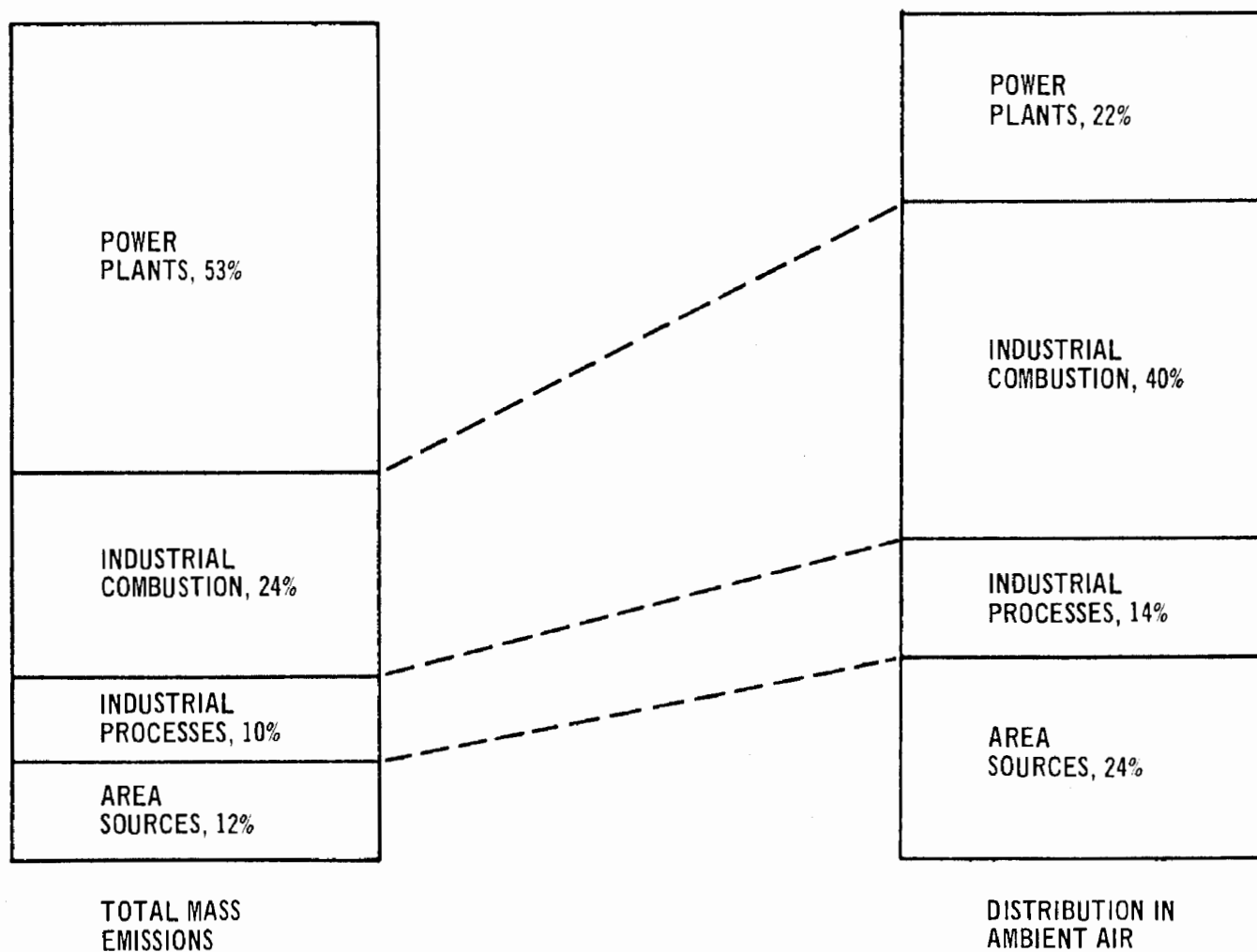


Figure 2. Distribution of SO_x emissions in ambient air.

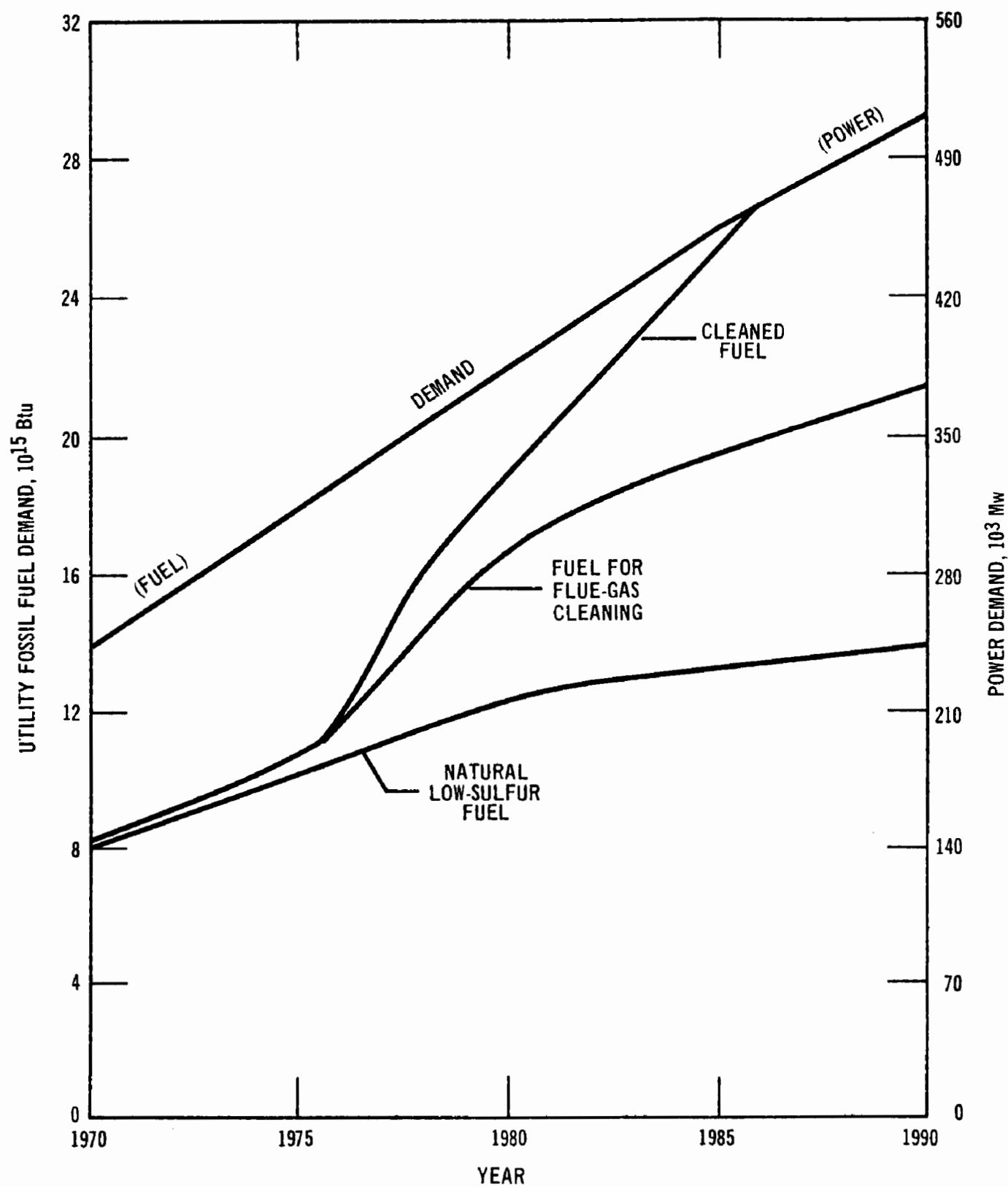


Figure 3. Power demand and utility fossil fuels required to achieve ambient air quality standards.

STATUS OF JAPANESE FLUE GAS DESULFURIZATION TECHNOLOGY

by

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Status of Japanese Flue Gas Desulfurization Technology

Jumpei Ando

Per-capita energy consumption in Japan is now about one-third that in the U.S.A. but consumption per acre of level land is eight times the U.S. figure resulting in serious environmental problems. Stringent regulation of SO_2 emissions has prompted the development of various desulfurization processes. More than 100 commercial and prototype plants for waste-gas desulfurization are on stream now. The present paper will chiefly describe seven of the processes which seem to be of more interest for possible application in the U.S.A.

1 Outline of SO_2 control activity

Recently, about 70% of energy supply in Japan has depended upon imported crude oil. Heavy oil, which is a residue from atmospheric distillation of crude and contains 2-4% sulfur, has been a major fuel for power generation as well as for other industrial activities. Hydrodesulfurization of heavy oil has been carried out since 1967. In 1971, nearly 200 million barrels of heavy oil, about one-fourth of the total quantity of heavy oil consumed in Japan, was subjected to hydrodesulfurization giving 287,000 tons of elemental sulfur as by-product. Still nearly 3 million tons of sulfur in heavy oil burned produced nearly 6 million tons of SO_2 , constituting the chief source of SO_2 emissions. Today's stringent controls on SO_2 emissions have rendered the desulfurized heavy oil, with its 1% or higher sulfur content, unsatisfactory for large power plants.

Under such situation, flue-gas desulfurization has assumed greater importance, which fact has led to construction of more than 100 commercial and prototype plants. Most of the plants built so far are of relatively small capacity, designed to treat waste gas from industrial boilers, chemical and smelting plants, etc. Some of the larger ones are listed in Table 1. Major plants under construction or being designed are listed in Table 2. Nine major power companies, supplying more than 70% of the total electric power needs in Japan, were originally interested in dry processes but have recently decided to build many plants using wet processes because wet processes with reheating of the treated gas have proved to be less expensive than dry processes. With some of the wet processes, moreover, trouble-free continuous operation has been demonstrated and wastewater has been eliminated. The total capacity of the desulfurization plants of the major power companies will increase from 375MW in 1972 to 2,700MW in 1974 and to 4,800MW in 1976.

Most of the desulfurization plants have produced salable by-products such as sodium sulfite, sulfuric acid, and gypsum, because Japan is subject to limitations in domestic supply of sulfur and its compounds as well as in land space available for disposal of useless by-products. As the desulfurization projects are making very rapid progress, however, it is likely that a considerable oversupply will occur in future necessitating abandonment of a substantial portion of the by-products.

Table 1 Major waste-gas desulfurization plants in operation

Process developer	Absorbent	Product	User	Plant site	Unit capacity (1,000scfm)	Date of completion
Kureha Chemical	NaOH	Na_2SO_3	Kureha Chemical	Nishiki	176 ^a , 176 ^a	1968
Showa Denko	NaOH	Na_2SO_3	Ajinomoto	Kawasaki	159 ^b	1971
Wellman-MKK	NaOH	H_2SO_4	Japan Synth. Rub.	Chiba	118 ^a	1971
Wellman-SCEC	NaOH	SO_2 , S	Toa Nenryo	Negishi	35 ^b	1971
Mitsubishi-JECCO	$\text{Ca}(\text{OH})_2$	Gypsum	Kansai Electric	Amagasaki	59 ^a	1972
Mitsubishi-JECCO	$\text{Ca}(\text{OH})_2$	Gypsum	Onahama Smelting	Onahama	54 ^c	1972
Chiyoda	H_2SO_4 , CaCO_3	Gypsum	Fuji Kosan	Kainan	93 ^a	1972
Chiyoda	H_2SO_4 , CaCO_3	Gypsum	Mitsubishi Rayon	Otake	53 ^a	1973
12 Nippon Kokan	NH_3 , $\text{Ca}(\text{OH})_2$	Gypsum	Nippon Kokan	Keihin	88 ^d	1972
Onahama Smelting	MgO	H_2SO_4	Onahama Smelting	Onahama	53 ^c	1972
Chemico-Mitsui	$\text{Ca}(\text{OH})_2$	CaSO_3	Mitsui Aluminum	Omuta	226 ^e	1972
Sumitomo S.M.	Carbon	H_2SO_4	Kansai Electric	Sakai	100 ^a	1971
Mitsubishi H.I.	MnO_x , NH_3	$(\text{NH}_4)_2\text{SO}_4$	Chubu Electric	Yokkaichi	193 ^a	1972
Hitachi Ltd.	Carbon, CaCO_3	Gypsum	Tokyo Electric	Kashima	250 ^a	1972

a: Oil-fired boiler

b: Claus furnace

c: Smelting furnace

d: Sintering plant

e: Coal-fired boiler

Table 2 Major flue-gas desulfurization plants under construction
or being designed (oil-fired boilers)

<u>Process developer</u>	<u>Absorbent</u>	<u>Product</u>	<u>User</u>	<u>Plant site</u>	<u>Capacity (MW)</u>	<u>Date of completion</u>
Wellman-MKK	NaOH	H ₂ SO ₄	Chubu Electric	Nishinagoya	220	1973
Wellman-MKK	NaOH	H ₂ SO ₄	Japan Synth. Rub.	Yokkaichi	160	1974
Wellman-SCEC	NaOH	H ₂ SO ₄	Sumitomo C.C.	Chiba	125	1973
Showa Denko	NaOH, CaCO ₃	Gypsum	Showa Denko	Chiba	200	1973
Shell	CuO	SO ₂ , S	Showa Y.S.	Yokkaichi	42	1973
Mitsubishi-JECCO	Ca(OH) ₂	Gypsum	Tohoku Electric	Hachinoe	125	1974
72 Mitsubishi-JECCO	Ca(OH) ₂	Gypsum	Kansai Electric	Kainan	150, 130	1974
Mitsubishi-JECCO	CaCO ₃	Gypsum	Tokyo Electric	Yokosuka	150	1974
Kureha-Kawasaki	NaOH, CaCO ₃	Gypsum	Shikoku Electric	Shintokushima	150	1974
Kureha-Kawasaki	NaOH, CaCO ₃	Gypsum	Tohoku Electric	Sendai	130	1974
Babcock-Hitachi	CaCO ₃	Gypsum	Chugoku Electric	Mizushima	100	1974
Chiyoda	H ₂ SO ₄ , CaCO ₃	Gypsum	Hokuriku Electric	Shinminato	250	1974
Chiyoda	H ₂ SO ₄ , CaCO ₃	Gypsum	Mitsubishi P.C.	Yokkaichi	240	1974

2 Mitsubishi-JECCO lime (limestone)-gypsum process^{1,2)}

Developer Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo
Japan Engineering Consulting Co.
1-4, Ogawamachi, Kanda, Chiyoda-ku, Tokyo

Process description Waste gas is first washed with water for dust removal and cooling to about 140°F. As the water becomes acidic and dissolves metallic components of dust, it is neutralized with milk of lime to precipitate metallic ions, which are filtered off together with the dust. The filtrate is used for slaking of lime. The cooled gas is then sent to an absorbing step. At three plants built recently two plastic-grid packed absorbers in series, which are put together in one tower, are used as shown in Figure 1. (For new plants which are being designed a one-absorber system will be used.) Milk of lime is fed to the No. 2 absorber. The gas is introduced into the No. 1 absorber and then into the No. 2 absorber. The slurry discharged from the No. 2 absorber is a mixture of calcium sulfite and unreacted lime with a small amount of gypsum. The slurry is then led to the No. 1 absorber, where the remaining lime is reacted to form calcium sulfite, a portion of the sulfite is converted to bisulfite. The pH of the slurry discharged from the No. 1 absorber is 4-4.5. The concentration of the slurries in the absorbers is about 15%. A relatively large liquid/gas ratio (20-50 gal/1,000scf) is used to prevent scaling.

The pH of the slurry is then adjusted to about 4 to promote oxidation in the following step. If required, a small amount of sulfuric acid, normally less than one ton per 100 tons of inlet SO₂, is added to the slurry for the adjustment. The slurry is then sent² to an oxidizing tower where the sulfite and bisulfite are converted to gypsum by air oxidation using rotary atomizers invented by Japan Engineering Consulting Co.(JECCO) at a pressure of 50-57psig and a temperature of 120-180°F. The atomizer is quite effective in producing fine bubbles and is free from scaling, erosion and corrosion. The gas leaving the oxidizer contains some SO₂, and is returned to the absorber. The gypsum is centrifuged. All of² the liquor and wash water are used for the gas washing and cooling step. The gypsum grows into large crystals; its moisture content after centrifugation is only 8-10%. The gypsum thus obtained is of high purity and good quality, which make it suitable for use in cement and gypsum board. The gas from the No. 2 absorber is passed through a demister, reheated, and led to a stack. Wash water of the mist eliminator is also used in the system. Normally no wastewater is emitted from the system. More than 90% of SO₂ is recovered.

State of development Four plants are in operation and five others are being constructed or designed as shown in the following table:

<u>User</u>	<u>Plant site</u>	<u>Capacity (scfm)</u>	<u>Absorbent</u>	<u>Number of absorbers</u>	<u>Year of completion</u>
Nippon Kokan	Koyasu	37,000	$\text{Ca}(\text{OH})_2$	2	1964
Kansai Electric	Amagasaki	59,000	$\text{Ca}(\text{OH})_2$	2	1972
Onahama Smelting	Onahama	54,000	$\text{Ca}(\text{OH})_2$	2	1972
Tomakomai Chemical	Tomakomai	35,000	$\text{Ca}(\text{OH})_2$	2	1972
Kawasaki Steel	Chiba	71,000	$\text{Ca}(\text{OH})_2$	1	1973
Tokyo Electric	Yokosuka	235,000	CaCO_3	1	1974
Kansai Electric	Kainan	235,000	$\text{Ca}(\text{OH})_2$	1	1974
Tohoku Electric	Hachinoe	224,000	$\text{Ca}(\text{OH})_2$	1	1974
Kansai Electric	Kainan	221,000	$\text{Ca}(\text{OH})_2$	1	1974

Status of technology Based on extensive studies with a pilot plant, Mitsubishi has succeeded in scale prevention. Scaling can be prevented by the use of a suitable material, shape, and arrangement of the grid in the absorber, by the adjustment of the slurry concentration and pH as well as of the liquid/gas ratio, by the addition of gypsum crystal seed and thorough mixing of lime and the circulating slurry.

The Amagasaki plant has been in continuous operation since its start in April 1972 except for the period of shutdown of the power plant. The desulfurization plant treats a fraction of flue gas 86,000scfm from a 156MW boiler containing about 700ppm SO_2 to recover about 90% of the SO_2 . The gas velocity in the absorber is about 11 feet/sec. The pressure drop in the whole system including the cooler, absorbers and demister is 6 in. H_2O . More than 95% of calcium sulfite is oxidized into gypsum in the absorbers due to the low SO_2 concentration; the oxidizing tower is almost unnecessary. The amount of water added to the system is maintained equal to that removed from the system by evaporation in the cooler, by hydration of gypsum, etc. No water is wasted from the plant.

The Onahama plant treats 54,000scfm of gas from a copper smelter containing 20,000-25,000ppm SO_2 . More than 99.5% of the SO_2 is recovered with a stoichiometric amount of lime by feeding milk of lime mainly to the No. 2 and partly to the No. 1 absorber. The SO_2 content of the outlet gas is less than 50ppm. The plant came on-stream at the end of October 1972 and has been in continuous operation without trouble except for a period of scheduled shutdown for inspection at the end of November. No scaling was observed at the inspection. The gas supplied from the smelter is a

wet gas at 155°F and results in less evaporation of water in the system. Therefore, the amount of water fed to the desulfurization plant slightly exceeds that by evaporation, hydration, etc. A small amount of water is wasted after being treated for pollution control. About 450 tons/day gypsum is produced; three oxidizing towers are provided for the oxidation of calcium sulfite into gypsum; little oxidation occurs in the absorbers due to the high concentration of SO_2 .

A one-absorber system will be used for the new plants to save investment cost. To ensure high SO_2 recovery excessive amounts of the absorbents, about 105% of stoichiometric for lime and about 110% for limestone, will be used. For pH adjustment prior to oxidation, a considerable amount of sulfuric acid will be required to convert the excessive absorbent to gypsum. Other facilities and treatments are the same as in the two-absorber system.

In the limestone scrubbing plant in Yokosuka, seawater will be used for cooling flue gas from an oil-fired boiler. The seawater is gradually concentrated in the gas-cooler and therefore should be wasted after being duly treated. Salable gypsum of high purity and good quality will be by-produced using limestone as absorbent.

Economics Investment cost for the Amagasaki plant (59,000scfm) was \$1.46 million including various equipment for automatic control and for tests, while that for Tomakomai Chemical (31,000scfm) was \$0.32 million. The cost for larger plants (224,000-235,000scfm) is estimated to be \$2.6-2.9 million in battery limits. The desulfurization cost for a plant to treat 100,000-150,000scfm gas from an oil-fired boiler is estimated at \$0.67-0.88/bl of oil containing 2.5-3.0% sulfur, including depreciation and credit on gypsum at \$6/t.

Advantages High recovery of SO_2 is attained and good-quality gypsum is obtained using either lime or limestone without scaling problems. The rotary atomizer is quite effective for oxidation, involving no operational problem. No water is wasted when gas at temperatures above 250°F is treated. Seawater can be used for cooling, although in this case the used seawater should be discharged.

Disadvantage Lime is more expensive than limestone. Although limestone is used for the absorbent, an appreciable amount of sulfuric acid is required to produce gypsum of high purity and good quality. Oversupply of gypsum might occur within several years if too many gypsum-producing desulfurization plants are built.

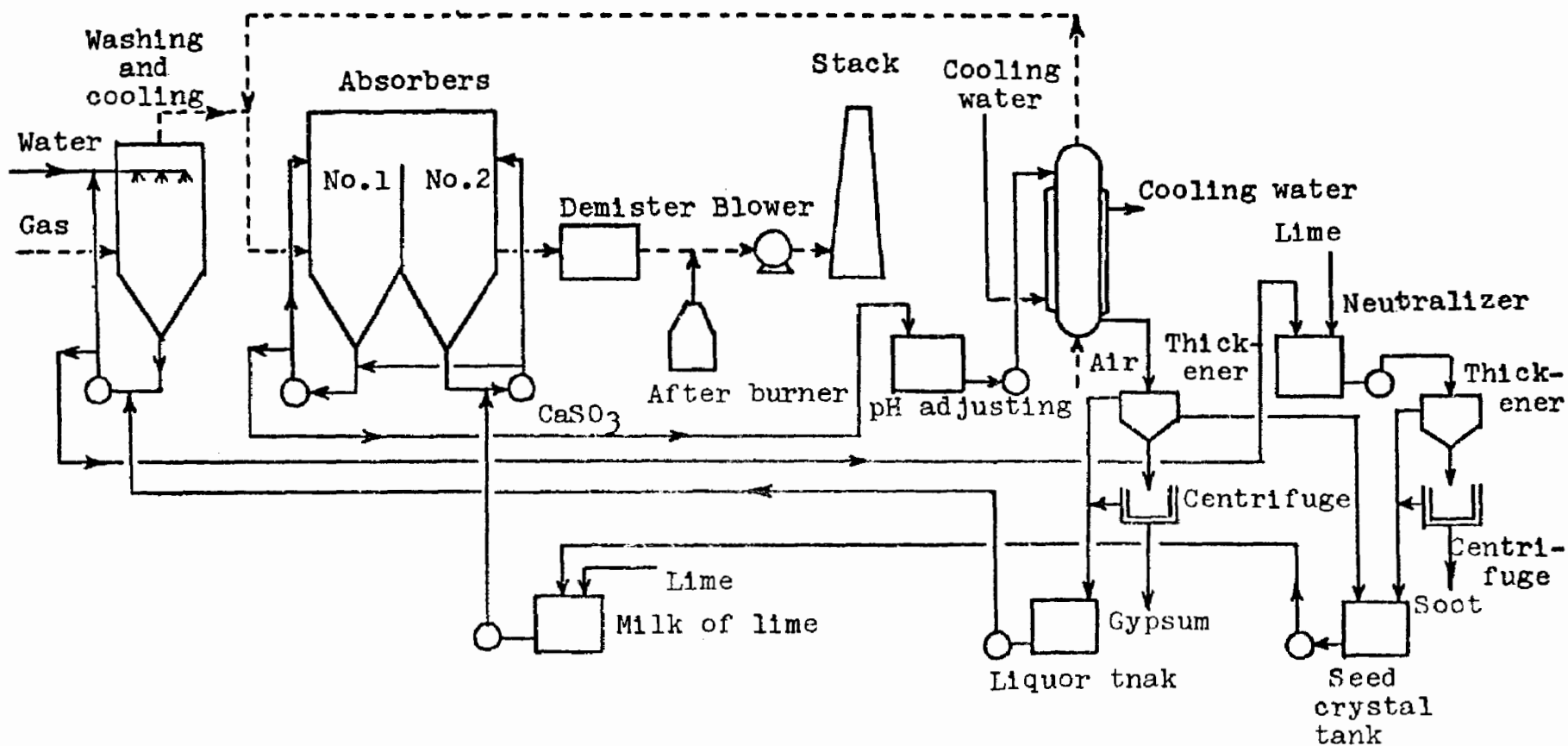


Figure 1 Flow sheet of Mitsubishi-JECCO lime-gypsum process

3 Chemico-Mitsui lime process^{1,2,5)}

Developer Chemico, U.S.A.

Mitsui Aluminum Co. (Miike Power Station), Omuta

Constructor Mitsui Miike Machinery Co. Ltd.

1-1, 2-chome, Muromachi, Nihonbashi, Chuo-ku, Tokyo

Process description Chemico scrubbers (two-stage venturi) are used for SO₂ and dust removal from flue gas from coal-fired boiler (156MW). Carbide sludge (primary calcium sulfite) is used as absorbent. Figure 2 presents a description of the total scrubber system. The flue gas (302,000scfm) after passing through an electrostatic precipitator contains 0.3 grain/scf of dust and 1,800 to 2,200ppm of SO₂ at 300°F. About 75% of the gas is handled by the scrubber. Two scrubbers were installed but one of them has been used with the other as a back-up. The gas flows down through the first venturi section, up through the mist eliminator section, then passes through the second venturi and mist eliminator sections, is reheated and exhausted to a stack along with the unscrubbed fraction of the gas. Milk of lime is mixed with the discharge from the second venturi; the mixed slurry is partly recycled to the second venturi and partly fed into a delay tank. The slurry in the delay tank is sent to the first-stage venturi. The discharge from the first venturi, consisting mainly of calcium sulfite with small amounts of calcium sulfate, unreacted calcium hydroxide and fly ash, is sent partly to a delay tank and partly to a disposal pond about a mile from the plant. The decanting or settling of the solids takes place there and the supernatant from the pond is recycled to the scrubbing system to prepare milk of lime and also to wash mist eliminators. The outlet gas from the scrubber contains 0.1 grain/scf of dust and 200 to 300ppm of SO₂.

Status of technology The scrubber is 33 feet in diameter and 66 feet high, is constructed of stainless steel, and is lined with glass flake reinforced polyester material. The following operation conditions have been used:

L/G (venturi + spray) 1st stage, 46 to 59 gal/1,000scf

2nd stage, 42 to 55 gal/1,000scf

Stoichiometry 100 to 105% as pure Ca(OH)₂

Percentage solids in slurry 3-5%

Total pressure drop 16 in.H₂O

Prior to the completion of the plant, extensive pilot plant tests were carried out by Mitsui Aluminum Co. leading to the establishment of operation know-how for scale prevention. Precise control of pH to a certain narrow range is important for the scale prevention.

State of development Operation of the commercial plant started in March 1972. After 8 months of satisfactory continuous operation, the plant was subjected to a scheduled shutdown for inspection, which revealed essentially no scaling. Operation was resumed soon and has since been

carried out smoothly. The waste disposal pond has a capacity for holding solids discharged over a period of several years. However, to eliminate any possible pollution with sulfite ion in wastewater which could be emitted when the facilities are cleaned in a periodical shutdown of the plant for inspection, some means of converting calcium sulfite to gypsum will be adopted within 1973. Tests have shown that the gypsum can be used for gypsum board and cement although it contains a small amount of fly ash.

Economics The commercial plant cost \$3.3 million including two scrubbers. The desulfurization cost is a little less than 1 mil/kWh. About 70% of the desulfurization cost is accounted for by depreciation and interest.

Advantages Stable operation without scale formation is achieved, removing both SO_2 and dust satisfactorily. Carbide sludge, a cheap source of lime, is used. The Chemico scrubber is suited for treating a large amount of gas.

Disadvantage Large amounts of slurry and water must be recycled because of the use of high L/G and low slurry concentration in order to ensure scale prevention.

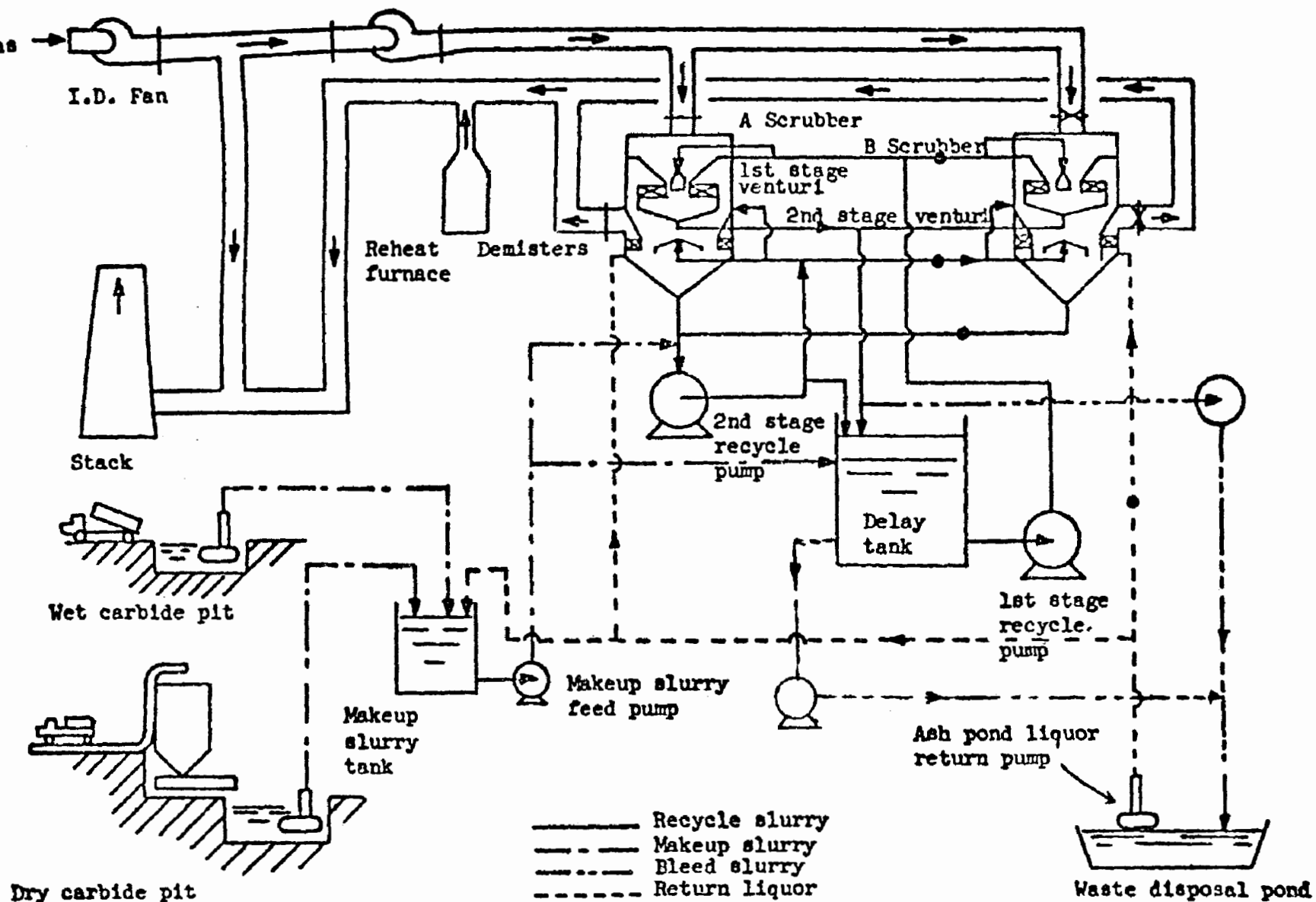


Figure 2 Mitsui-Chemico lime process

4 Chiyoda dilute sulfuric acid process ^{1,2,3)} (Thoroughbred 101 process)

Developer Chiyoda Chemical Engineering & Construction
1580 Tsurumi-cho, Tsurumi-ku, Yokohama

Outline of the process Flue gas is washed with dilute sulfuric acid which contains an iron catalyst and is saturated with oxygen. SO_2 is absorbed and converted to sulfuric acid. Part of the acid is reacted with limestone to produce gypsum. The rest is diluted with gypsum wash water and returned to the absorber.

Description A flow sheet is shown in Figure 3. Flue gas is first treated by a prescrubber to eliminate dust and to cool the gas to 140°F . The cooled gas is led into a packed tower absorber containing 1 inch Telleretts. Dilute sulfuric acid (2 to 5% H_2SO_4) which contains ferric ion as a catalyst and is nearly saturated with oxygen, is fed to the packed tower. About 90% of SO_2 is absorbed, and partly oxidized into sulfuric acid.

The product acid is led to the oxidizing tower into which air is bubbled from the bottom to complete the oxidation. Most of the acid at $120\text{--}150^\circ\text{F}$ nearly saturated with oxygen is returned to the absorber. Part of the acid is treated with powdered limestone (minus 200 mesh) to produce gypsum. A special type of crystallizer has been developed to obtain good crystalline gypsum 100 to 300 microns in size. The gypsum is centrifuged from the mother liquor and washed with water. The product gypsum is of good quality and salable.

The mother liquor and wash water are sent to the scrubber. The amount of input water--wash water and the water to the prescrubber--is kept equal to the amount of water lost by evaporation in the scrubbers and by hydration of gypsum. No wastewater is emitted.

State of development The operation of a pilot plant (6,000scfm) has led to the construction of the following commercial plants:

Commercial plants by Chiyoda process

<u>User</u>	<u>Plant site</u>	<u>Source of gas</u>	<u>Size, scfm</u>	<u>Completion</u>
Nippon Mining	Mizushima	Claus furnace	20,600	October 1972
Fuji Kosan	Kainan	Oil-fired boiler	94,100	October 1972
Mitsubishi Rayon	Otake	Oil-fired boiler	52,900	December 1973
Tohoku Oil	Sendai	Claus furnace	8,200	January 1973
Daicel Ltd.	Aboshi	Oil-fired boiler	59,000	October 1973
Hokuriku Electric	Shinminato	Oil-fired boiler	442,000	June 1974
Mitsubishi Petrochem.	Yokkaichi	Oil-fired boiler	413,000	December 1974

Status of technology The iron catalyst is less reactive at low temperature but is as reactive as manganese catalyst at operation temperatures above 120°F (Figure 4). It is not poisoned by impurities in the gas, even when flue gas from a coal-fired boiler is used. Catalyst loss is very small (Figure 5). The towers of the commercial plants are provided with rubber or FRP linings. Stainless steel is also usable; the ferric catalyst works also as a corrosion inhibitor.

A large L/G ratio is required to attain high SO₂ recovery as shown in Figure 6; large pumps and fairly large absorber and oxidizer are required as shown in the following table.

Size of towers (feet)

<u>Capacity (scfm)</u>	<u>Absorber</u>		<u>Oxidizer</u>	
	<u>Diameter</u>	<u>Height</u>	<u>Diameter</u>	<u>Height</u>
117,600	29.7	49.5	13.4	62.7
294,100	49.5	49.5	21.1	62.7

A double-cylinder type reactor (Figure 7) including an oxidizing section in the center and a scrubbing section in the outer part has been developed recently instead of using two towers. The absorbing liquor goes down the scrubbing section, then goes up in the oxidizing section and overflows to the scrubbing section. The reactor enables some savings to be made in floor space and investment cost.

Advantages The process is simple and the plant is easy to operate. Even in the event that the gypsum-producing system has to be stopped for a day or two for repairs, the absorbing system can be operated continuously. The concentration of sulfuric acid increases by 1 or 2% in this case but SO₂ recovery is not decreased. Catalyst is cheap and is not poisoned by impurities in the gas. Salable gypsum of good quality is obtained from limestone without scaling problems.

Disadvantage Large pumps and a fairly large scrubber and oxidizer are required. A large L/G is required when SO₂ concentration of inlet gas is high.

Cost estimation* (\$1 = ¥308)

(Inlet gas SO₂ 1,000ppm, dust 0.08 grain/scf)

(Outlet gas SO₂ 100ppm, dust 0.04 grain/scf)

	<u>Capacity</u>		
	800MW (1.51 x 10 ⁶ scfm)	500MW (0.95 x 10 ⁶ scfm)	250MW (0.475 x 10 ⁶ scfm)
Plant cost (\$) (A)	17.2 x 10 ⁶	12.5 x 10 ⁶	7.0 x 10 ⁶
Fixed cost (\$/year) (B)	3.10 x 10 ⁶	2.25 x 10 ⁶	1.26 x 10 ⁶
Direct cost (\$/year)			
Limestone (0.25¢/lb)	430,000	272,000	135,600
Electricity (0.7¢/kWh)	789,000	529,000	308,000
Water (8¢/1,000 gal.)	25,400	17,000	8,400
Fuel oil (\$3.18/bl)	1,035,400	648,700	325,600
Steam (0.12¢/lb)	39,700	25,100	12,600
Catalyst (6¢/lb)	11,000	8,000	4,000
Labor (\$12,000/year/capita)	144,000	96,000	96,000
Maintenance	344,000	250,000	140,000
Subtotal (C)	2,818,500	1,845,800	1,030,200
Net running cost (B + C = D)	5,918,500	4,095,800	2,290,200
Overhead (E) (12% of C)	338,200	221,500	123,600
Running cost (D + E)	6,256,700	4,317,300	2,413,800
Desulfurization cost { (\$/bl)	0.645	0.712	0.797
without by-product credit { (\$/MWhr)	0.992	1.095	1.225

* Estimation made by Chiyoda in February 1973

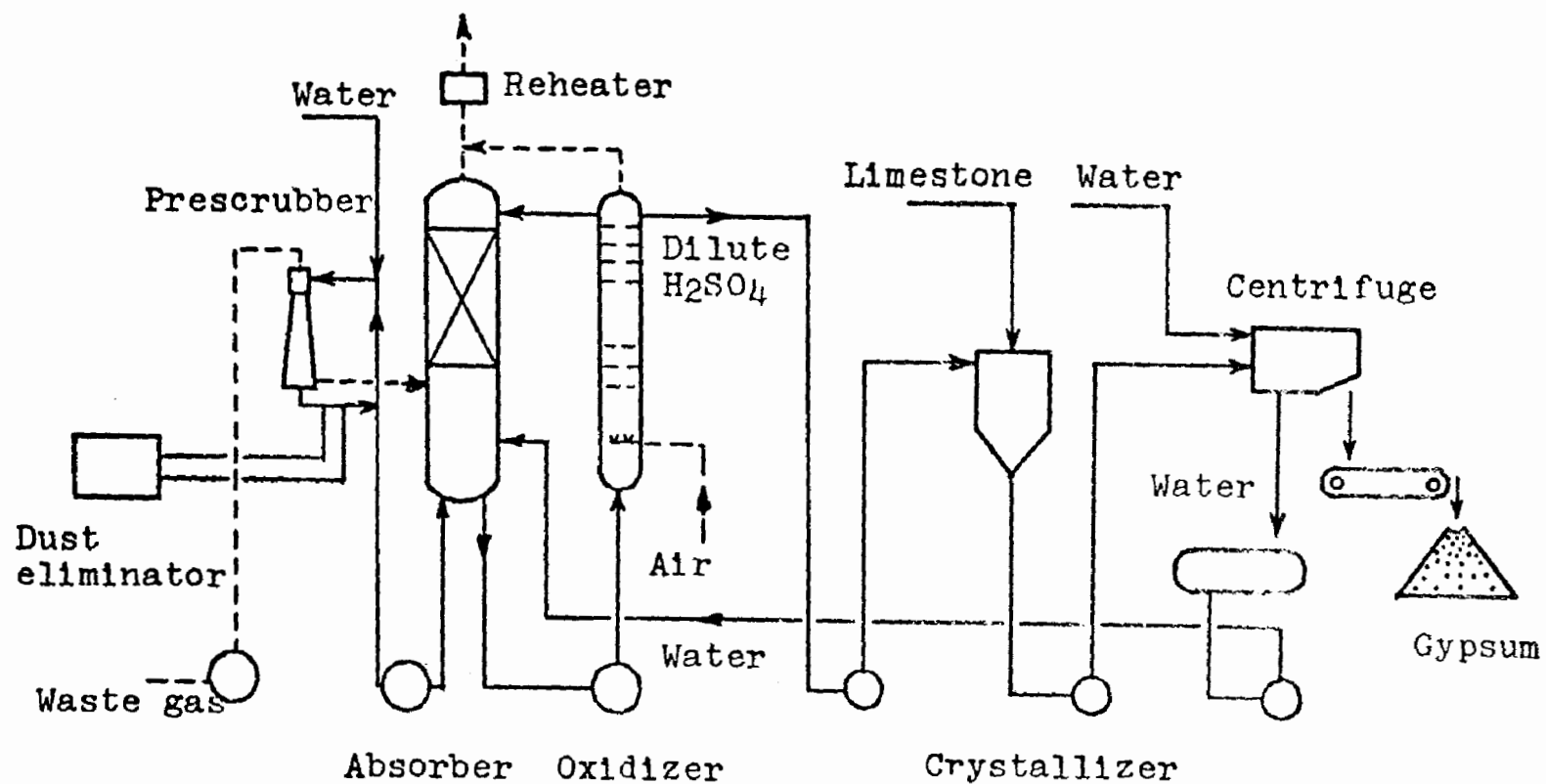


Figure 3 Flow sheet of Chiyoda Thoroughbred 101 process

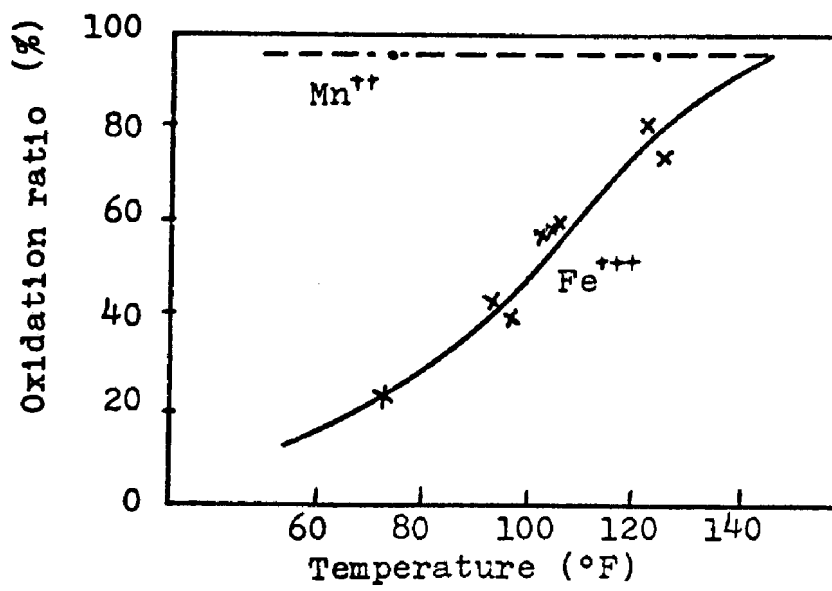


Figure 4 Temperature and oxidation ratio with catalysts

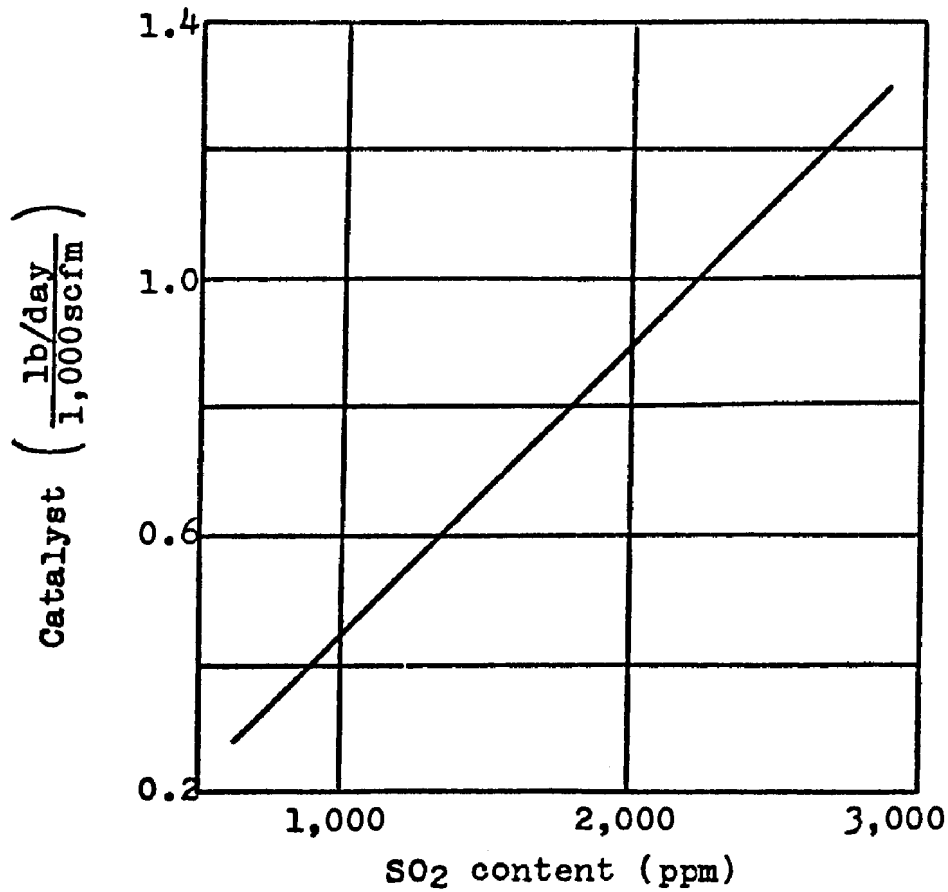


Figure 5 Catalyst requirement

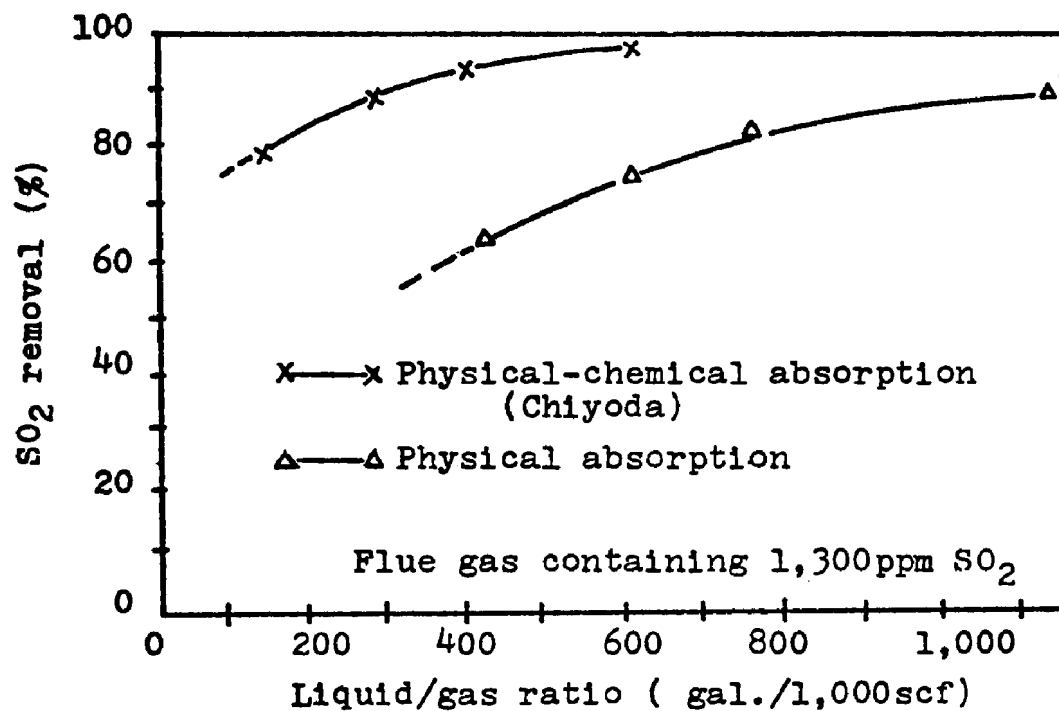


Figure 6 Liquid/gas ratio and SO₂ removal

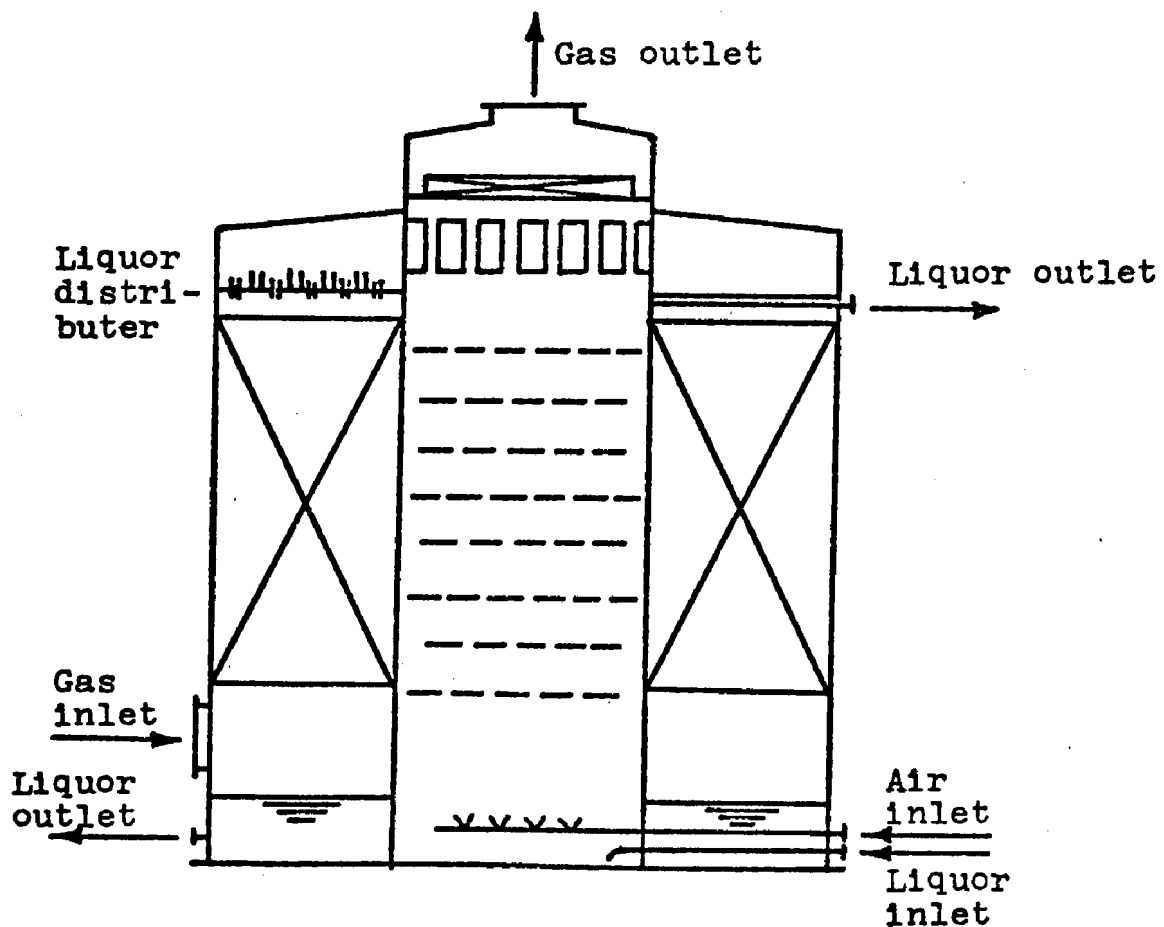


Figure 7 Double-cylinder type reactor

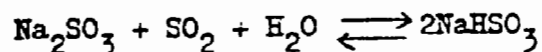
Developer Wellman-Lord, U.S.A.

Mitsubishi Chemical Machinery (MKK)

6-2, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description Flue gas is first washed by a prescrubber installed in the lower part of the sieve tray absorption tower (Figure 8).

The partially cleaned gas rises in the tower while contacting a countercurrent flow of a concentrated sodium sulfite solution which eliminates more than 90% of the inlet SO_2 to form sodium bisulfite. Mist droplets are removed by the eliminator and demister combination in the upper part of the tower and the gas is discharged at about 265°F after reheating in the oil-fired after-burner. A sodium bisulfite solution is discharged from the absorption tower and is stored in a surge tank before it is sumped to an evaporator. In the evaporator the sodium sulfite solution is heated with steam and decomposed into SO_2 gas and sodium sulfite.



The SO_2 concentration in the gas leaving the evaporator is 90% after the water vapor is condensed in a cooler. In this evaporator, sodium sulfite is gradually concentrated and crystallized. The crystalline sodium sulfite is centrifugally separated from the mother liquor, dissolved in a condensate from the cooler, and the solution is recycled to be used as absorbent. The recovered SO_2 is used for sulfuric acid production. Tail gas from the acid plant is led into the absorption tower.

Sodium sulfite is gradually oxidized into sulfate by the oxygen in the flue gas. To keep Na_2SO_3 concentration to a minimum and optimum figure, a small portion of the mother liquor is purged; this purge liquor is used for gas cleaning in the prescrubber. The bleed is taken off this prescrubber circuit for the purpose of removing contaminants, which otherwise would build up in the system. The major contaminants are sodium sulfate and sodium polythionate. The purge stream is subjected to wastewater treatment that involves the following: (1) addition of H_2SO_4 to convert NaSO_3 and NaHSO_3 to Na_2SO_4 ; SO_2 evolved is sent to the sulfuric acid plant; (2) alkali is added to form the hydroxide of soluble metal ions (vanadium, nickel, iron); this precipitates them as hydroxides; (3) removal of solids by filtering; (4) neutralization by adding H_2SO_4 . The final wastewater is a largely clear concentrated solution of sodium sulfate. This effluent eventually is sent to the bay.

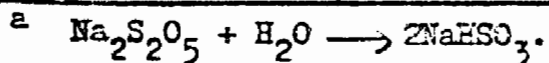
State of development A commercial plant designed to treat 118,000scfm of flue gas from oil-fired boilers has been in operation since June 1971 at Chiba plant, Japan Synthetic Rubber Co. A larger plant with a capacity of treating 365,000scfm of flue gas from oil-fired boilers is under construction at Nishinagoya Station, Chubu Electric Power Co. to start operation in July 1973. It has been recently decided to build a 237,000scfm plant (flue gas from oil-fired boiler) for Japan Synthetic Rubber Co. at Yokkaichi.

Status of technology In Chiba plant, Japan Synthetic Rubber, flue gas from two oil-fired boilers (130 tons/hr each) is treated by two 16-ft

square sieve tray absorption towers at a rate of 90,000scfm per absorber. The plant came on-stream in June 1971 and has been operated for more than 8,000 hours in a year. The SO_2 concentration in inlet gas normally ranges from 1,000 to 2,000ppm and that in outlet gas from 100 to 200ppm.

The major problem associated with the process is the necessity to bleed a waste stream from the absorber liquor circuit to avoid build-up of contaminants, primarily sodium sulfate. The following tabulation summarizes the present composition of absorber and waste streams:

	<u>Absorber feed</u>	<u>Absorber out</u>	<u>Wastewater to treatment</u>	<u>Wastewater after treatment</u>
Na_2SO_3	16-19% by wt	2-4%	0	0
$\text{Na}_2\text{S}_2\text{O}_5^a$	0	14-17%	4-6%	0
Na_2SO_4	5-7%	5-7%	3-6%	7-16%
Suspended solids	-	-	1-2% (10,000-20,000ppm)	2-10ppm
pH	-	-	5-5.5	7±0.1
COD	-	-	20,000ppm	200ppm
Flow rate	-	-	-	1-1.5 tons/hr



Clear sodium sulfate solution is emitted from Chiba plant. In new plants to be built in future, the sodium sulfate solution will be evaporated to produce solid sodium sulfate as a by-product or treated with lime to precipitate gypsum and to recover a sodium hydroxide solution, thus eliminating the wastewater.

Economics The investment cost of the Chiba plant was \$2,600,000 including the cost for sulfuric acid plant. The plant consumes approximately 755,000bbl/year of fuel and produces 13,200 tons/year of sulfuric acid. The requirements of the desulfurization plant are shown below.

Make-up caustic soda	3-4 lb/bl oil for 86-93% recovery of SO_2
After-burner fuel	10.5 lb/bl oil to heat to 266°F
Steam	175 lb/bl oil
Cooling water	6.5 tons/bl oil

The investment cost for Nishinagoya plant, Chubu Electric (365,000scfm) is \$5,200,000 including the sulfuric acid plant with a capacity of 90 tons/day.

Advantages Stable reliable operation. High recovery of SO_2 . The sulfuric-acid plant is much smaller than usual because the concentrated SO_2 recovered is used.

Disadvantage The treatment of sodium sulfate formed by the oxidation is not simple.

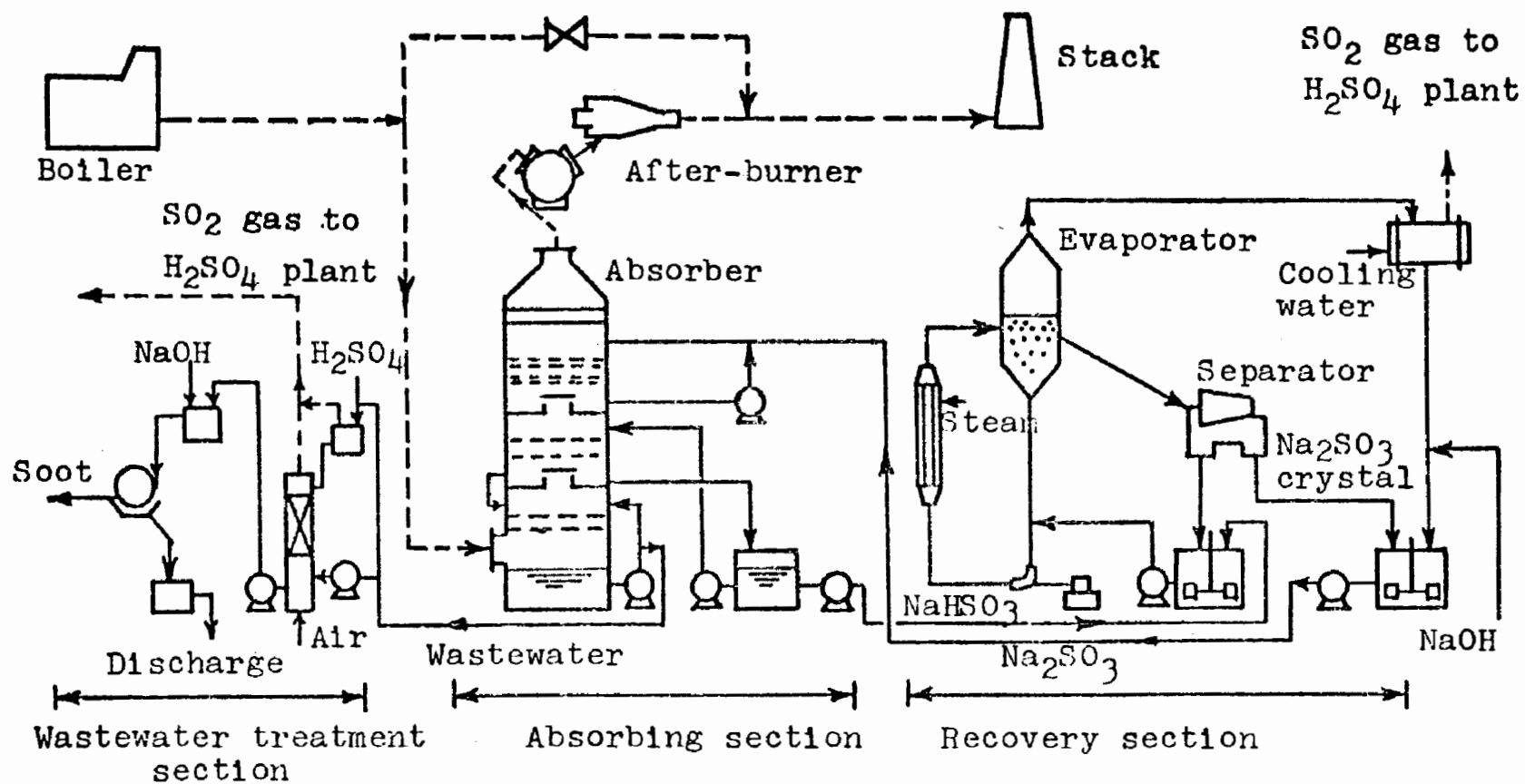


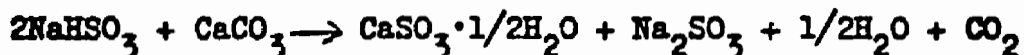
Figure 8 Wellman-MKK process

6 Kureha sodium-limestone process 1.2)

Developer Kureha Chemical Industry Co.
1-8, Horidomecho, Nihonbashi, Chuo-ku, Tokyo

State of development Kureha first developed a sodium scrubbing process to produce solid sodium sulfite to be sold to paper mills. In addition to two 176,000scfm plants operated by Kureha since 1969, two plants have been licensed, one to Mitsui Toatsu Chemical (112,000scfm) which began operation in September 1971, and the other to Konan Utility (123,000scfm) which started operation in late 1972. Since the demand for sodium sulfite is limited, Kureha has recently developed a sodium-calcium double-alkali process. Tests with a small pilot plant led to the construction of a larger pilot plant (3,000scfm) which has been in operation since July 1972. The larger pilot plant program is a joint effort with Kawasaki Heavy Industries. Two commercial plants will be completed in 1974 to treat flue gas from oil-fired boilers at power companies, one at Shinsendai station, Tohoku Electric Power (150MW), and the other at Shintokushima station, Shikoku Electric Power (150MW).

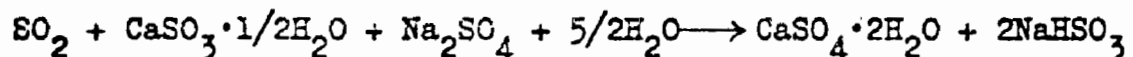
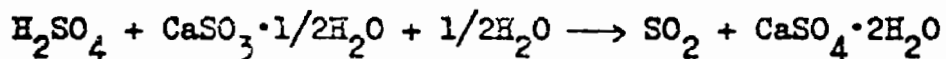
Process description A flow sheet of the sodium-calcium process is shown in Figure 9. The scrubbing system consists of a venturi scrubber where water is used to remove particulates and to cool the gas followed by a rubber-lined, grid-packed scrubber where SO_2 is absorbed in a sodium sulfite solution. The water from the dust scrubber is discharged at a pH of about 2.5. The pH of the liquor from the absorber is controlled to 6.0-6.5. With an inlet concentration of 1,500ppm SO_2 , 98% removal is achieved; the liquid gas ratio is 7gal/1,000ft³ of gas. The feed to the absorber contains 20-25% sodium sulfite and has a pH of 7-8; the calcium content was reported to be about 30ppm. The scrubber discharge contains about 10% sodium sulfite, 10% sodium bisulfite, and 2-5% sodium sulfate. Limestone pulverized in a wet mill equipped with a cyclone classifier is fed continuously along with scrubber liquor into an atmospheric pressure vessel where sodium bisulfite reacts with limestone to form calcium and sodium sulfites.



The reaction temperature is somewhat higher than the scrubber temperature which is about 140°F; residence time for conversion is about 2 hours. The slurry from the decomposer is passed through a centrifuge where the calcium sulfite crystals are separated from sodium sulfite liquor, which is then returned to the scrubber.

The calcium sulfite is reacted with air at atmospheric pressure in an oxidizer developed by Kureha. Gypsum is removed from the oxidizer discharge stream by a centrifuge. The product is suitable for use in wallboard and cement.

Oxidation of sulfite in the scrubbing and decomposition steps results in the formation of sodium sulfate which cannot be regenerated by reaction with limestone. In order to control the sulfate level, a sidestream from the scrubber discharge is mixed with calcium sulfite crystals and sulfuric acid is added. The net effect is to convert the sodium sulfate to calcium sulfate and produce sodium bisulfite for recycle. Gypsum is separated by a centrifuge and added to the oxidizer loop.



Status of pilot plant operation The pilot plant (3,000scfm) has been operated continuously since its completion in July 1972 except for the scheduled shutdown for inspection in September and December. Almost no scaling was observed. Operation of the centrifuges has given effective separation of solid and liquid phases. Both calcium sulfite and gypsum discharged from the centrifuge are dump solids which can be transported by solid-handling equipment, if desired. The crystals of gypsum grow to around 100 microns. The flue gas contains about 6% oxygen. About 7% of the recovered SO_2 is oxidized to form sodium sulfate. The sulfuric acid requirement for the decomposition of the sulfate is 125% of the theoretical amount. Therefore, about 8.7% of the product gypsum is derived from sulfuric acid.

Economics For the production of a ton of gypsum, 1,200 lb of limestone, 18 lb of caustic soda (100%) for make-up, 100 lb of sulfuric acid (98%), 340kWh of electric power, 1,460 lb of steam, and 18 tons of water are required. Investment cost is uncertain, but the investment requirement would be split among the process steps as follows:

Absorption 30%, Decomposition 30%, Sulfate conversion 10%,
Oxidation 30%.

Advantages High recovery of SO_2 is achieved with limestone. No scaling. Sodium sulfate is decomposed to recover sodium bisulfite and gypsum. Good quality of salable gypsum is obtained. Both gypsum and calcium sulfite discharged from the centrifuge have less moisture and are easy to handle.

Disadvantages The process is less simple than the lime-gypsum process. The use of a considerable amount of sulfuric acid is disadvantageous for plants where the product calcium sulfite or gypsum must be discarded.

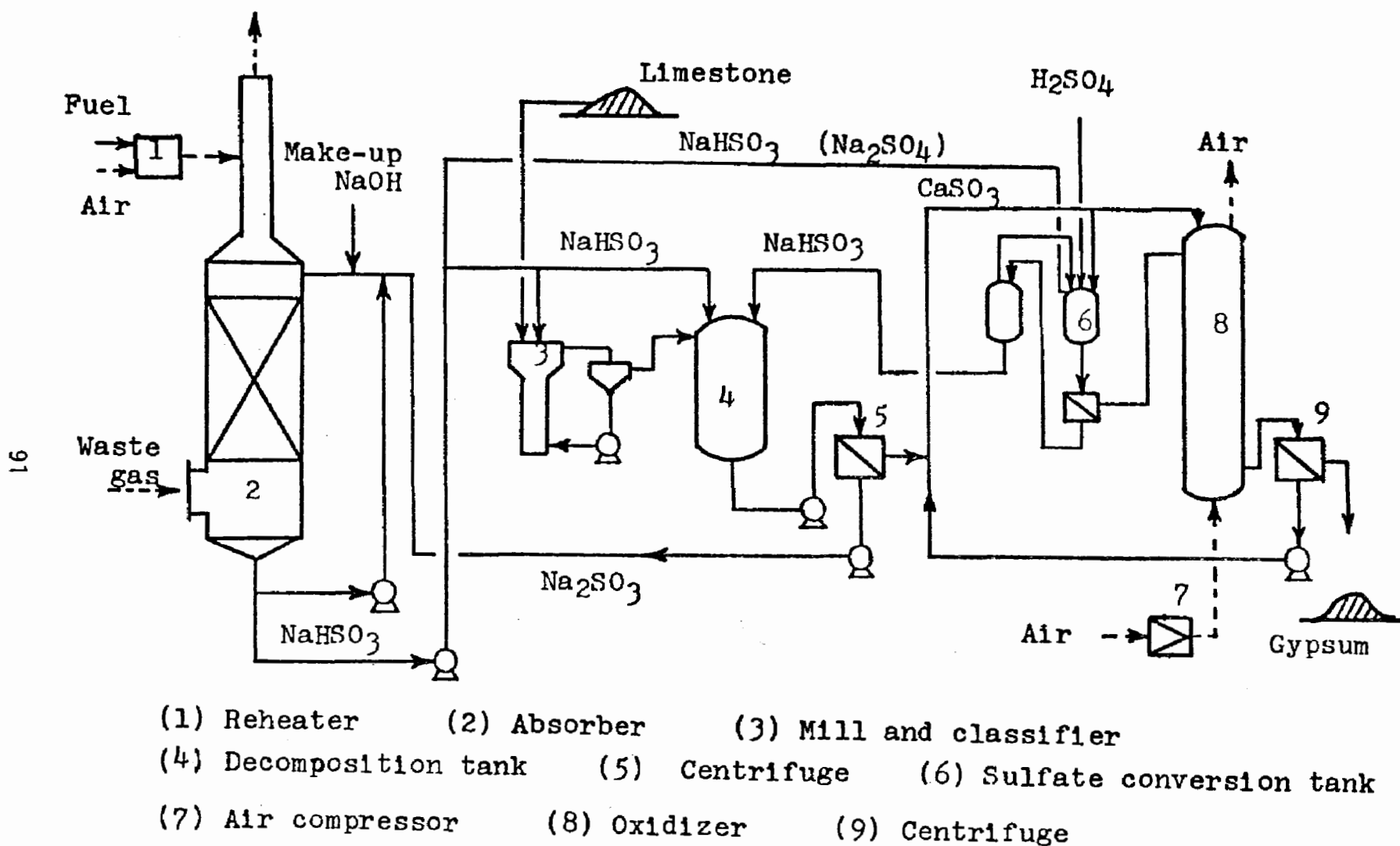


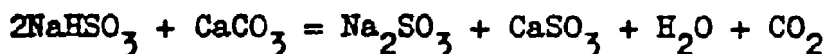
Figure 9 Flow sheet of Kureha sodium-limestone process

7 Showa Denko sodium-limestone process^{1,2)}

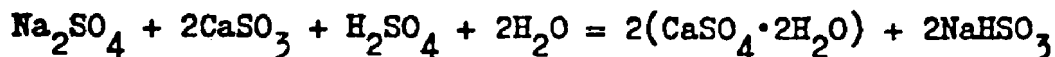
Developer Showa Denko K.K.
34, Shiba Miyamotocho, Minato-ku, Tokyo
Ebara Manufacturing Co. Ltd.
11-1, Asahimachi, Haneda, Ota-ku, Tokyo

State of development Showa Denko, jointly with Ebara, recently constructed commercial plants for SO₂ recovery by sodium scrubbing to produce sodium sulfite for paper mills.² The plants include Kawasaki plant (88,000scfm) of Showa Denko, Kawasaki plant (159,000scfm) of Ajinomoto, and Yokohama plant (142,000scfm) of Asia Oil for flue gas from oil-fired boilers, and Sodegaura plant (47,000scfm) of Nippon Phosphoric Acid to treat tail gas from a sulfuric acid plant. As demand for sodium sulfite is limited, Showa Denko and Ebara have started joint tests on sodium-calcium process to by-produce salable gypsum. A pilot plant (5,900scfm) has been in operation at Kawasaki plant of Showa Denko since 1971. A commercial plant to treat 340,000scfm of flue gas is being constructed at Chiba plant, Showa Denko, to start operation in June 1973.

Process description The Showa Denko-Ebara process features the use of a vertical-cone type absorber as shown in Figures 10 and 12. A liquid (sodium sulfite solution) is charged from the bottom, blown up by the gas to absorb SO₂, and flows back to the liquor inlet by gravity. Very good contact between gas and liquid particles is attained ensuring 95-98% desulfurization at a liquid/gas ratio of 7-14 gal./1,000scf (Figure 11). Pressure drop ranges from 8 to 15 in.H₂O. A flow sheet of the sodium-calcium process is shown in Figure 12.² Flue gas from an oil-fired boiler containing 1,500ppm SO₂ and about 1 grain/cf dust is led directly into the scrubber; 95% of the SO₂ and about 60% of the dust is removed by a sodium sulfite solution. Most of the liquor discharged from the scrubber is recycled to the scrubber. A portion of the liquor is led to a reactor and treated with pulverized limestone.



The calcium sulfite is separated from the sodium sulfate solution; the solution is returned to the scrubber. Calcium sulfite is oxidized in an oxidizer to form gypsum. As sodium sulfate gradually forms in the solution and tends to accumulate, a portion of the liquor discharged from the scrubber is sent to a sulfate conversion step to maintain the sulfate concentration at a certain level. In the conversion step, the sulfate is treated with calcium sulfite and sulfuric acid to produce gypsum and sodium bisulfite.



The bisulfite solution is led to the reactor.

Status of technology The pilot plant has been operated for more than one year without serious trouble. Both lime and limestone have been used for comparison. Limestone reacts slowly with sodium bisulfite requiring a few hours. By using lime the reaction proceeds rapidly. However, limestone will be used in the commercial plant because it is much cheaper than lime, and moreover, larger crystals of gypsum is obtained with limestone. An oxidizer developed by Showa Denko and Ebara will be used in the commercial plant. The oxidation proceeds a little more slowly but the crystals of gypsum grow larger than with a rotary atomizer developed by JECCO.

Advantages The scrubber is very effective for desulfurization. High recovery of SO_2 is achieved consuming limestone.

Disadvantages The process is less simple than the lime-gypsum process. The use of a considerable amount of sulfuric acid is a demerit for plants whose by-product gypsum or calcium sulfite must be discarded.

Economics The estimated desulfurization cost for a 120,000scfm plant for 95% removal of SO_2 is shown below.

Plant cost \$1.7 million
 7,000 hours operation in a year
 By-product gypsum 192,000 tons/year

		Requirements (lb per bl oil)			
NaOH	H_2SO_4	CaO	Water	Steam	Electricity
0.56	5.0	35.8	560	0.38	10(kWh)
Variable cost		\$0.331/bl oil			
Fixed cost		\$0.687/bl oil			
Desulfurization cost		\$1.018/bl oil (without credit for gypsum)			
		\$0.936/bl oil (with credit for gypsum)			

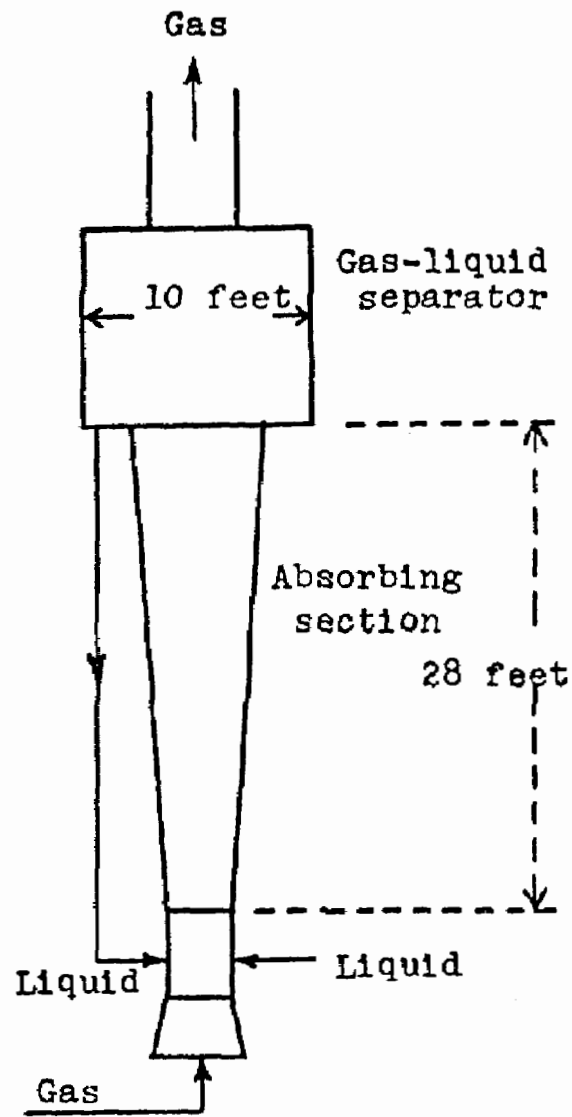


Figure 10 Vertical-cone type absorber for 60,000acfm

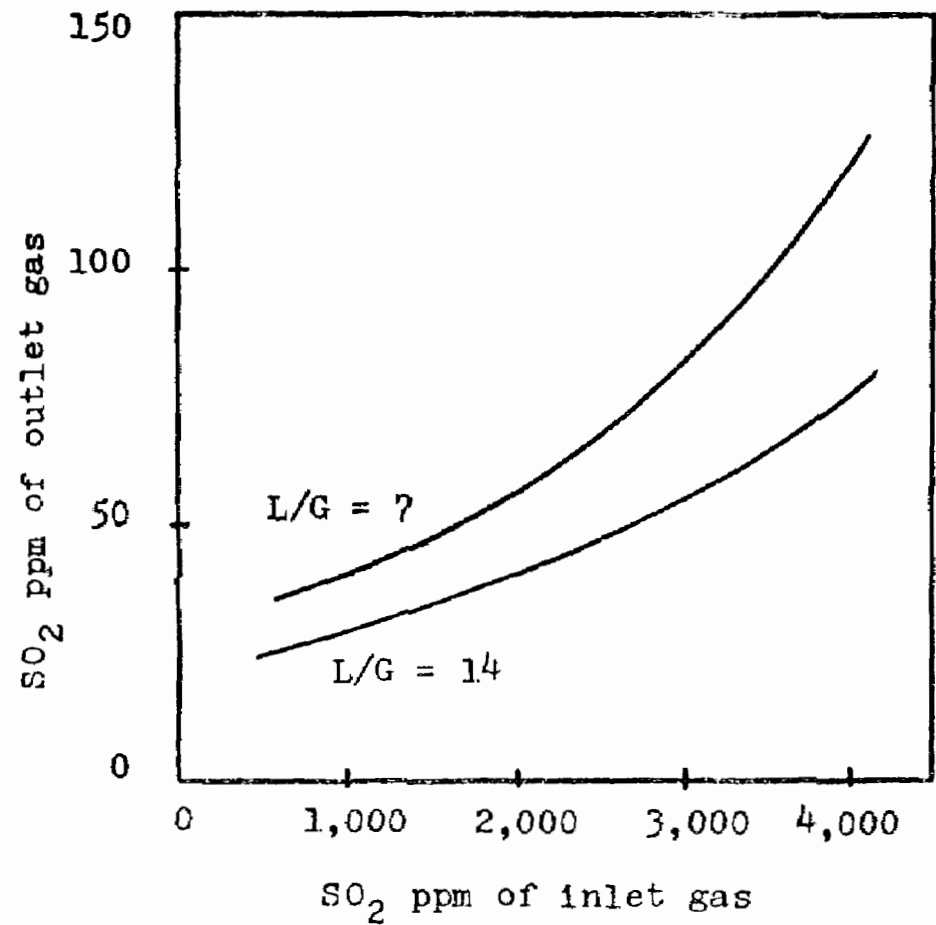


Figure 11 Relation between liquid/gas ratio (gal./1,000scf) and SO₂ removal (pH 6.5)

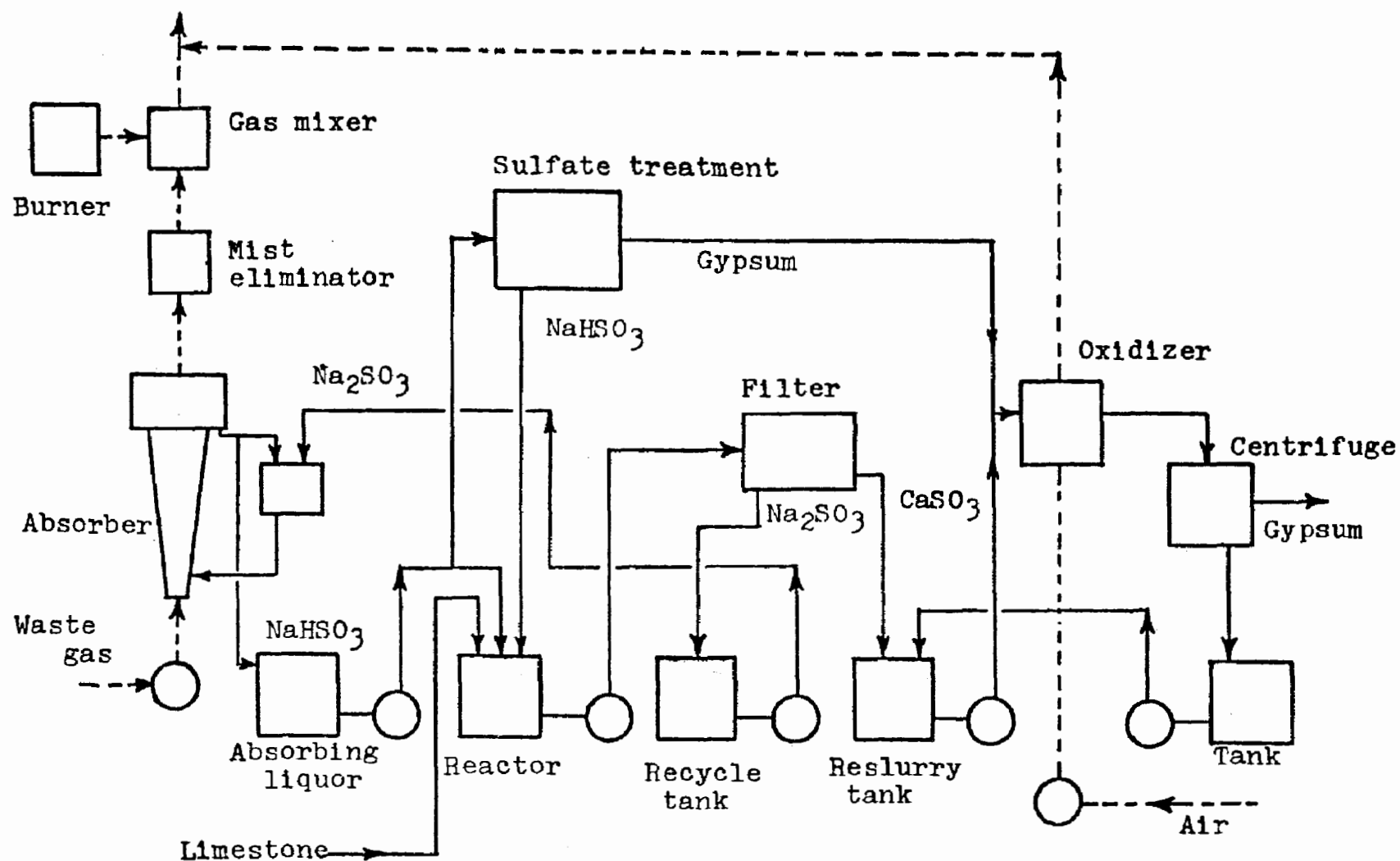


Figure 12 Showa Denko sodium-limestone process

8 NKK ammonia process and ammonia-lime process ^{2,4)}

Developer Nippon Kokan Kabushiki Kaisha
1-1-3, Otemachi, Chiyodaku, Tokyo

Process description Waste gas at 250°F from an iron ore sintering plant, containing 400 to 1,000ppm SO₂ is first led into an electrostatic precipitator and then cooled to 140°F in a cooler with water spray (Figure 13). The gas is then led into a screen type scrubber (Jinkoshi type scrubber) for the absorption of SO₂ by a liquor containing ammonium sulfite. In the scrubber 16 mesh screens of stainless steel are placed with some inclination in five stages. On three of the screens placed at the middle of the scrubber, the ammonium sulfite solution flows slowly forming a liquor film which readily absorbs SO₂. On the other two screens placed at the upper part of the scrubber, water flows slowly forming a water film to decrease plume formed by the reaction of SO₂ and ammonia. About 95% of SO₂ is removed when the pH of the circulating liquor is about 6. Virtually no ammonia is lost when the pH of the liquor is 6 or below.

The outlet liquor containing ammonium bisulfite is sent to an ammonia absorber. Coke oven gas containing a small amount of ammonia is introduced into the absorber. The liquor is sprayed to absorb ammonia and to form an ammonium sulfite solution. A large portion of the solution is returned to the scrubber to absorb SO₂. The rest of the solution is sent to an oxidizer where the sulfite is oxidized into sulfate by air bubbles produced by rotary atomizers. The ammonium sulfate solution is evaporated to produce crystal ammonium sulfate.

Nippon Kokan has recently developed an ammonia-lime double alkali process (Figure 14). The SO₂ absorbing part is the same as in the ammonia process except that no coke oven gas is used. The liquor from the scrubber contains about (NH₄)₂SO₃ 7.5%, NH₄HSO₃ 7.5% and (NH₄)₂SO₄ 15%. A portion of the liquor is sent to a reactor and is reacted with milk of lime (10% concentration) under normal pressure at 210°F. The ammonia released here is sent to the ammonia absorber to be absorbed by the liquor from the scrubber. Calcium sulfate and sulfite are precipitated in the reactor. The slurry from the reactor is acidified with sulfuric acid to adjust the pH to 4 to promote oxidation. The slurry is then led into an oxidizer equipped with rotary atomizers to convert calcium sulfite to gypsum, which is then centrifuged. Salable gypsum with a good quality is obtained. The gas from the oxidizer contains SO₂ and is sent to the scrubber.

State of development After tests with a pilot plant to treat 17,000scfm of waste gas from the iron ore sintering plant, a prototype plant to treat 88,000scfm gas to produce ammonium sulfate by reaction with coke oven gas was completed in early 1972 at the Keihin works of Nippon Kokan.

Additional units for the ammonia-lime double alkali process were completed in November 1972. The construction and the operation of the plants have been carried out as a research project by Japan Iron & Steel Federation.

Status of technology The Jinkoshi type scrubber capable of treating 88,000scfm gas is 56 feet high with a cross section of 14 feet x 23 feet. The following conditions are used for SO₂ absorption:

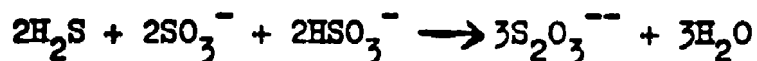
L/G 12gal/1,000scf Gas velocity 7 to 13ft/sec.

Pressure drop 10 to 12 inches H₂O

Inlet SO₂ 400 to 1,000ppm Outlet SO₂ 15 to 50ppm

The outlet gas is at 140°F and is not preheated; heavy plume is observed from the stack. Tests have indicated that the plume becomes slight when the gas is reheated to 180°F and nearly invisible at 240°F.

When coke oven gas is used as the source of ammonia, H₂S in the gas is absorbed to form thiosulfate.



The thiosulfate is not oxidized into sulfate in the oxidizer. It is decomposed by addition of sulfuric acid to the liquor discharged from the oxidizer.



By the decomposition SO₂ is released which is sent to the scrubber. Elemental sulfur formed² by the reaction is removed by filtration.

In the ammonia-lime process, the oxidation of calcium sulfite into sulfate is hindered under the presence of thiosulfate. Therefore, it is better not to use coke oven gas in this case. To make up a small amount of ammonia (about 5%) lost from the system, ammonium sulfate is added to the reactor to react with lime and to generate ammonia. The pH in the reactor is maintained at about 11 to ensure gypsum crystal growth in the reactor. To promote the oxidation of calcium sulfite present in the slurry from the reactor, the slurry is acidified to pH 4 by addition of sulfuric acid and then led into the oxidizer. Gypsum grows into big crystals (100 to 300 microns) and can easily be centrifuged to a low moisture content (about 10%). The liquor from the centrifuge which is acidic is neutralized, clarified and returned to the system. No wastewater is emitted.

Advantages The screen type scrubber is effective for SO₂ removal with a relatively low pressure drop. A large amount of gas, up to about 300,000scfm can be treated in one scrubber. By the ammonia process, both SO₂ in waste gas and ammonia in coke oven gas are utilized to produce salable ammonium sulfate. By the ammonia-lime process, salable gypsum of good quality is obtained with no scaling problem. No wastewater is emitted.

Disadvantages When coke oven gas is used, hydrogen sulfide in the gas necessitates additional facilities. The screen in the scrubber is subject to corrosion under inadequate operating condition.

Cost estimation A cost estimation for the ammonia-lime process to treat flue gas from an oil-fired boiler is shown in the following table in comparison with that for the lime-gypsum process developed by Nippon Kokan which is similar to the Mitsubishi-JECCO lime gypsum process.

Cost estimation (\$1 = ¥308)

(SO₂ in inlet gas 1,400ppm, in outlet gas 70ppm)

	<u>Ammonia-lime process</u>		<u>Lime-gypsum process</u>	
Amount of gas treated (scfm)	<u>235,000</u>	<u>882,000</u>	<u>235,000</u>	<u>882,000</u>
Investment cost (\$1,000)	2,110	4,545	2,273	5,844
Fixed cost (\$1,000/year)				
Depreciation	382	822	409	1,055
Labor (7 persons)	45	45	45	45
Repair	63	136	68	175
Insurance	2	5	3	7
Management	95	353	84	295
Variable cost (\$1,000/year)				
Electric power (@11 mil/kWh)	168	634	191	822
Steam (@\$1.5/ton)	96	383		
Industrial water (@15 mil/ton)	4	14	3	11
Seawater (@3 mil/ton)			1	2
Quick lime (@\$13.1/ton)	168	688		
Slaked lime (@\$15.1/ton)			276	951
Sulfuric acid (@\$28.3/ton)	45	180		
Ammonia (@\$87.6/ton)	37	148		
Fuel (@\$35.1/ton)	326	1,295	262	1,006
Product gypsum (@\$5.8/ton)	-226	-899	-220	-883
Desulfurization cost (\$/tl)				
With revenue from gypsum	0.69	0.58	0.64	0.52
Without revenue from gypsum	0.82	0.72	0.77	0.66

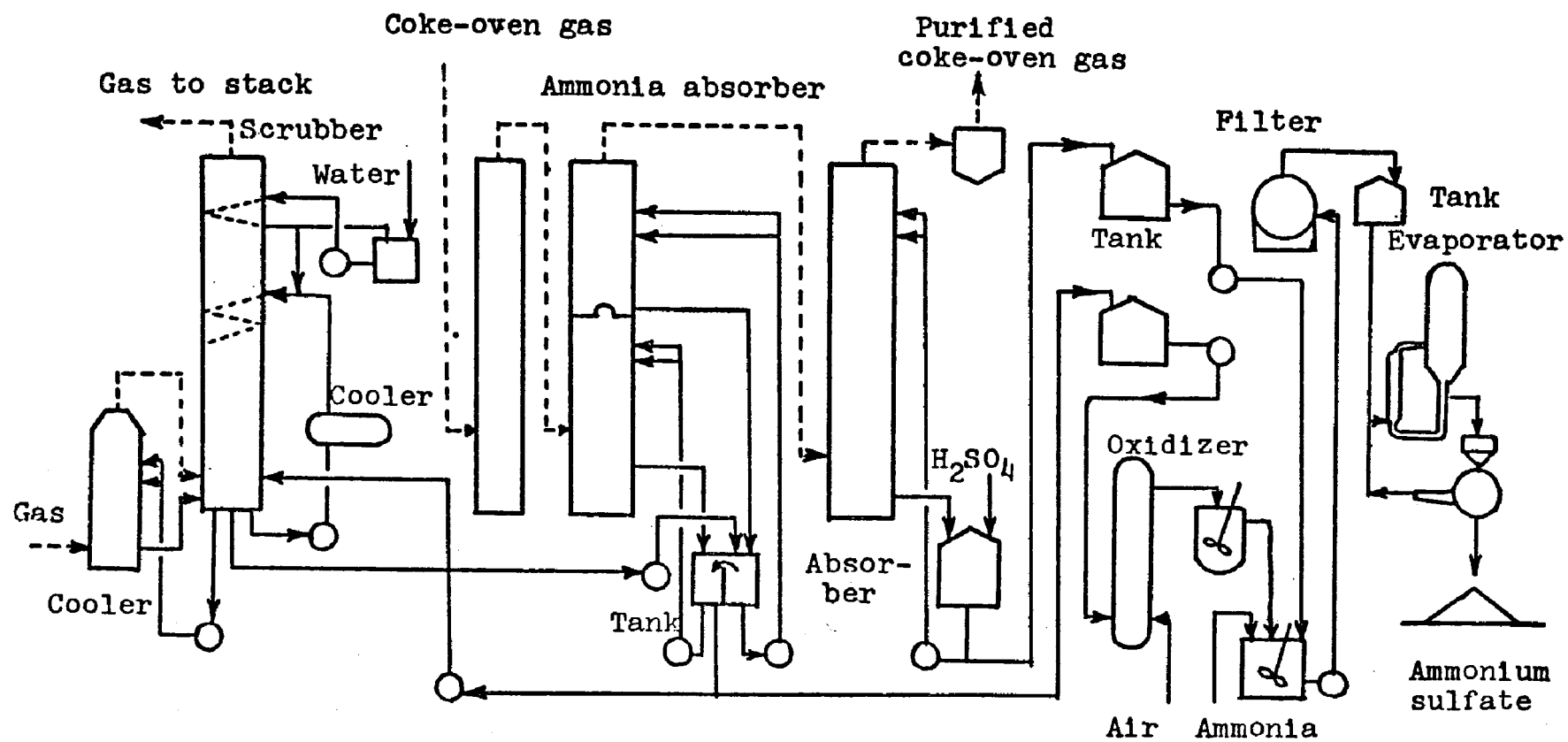


Figure 13 Nippon Kokan ammonium sulfate process

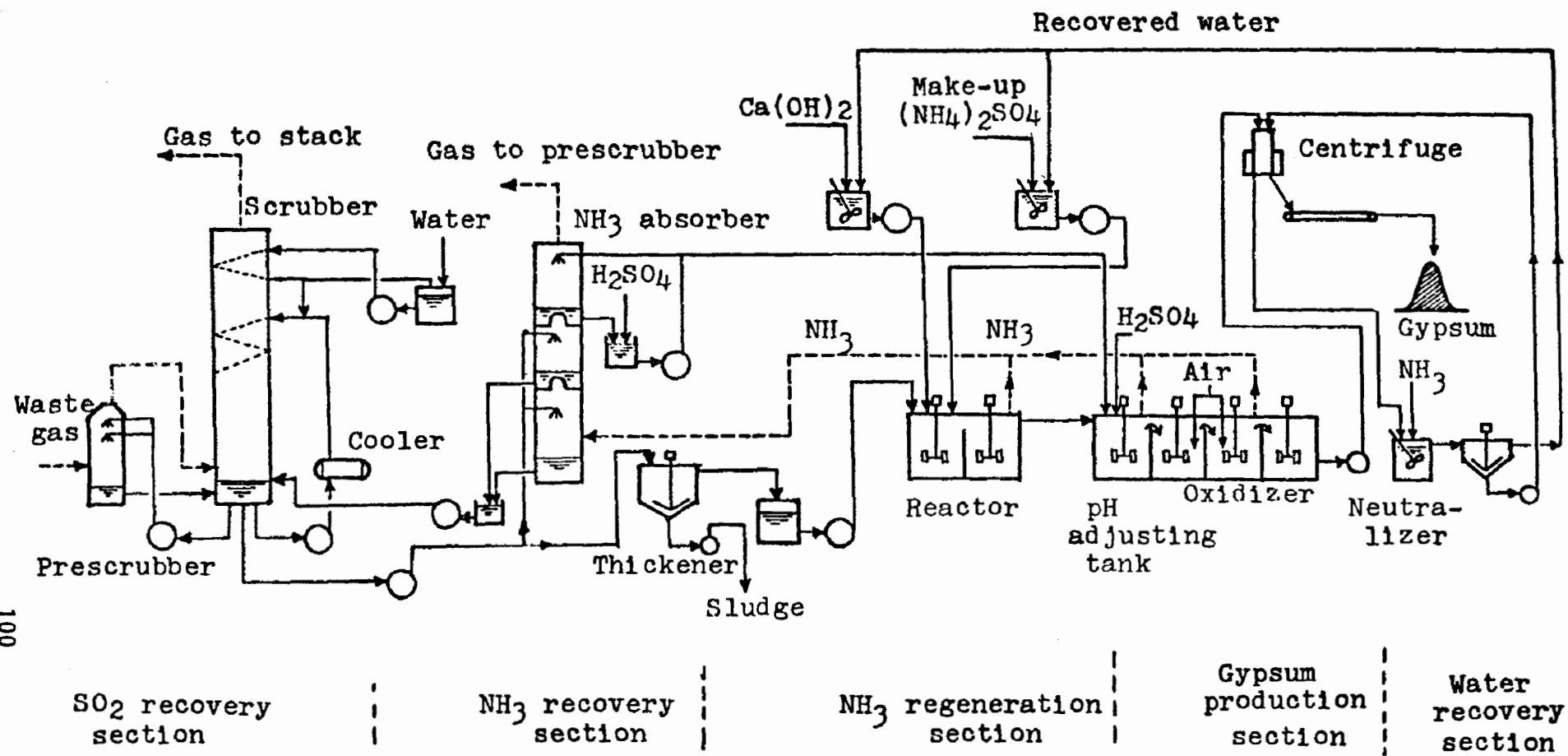


Figure 14 Nippon Kokan ammonia-lime process

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- 3) Haiendatsuryu no Subete (All About Waste-gas Desulfurization), Jukogyo Shimbunsha, Nov. 1972
- 4) M. Yokoi, Ryusan to Kogyo (Sulfuric Acid and Industry), Vol. 26, No. 1, 1973
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ECONOMICS OF FLUE GAS DESULFURIZATION

by

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Summary and Conclusions

This paper summarizes the results and conclusions of an analysis of the costs of flue gas desulfurization for fossil fuel boiler plants. Cost details of the desulfurization processes have been evaluated and presented as a consistent set of data from which it is possible to estimate capital and annualized costs for any given plant conditions. The following conclusions were derived from that data.

- 1) Flue gas desulfurization can be applied to 75% of existing fossil fuel utility capacity at an annualized cost of 1.5 to 3.0 mills/kwh, which is less costly than substitute low-sulfur fuels, typically costing 3.0 to 6.0 mills/kwh.
- 2) Regenerable processes are generally less costly than throwaway processes at waste disposal costs above \$3/ton wet sludge.
- 3) Newer processes such as citrate and double alkali may be up to 20% less costly than currently available processes such as Wellman-Lord and limestone scrubbing.
- 4) Annualized costs for a given process can easily vary from 2 to 6 mills/kwh with typical variations of plant sizes and load factors.
- 5) Flue gas desulfurization can be significantly cheaper to use with medium sulfur coals if only a portion of the flue gas needs to be treated in order to meet emission standards.
- 6) Extrapolation of this costing technique to industrial boiler conditions indicates annualized costs of 60 to 130 ¢/MMBTU with throwaway processes.
- 7) This cost data base consistently predicts actual first-of-a-kind project capital costs within 10 to 20%.

Introduction

A thorough evaluation of technology for control of SO_2 from power plants must include consideration of numerous processes and approaches as well as several criteria of usefulness. The scope of such an evaluation is illustrated in Figure 1. The technology to be considered includes not only flue gas cleaning and low sulfur fuels for short term solutions, but also longer term alternatives such as gasification, fluidized bed combustion, or solvent refining of coal. This technology must be evaluated on the basis of the following criteria:

- 1) environmental impact
- 2) stage of development
- 3) economics

This paper evaluates flue gas cleaning processes on the basis of economics. Its scope is indicated by the dotted line in Figure 1.

For purposes of evaluation the flue gas cleaning processes considered here can be divided into three groups:

- 1) Available throwaway - Limestone scrubbing and lime scrubbing
- 2) Available regenerable - Wellman-Lord, MgO scrubbing, and Cat-Ox
- 3) New/developing
 - a) Throwaway - Double alkali
 - b) Regenerable - Citrate and Stone & Webster/Ionics

These processes were selected as being representative; they do not include all potentially important systems.

Each of the three groups appears to be identified with one of the evaluation criteria listed above. Throwaway processes have serious problems with environmental impact of waste disposal. Regenerable processes are often cited as

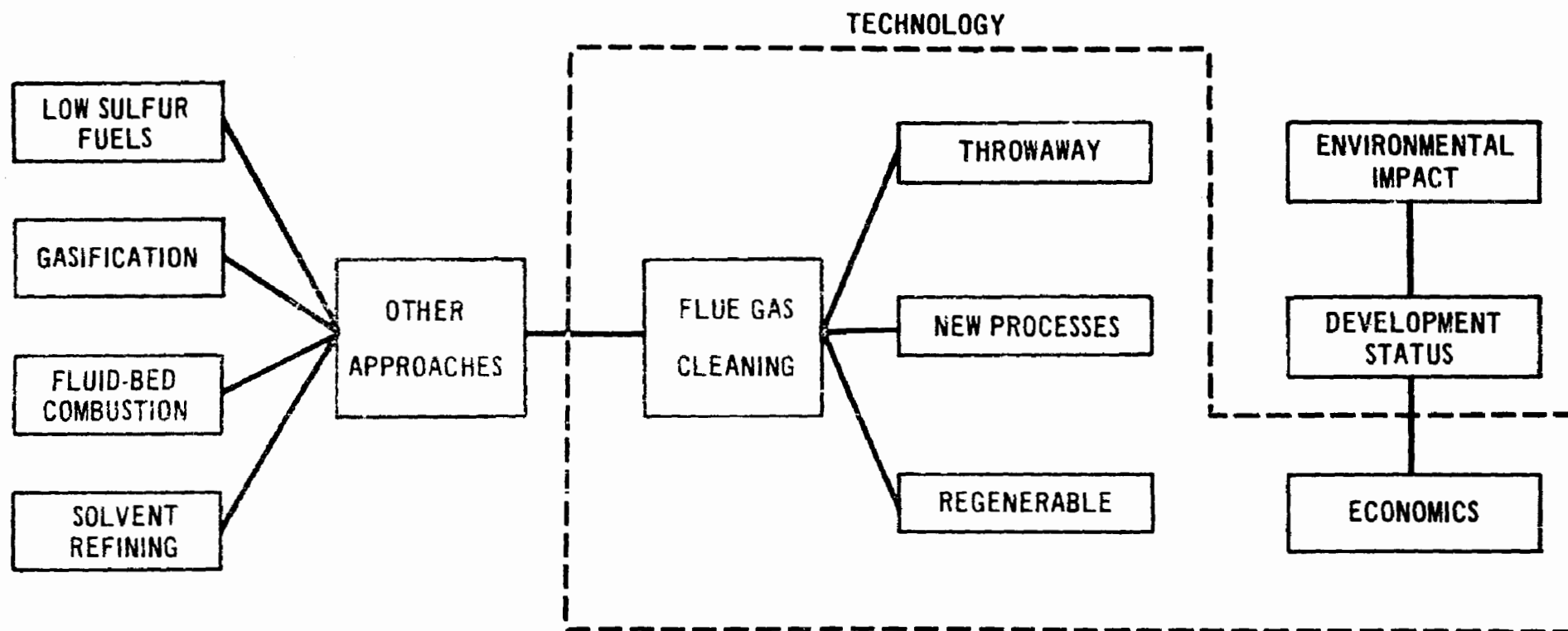


Figure 1. Evaluation of SO₂ control technology.

having higher costs. New processes have not yet reached a stage of development adequate for commercial applications. To provide a quantitative evaluation for process selection, these different criteria must be quantified for all of the process groups. This paper concentrates upon quantifying the economics of flue gas cleaning processes, so that they can be compared with each other and with other approaches to SO₂ control. Flue gas cleaning will be evaluated on the basis of all three criteria in a paper to be presented at the APCA annual meeting in June 1973.

In a paper presented in Fall 1972,⁽¹⁾ we summarized and analyzed the cost data for five wet scrubbing processes: limestone scrubbing, lime scrubbing, Wellman-Lord, MgO scrubbing, and Stone & Webster/Ionics. That data base has been expanded to include the double alkali and citrate processes as well as preliminary information on Cat-Ox. The capital cost data for Wellman-Lord and Stone & Webster/Ionics has been modified to reflect the higher costs of purge handling and SO₂ reduction being estimated for the NIPSCO Wellman-Lord demonstration. Corrections and supplements to the 1972 paper are being prepared and will be available shortly. This paper summarizes the results and conclusions of the revised cost analysis.

The major sources of cost data are given in Table 1. The primary sources are important, detailed estimates. The secondary sources include project, scoping, and open literature references of lesser detail or importance.

The Cost Model

On the basis of the aggregated cost data, CSL has developed a series of equations and graphs that allow cost estimates to be generated as a function of process type and conditions of specific installations. For ease of representation, the scrubbing processes are divided into two process areas:

Table 1. SOURCES OF COST DATA

Primary

- Catalytic, Inc. -- Limestone scrubbing⁽²⁾
- TVA -- MgO conceptual study; includes limestone⁽³⁾
- Davy-Power Gas -- Demonstration project costs and proprietary data⁽⁴⁾
- Allied Chemical -- Proprietary data on sulfur production⁽⁵⁾

Secondary

- M. W. Kellogg -- Cost study of 12 processes⁽⁶⁾
- Stone & Webster/Ionics -- Costs of electrolytic regeneration⁽⁷⁾
- TVA -- Widow's Creek project estimate (limestone)⁽⁸⁾
- Monsanto/Illinois Power -- Cat-Ox project costs⁽⁹⁾
- Chemico/Boston Edison -- MgO project costs⁽¹⁰⁾
- Bechtel -- Limestone scrubbing costs⁽¹¹⁾

scrubbing and alkali handling. Scrubbing costs are dependent on the flue gas rate but not on the amount of sulfur removed. Alkali handling costs vary with sulfur rate but are independent of flue gas rate.

The structure of economics is illustrated in Figure 2. Capital costs are made up of four segments: process direct, other direct, contractor indirect, and user indirect. The process direct costs include labor and material for process equipment. For scrubbing, process direct costs are represented as a function of process type, flue gas rate, and retrofit conditions. Alkali handling process direct costs are a function of process type and the amount of sulfur removed per hour. The other direct costs and indirect costs are estimated as a percentage of process direct costs. In this analysis total capital costs are computed as 170% of process direct costs, unless otherwise noted. Capital costs can be expressed as absolute dollars or \$/kw of generating capacity.

Annualized costs include contributions from utilities and raw materials, labor, maintenance and capital charges. Utilities and raw materials cost per year are functions of gas rate or sulfur rate, process type, and load factor. Labor is assumed to be \$225,000/year regardless of plant size. Maintenance cost is estimated as 4.5% of capital cost per year. Capital charges at 17.5% of capital cost are meant to include depreciation, return on investment, taxes, and insurance. Annualized costs can be expressed as absolute dollars per year or as cost per unit throughput, such as mills/kwh, ¢/MMBTU, or \$/ton sulfur. Generally CSL has used mills/kwh. Variations of annualized cost with load factor depend on the units used. At lower load absolute costs per year will decrease, but relative costs per unit throughput will increase.

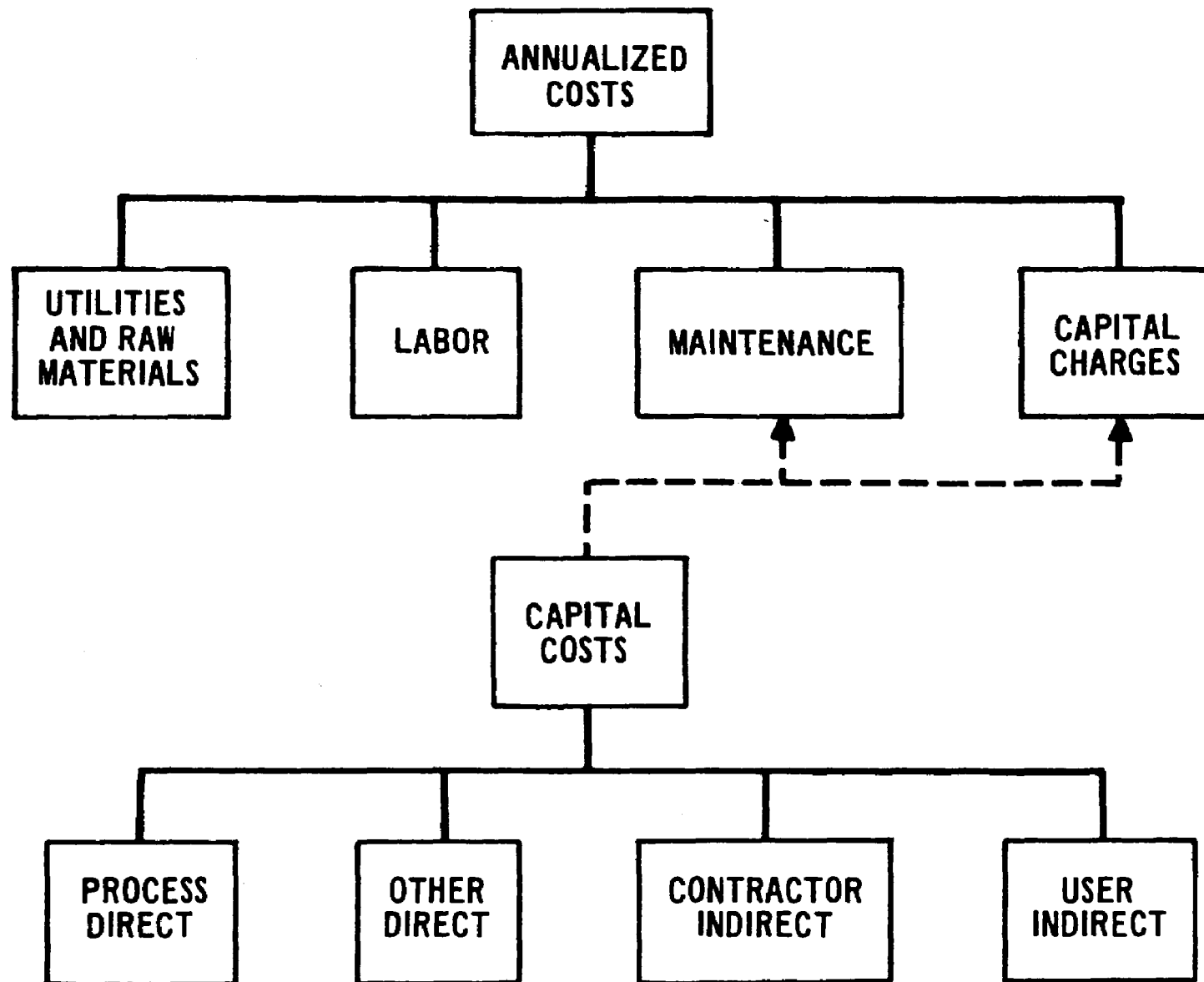


Figure 2. Structure of economics.

Estimated Versus Actual Costs

Using this cost data base and estimating techniques CSL has evaluated the costs of six actual construction projects. The results of these evaluations are given in Table 2. Generally all but 10 to 20% of the actual or contractor estimated investment costs were predicted from process configurations and site conditions. This consistently good prediction of costs was maintained over a wide range of retrofit conditions, plant size, fuel type, and process type. Therefore this technique of cost prediction should be accurate in predicting variations in process costs and can be relied upon for process comparisons.

However, the estimated costs are consistently about 15% lower than the actual project costs. This error may result from insufficient detail on actual contractor estimates or from real costs for first-of-a-kind installations. When cost detail is lacking, assumptions must be made for the extent of inflation and other direct and indirect costs. These assumptions will probably be more conservative than the assumptions of a contractor trying to make a profit. The costs presented here are meant to be accurate for widespread commercial applications and do not include first-of-a-kind costs. Nevertheless, we recognize that the bias in our estimated capital costs may be partially real. At the worst however, the 15% lower capital cost projects would result in annualized costs that are 5 to 10% low.

In order to better illustrate project cost estimating, two of the cases will be discussed in greater detail. Calculations for the Will County limestone scrubbing facility are summarized in Table 3. The power plant is designed for a new generation of 163 Mw, but its gross capacity is 177 Mw. We have estimated the design flue gas rate at 360,000 SCFM or 180 Mw gas equivalent. The actual

Table 2. ESTIMATED CAPITAL COSTS OF DEMONSTRATION PROJECTS (\$MM)

	Will County	Widow's Creek	Sherburne County	LaCygne	Mystic	Mitchell
Explained costs	11.3	27.6	31.0	29.5	5.6	7.7
Actual costs	13.3	35.0	36.1	32.5	6.2	9.6
Unexplained costs, % of actual costs	15%	21%	14%	9%	10%	20%
Plant characteristics	Limestone Retrofit	Limestone Retrofit	Limestone New	Limestone New	MgO Retrofit	Wellman-Lord Retrofit
	3% S Coal	4% S Coal	1% S Coal	5% S Coal	2% S Oil	3% S Coal
	177 Mw	550 Mw	1360 Mw	820 Mw	155 Mw	115 Mw

Table 3. ESTIMATED COSTS OF WILL COUNTY LIMESTONE DEMONSTRATION

(Basis: 180 Mw (360,000 SCFM), 15 tons limestone/hour, difficult retrofit.)

Process area	Cost, \$MM
Scrubber, two modules	8.6
Alkali handling, without pond, grinding for 24 tons limestone/hr	<u>2.7</u>
Total	11.3
Actual Costs (includes considerable overtime)	13.3

Table 4. ESTIMATED COSTS OF THE NIPSCO WELLMAN-LORD DEMONSTRATION

Process area	Comments	Estimated ^a by model	Actual Estimate	Unexplained
Scrubber	Single shell with particulate scrubbing	3.00	3.0	--
Evaporator	---	1.65	1.8	+ 0.15
Purge handling	Very small, almost pilot scale	0.65	1.3	+ 0.65
	Earlier paper	(0.30)	-	(+ 1.0)
Sulfur plant	Very small, almost pilot scale	1.50	2.6	+ 1.10
	Earlier paper	(0.95)	-	(+ 1.8)
Boiler	Not usually required	<u>0.90</u>	<u>0.90</u>	<u>-</u>
Total		7.7	9.6	1.9

^aIncludes actual indirect cost rates with predicted direct costs.

sulfur design rate is not disclosed, but the limestone rate is 15 tons/hr, equivalent to about 3 tons/hr of sulfur. The scrubbers were installed under severe space limitations and are therefore rated as difficult retrofits. Normally, the total gas flow could possibly go through a single large scrubber, but two smaller modules have been used. Furthermore, the limestone grinding facilities were designed for almost double capacity (24 tons/hr). The actual costs are about \$2 MM more than the estimated costs, but include a large amount of overtime labor not usually accounted for by the estimating procedure. A similar facility designed for 180 Mw, 3 tons S/hr with easy retrofit conditions and using only one scrubber and matching sized limestone grinding should cost only \$7.0 MM compared to the estimated cost of \$11.3 MM for this facility.

The estimated costs for the Mitchell Station Wellman-Lord process are given in Table 4. The costs are compared on an area by area basis with the actual contractor estimates. Costs for the scrubber and evaporator agree very well. Costs for purge handling and the sulfur plant reported in the earlier CSL paper were not well founded and have actually been modified for this paper to reflect the much higher costs estimated for the Mitchell Station. Even as modified, the contractor costs for these two areas are almost a factor of two greater than our estimated costs. However, both the purge handling and sulfur plant are very small, first-of-a-kind, almost pilot plant facilities. Since the estimating technique is intended to be most representative of larger, widespread applications, the lack of accuracy under these extreme conditions is not unexpected. The Mitchell estimate also includes provision for a package boiler which would normally not be required. Another factor of great importance is inflation. The Mitchell estimate includes actual costs through 1975. Our time basis is late 1972, so as much as 15% should be added to our

estimated costs to account for inflation. This would put estimated costs within 5% of actual project estimates.

Comparative Process Costs

In order to provide a point of process comparison, capital and annualized costs for a single, base case power plant are given in Table 5. The range of annualized costs between processes is quite small, varying from 1.95 to 2.75 mills/kwh. At the conditions selected, lime and limestone scrubbing are somewhat less expensive than the regenerable processes. The new processes, double alkali and citrate, appear to offer savings up to 20% in annualized costs over available throwaway and regenerable processes. The costs for the Cat-Ox process have been scaled from the actual demonstration project costs and are therefore somewhat preliminary. Nevertheless, the estimated annualized cost of Cat-Ox is within 5 to 10% of the other regenerable systems, and actual costs could easily turn out to be competitive. At conditions different from the base case, the relative cost ranking can change. For example, higher costs of waste disposal would make throwaway processes more expensive.

Regenerable Versus Throwaway - The comparative costs of regenerable and throwaway processes are typified by the annualized costs of Wellman-Lord and limestone scrubbing as compared in Table 6. In the scrubbing area limestone is more expensive because of the higher capital expense of using limestone slurry with larger liquid recirculation, more complicated demisting, and erosion resistant materials. On the other hand the annualized costs of alkali handling appear to be greater for Wellman-Lord, because of contributions from large capital expense and utility requirements. Therefore the major cost components balance out, and overall annualized costs differ by only 10%.

Table 5. COMPARATIVE PROCESS COSTS

(Basis: 500 Mw, 3.5% S coal, retrofit, 60% load, waste at \$3/ton wet sludge, sulfur credit at \$15/ton, particulate removal included.)

Process	<u>Comparative Process Costs</u>	
	Capital, \$/kw	Annualized, mills/kwh
Throwaway^a		
Double alkali	24	1.95
Lime scrubbing	35	2.40
Limestone scrubbing	36	2.45
Regenerable		
Citrate	39	1.95
MgO (to S)	49	2.40
Wellman-Lord (to S)	50	2.65
Stone & Webster/Ionics (to S)	50	2.70
Cat-Ox	55	2.75

^aCapital costs do not include disposal facilities, usually \$5-15/kw.

Table 6. ANNUALIZED COSTS OF LIMESTONE SCRUBBING AND WELLMAN-LORD

	Annualized costs (mills/kwh)	
	Limestone scrubbing	Wellman-Lord
<hr/>		
Scrubbing		
Operating utilities and labor	0.21	0.21
Capital charges and maintenance	<u>1.33</u>	<u>1.08</u>
Subtotal	1.54	1.29
Alkali handling		
Operating utilities and raw materials	0.23	0.45
Labor	0.06	0.06
Capital charges and maintenance	0.18 ^a	0.99
Waste disposal costs and sulfur credit	<u>0.45</u>	<u>- 0.15</u>
Subtotal	0.92	1.35
Total annualized cost	2.46	2.64

^aCapital charges are not included for a disposal pond. Its costs are represented by waste disposal costs.

The assumed sulfur credit for Wellman-Lord is \$15/ton, but at that level it only amounts to 0.15 mills/kwh. If acid were produced rather than sulfur, the costs would be reduced about 0.15 mills/kwh in addition to the byproduct credit which could amount to as much as 0.30 mills/kwh. Therefore, acid production could be as much as 0.30 mills/kwh less costly than sulfur production.

The key assumption affecting the relative costs of regenerable and throwaway processes is the cost of waste disposal. The assumed cost in Table 6 is \$3/ton wet sludge (\$1.50/ton dry solids) and corresponds to the typical costs of a disposal pond. Figure 3 illustrates the variation of the annualized costs of lime and limestone scrubbing with waste disposal costs. The middle range of regenerable process costs is also shown. The range of disposal costs at which regenerable processes are competitive varies from \$1 to 3/ton wet sludge. In practice, costs for disposing of sludge via dewatering and hauling can run as high as \$7/ton sludge. Therefore, it is certainly not accurate to say that throwaway processes are less expensive than regenerable systems, though there will certainly be localities of low-cost waste disposal where throwaway systems will be 5 to 20% less expensive.

New Processes - The double alkali and citrate processes are typical of the cost benefit to be achieved by new systems. The capital cost of double alkali is compared with lime scrubbing in Table 7. The double alkali scrubbing system is much cheaper because it can achieve SO_2 and particulate removal in a very simple single stage venturi scrubber with little concern for entrainment and erosion problems. Of course the double alkali process requires more equipment for alkali handling, but the overall capital cost is still 15 to 30% less expensive than lime scrubbing. Utility and raw materials costs are the same

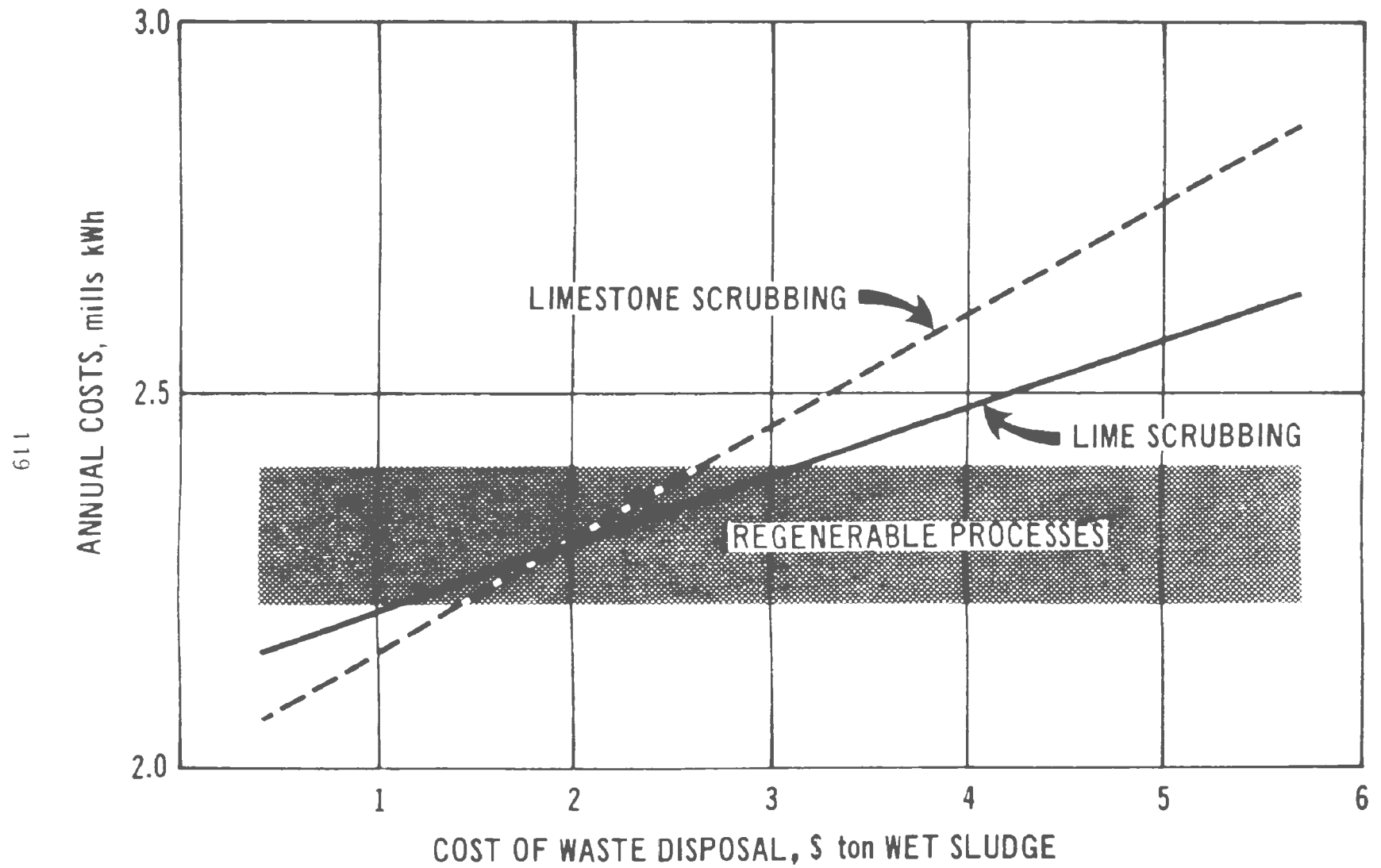


Figure 3. Process costs versus waste disposal costs.

Table 7. CAPITAL COSTS OF DOUBLE-ALKALI AND LIME SCRUBBING

(Basis: 500 Mw, 3.5% S coal, typical retrofit, includes particulate scrubber.)

Process area	Capital Costs, \$/kw	
	Double alkali/lime	Lime scrubbing
Scrubbing	18.1	32.0 (25.9) ^a
Alkali handling (not including pond)	<u>6.8</u>	<u>2.7</u>
Total	24.9	34.7 (28.6) ^a

^aWithout particulate scrubber.

Table 8. ALKALI HANDLING COSTS OF CITRATE AND WELLMAN-LORD

(Basis: 500 Mw, 3.5% S coal, 60% load.)

Cost factor	Annualized costs, mills/kwh	
	Citrate	Wellman-Lord
Operating utilities and raw materials	0.20	0.45
Labor	0.06	0.06
Capital charges and maintenance	0.57	0.99
Sulfur credit	<u>-0.15</u>	<u>-0.15</u>
Total (alkali handling)	0.68	1.35

for both processes, so the difference in annualized costs is a result of capital cost differences.

The scrubbing costs of citrate and Wellman-Lord are essentially the same since both processes use clear solution scrubbing. The annualized costs of alkali handling are compared in Table 8. The citrate process regenerates scrubbing solution with H_2S to sulfur, so no steam is required as with Wellman-Lord. Furthermore, the regeneration reactor is quite a bit simpler than the Wellman-Lord evaporator. The citrate process requires a unit to produce H_2S from sulfur, but it should be cost equivalent to the Wellman-Lord unit for production of sulfur from SO_2 . Therefore, the capital costs, and hence maintenance and capital charges, are 40% less for citrate. The overall costs for alkali handling are about 50% lower for citrate.

The reduced costs for new processes may not totally materialize. The cost estimates are necessarily based on preliminary information. Additional processing equipment may be identified as the processes become better developed.

Cost Variations with Source Parameters

As just explained, the total variation of annualized costs with process type at the base conditions is limited to a factor of about 1.4 from double alkali to Cat-Ox. However variation of costs with source parameters such as plant size, fuel sulfur content, and load factor is much more pronounced. The variation of total capital costs (including waste disposal) with plant size is illustrated in Figure 4. Costs for the available systems, Wellman-Lord and limestone, vary a factor of 1.65 from \$65-75/kw at 100 Mw to \$45/kw at 1000 Mw. Citrate and double alkali capital costs are 20 to 50% lower.

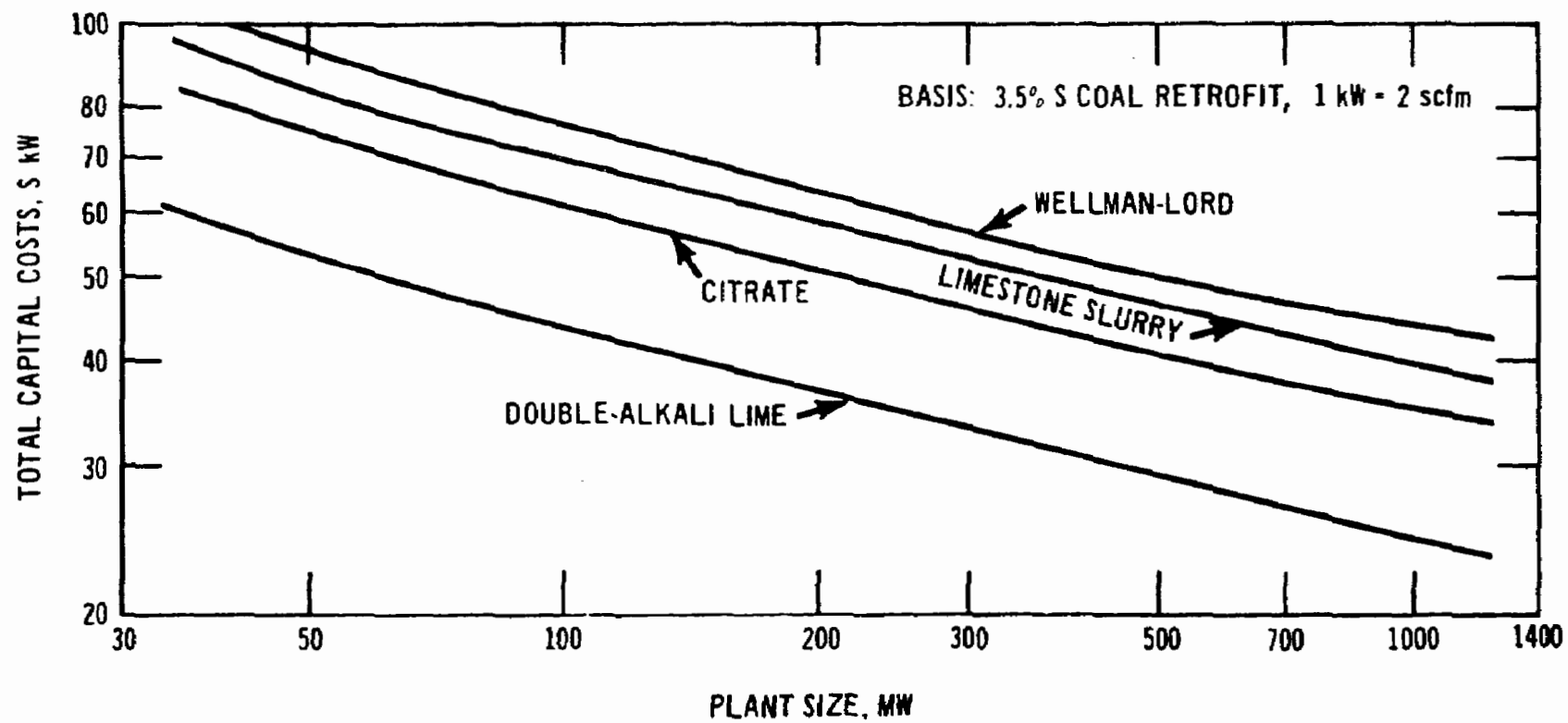


Figure 4. Total capital costs.

The variation of annualized costs with plant size and load factor is illustrated in Figure 5. Over a range of 100 to 1000 Mw, 40 to 70% load factor, the annualized costs for a typical retrofit plant with 3.5% S coal vary a factor of 3 from 2 to 6 mills/kwh. The sludge waste disposal cost was treated in Figure 5 as a materials operating cost rather than capital cost. Therefore the limestone process is relatively less costly than Wellman-Lord at smaller plant sizes and lower load where capital costs have a greater impact than materials costs.

Figure 6 illustrates the variation of annualized costs of limestone scrubbing with sulfur content. In most estimates it is assumed that all of the gas will pass through the scrubber, in which case the cost varies a factor of 1.4 in going from 1 to 5% S coal. The other curves in Figure 6 represent costs if some flue gas can be bypassed around the scrubber while maintaining a sulfur emission standard. Clearly the cost to treat flue gas from combustion of 1% S coal will be zero if the sulfur emission standard requires 1% S. Actual costs for 3.5% S coal with a 2% S standard can be as much as 50% less than costs for treatment of all the flue gas. With a 1% S standard, the cost of using 2% coal with flue gas scrubbing would only be 1.25 mills/kwh (12.5¢/MMBTU). Therefore, substitution of low sulfur fuel is economical only if its incremental cost is less than 12.5¢/MMBTU. With a 1% S standard, annualized costs vary a factor of 2 from 1.25 mills/kwh at 2% S to 2.5 mills/kwh at 5% S.

Actual Distribution of Annualized Costs

It is somewhat academic to discuss process costs over a range of source conditions as discussed earlier. In real life, costs must be considered as applied to actual plants. Figure 7 represents a distribution of calculated annualized

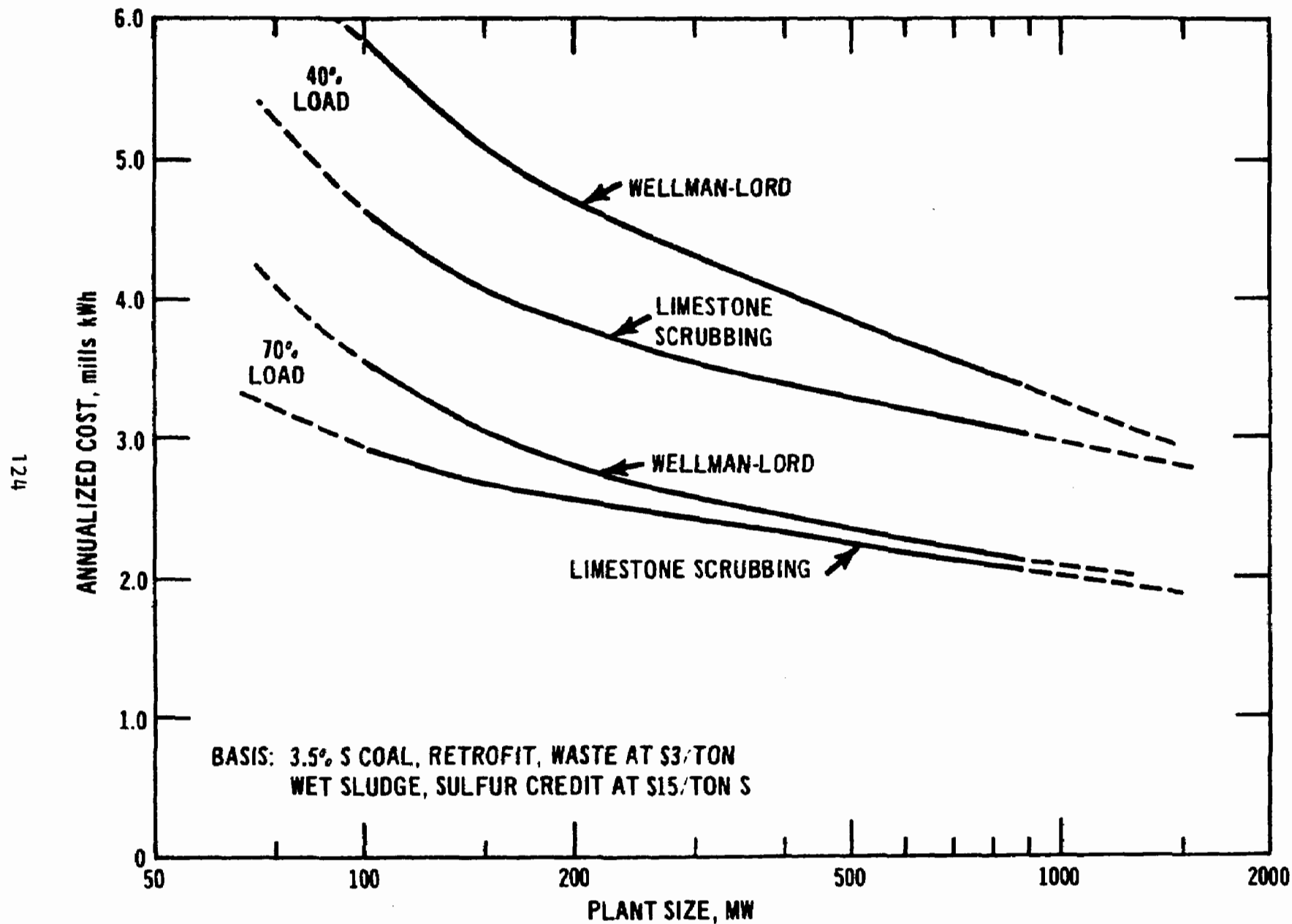


Figure 5. Annualized costs versus plant size and load factor.

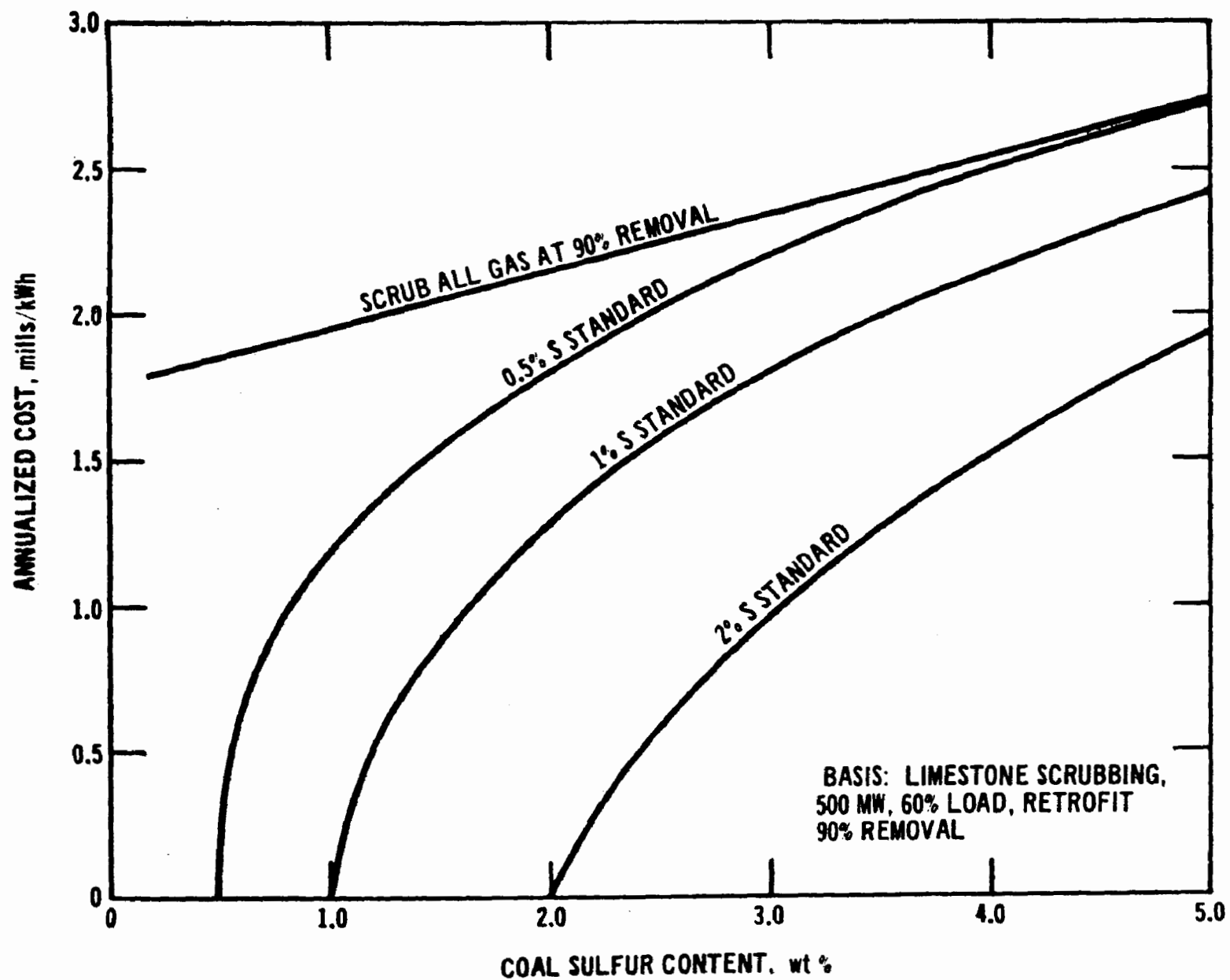


Figure 6. Annualized costs versus sulfur content.

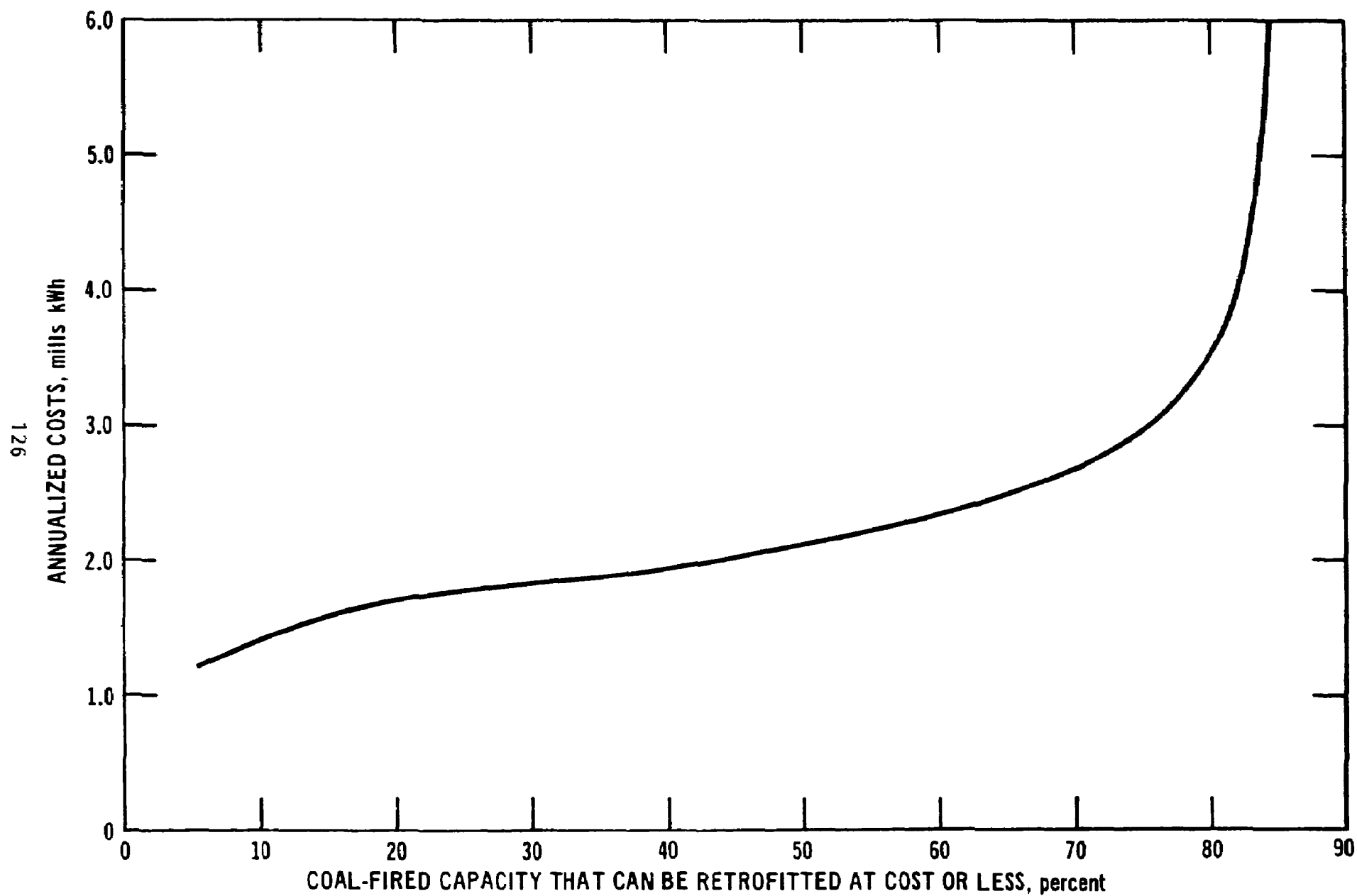


Figure 7. Distribution of annualized costs over utility population, limestone scrubbing.

costs over a random sample of coal-fired utility plants including 25% of the plants in the 1969 FPC form 67 survey. Costs of limestone scrubbing for each plant were calculated as a function of plant size, load factor, and fuel sulfur content. Retrofit factors were estimated on the basis of unit age and size. Each system was assumed to treat all of the flue gas for SO_x and particulate removal. Waste disposal was represented as an operating cost at \$3/ton sludge. In addition a random variation of plus or minus 15% (over two standard deviations) was incorporated into the costs to account for variations in waste disposal costs and retrofit factors that could not be correlated with plant parameters.

As shown in Figure 7, 75% of the coal-fired utility capacity in the U. S. could be retrofitted with limestone scrubbing at a cost of 3.0 mills/kwh or less, 50% at a cost of 2.0 mills/kwh or less. Thus representative costs for widespread application of flue gas cleaning would be 1.5 to 3.0 mills/kwh. It is also apparent from Figure 9 that 25% of the capacity would cost more than 3.0 mills/kwh (about 30¢/MMBTU) to retrofit with flue gas scrubbing. This capacity would probably be most economically controlled by the use of low-sulfur fuels, if available at costs less than the cost of flue gas scrubbing. It would appear from Figure 9 that 15% of the capacity would cost more than 6 mills/kwh (60¢/MMBTU). This capacity would certainly consider clean fuels or another more economic approach to sulfur emission abatement. Since substitution of low-sulfur fuels is expected to add an incremental cost of 30 to 60¢/MMBTU, flue gas cleaning would be the better economic choice for 75 to 85% of current coal-fired capacity.

As shown in Table 9, costs for typical new plants would be about 1.85 mills/kwh (18.5¢/MMBTU) for coal or 1.3 mills/kwh (13¢/MMBTU) for residual

Table 9. COST OF LIMESTONE SCRUBBING FOR NEW PLANTS

(Basis: 500 Mw, 70% load factor, no particulate scrubbing, 70% indirect costs, and 1972 dollars.)

Fuel	Annualized, mills/kwh	Capital, ^a \$/kw
Coal, 3.5% S	1.85	25
Oil, 2.5% S	1.31	20

^aWaste disposal included in operating cost, but not in capital cost.
Disposal ponds would cost \$5-10/kw.

oil. Thus the use of substitute low-sulfur coals or even desulfurized oil at incremental costs over 20¢/MMBTU would not be economically favored. Therefore most new fossil-fired plants will probably use flue gas cleaning until a cheaper alternative (such as fluidized bed combustion) can be developed.

Costs with Industrial Boilers

Generally the costs presented thus far have related primarily to applications on utility boilers. Coal-fired industrial boilers present a different picture. A typical coal-fired industrial boiler plant has three boilers with a total capacity of 500 MMBTU/hr (50 Mw). The average load factor is probably about 50%. Higher excess air (50% compared to 20% for utilities) is used with the typical stoker-fired boilers, so larger scrubbers must be used. Capital expense is a major factor that can have more than twice as great an impact on industrial boiler annualized costs. Industrial facilities are built primarily with equity, not 50% debt/50% equity as with utilities; therefore taxes are substantially higher. Furthermore, non-regulated industry necessarily requires higher return on investment, because of the risk involved. The combined effect of equity financing and higher investment returns is that capital charges for depreciation, return on investment, and taxes amount to 33% of the capital cost per year, not 17.5% as with utilities. Also, the relative impact of capital costs is increased because of the small scale of operation.

Figure 8 presents the annualized costs of lime scrubbing and double alkali as applied to coal-fired industrial boilers. The capital costs were extrapolated from utility costs. Actual capital costs may be lower if shop-fabricated

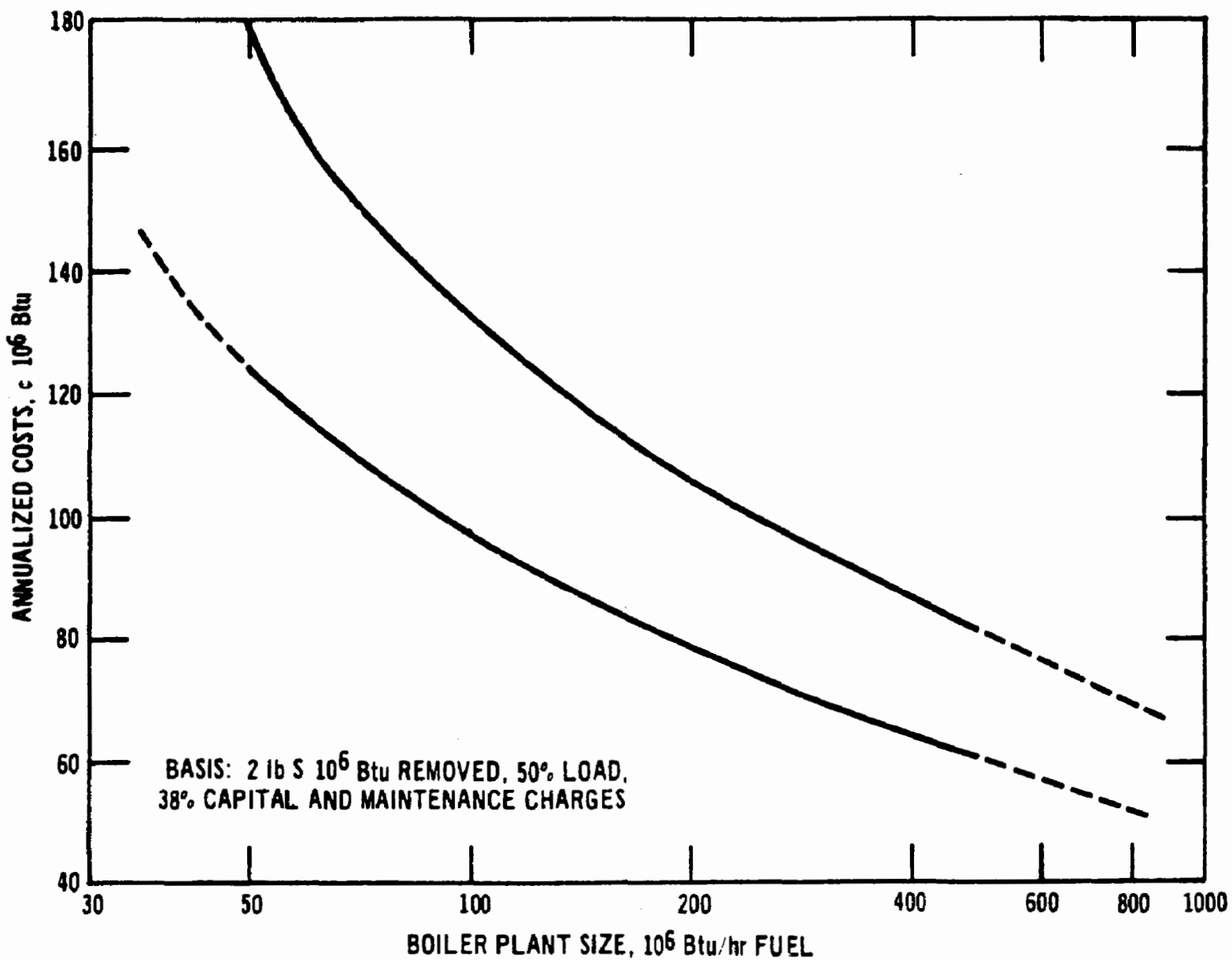


Figure 8. Annualized costs of throwaway processes on industrial boilers.

systems are practical. Labor and overhead costs were assumed to be constant at \$40,000/year. Waste disposal costs were assumed to be \$5/ton of wet sludge. The annualized costs on a boiler plant of 500 MMBTU/hr are 60 to 80¢/MMBTU. On a plant of 100 MMBTU/hr the costs are 100 to 130¢/MMBTU. Such prohibitive costs indicate that substitute low-sulfur fuels will probably be used if they are available.

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Notes

1. The mention of company names or products is not to be considered as endorsement or recommendation for use by the U. S. Environmental Protection Agency.
2. EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report these factors are:

<u>British</u>	<u>Metric</u>
1 SCFM (60°F)	1.61 NM ³ /hour (0°C)
1 short ton	.91 metric tons
1 MMBTU	252,000 kilocalories

**STATUS OF TECHNOLOGY OF COMMERCIALY
OFFERED LIME AND LIMESTONE FLUE
GAS DESULFURIZATION SYSTEMS**

by

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SUMMARY

The status of technology for commercially offered lime/limestone SO_2 removal processes has been evaluated. Suppliers have been contacted to determine the present status of design criteria. It is important to note that most commercial system suppliers will guarantee 80- and 90-percent SO_2 removals using limestone and lime scrubbing, respectively.

Between 1970 and 1973, liquid-to-gas ratio has increased from 20-30 to 40-80 gallons per thousand cubic feet, and stoichiometry has decreased from 1.7 to as low as 1.2. The new values for both parameters tend to make designs more reliable and free of scaling.

There are 21 full-size units being designed or constructed. The number of SO_2 removal systems (using alkali addition into scrubber) operating for any period of time is quite limited. The Will County Station of Commonwealth Edison is the only domestic coal-fired unit with scrubber addition that has operated for a significant period. The facility has shown high SO_2 removal but has been plagued with mechanical problems. Much has been learned from its operation to advance commercial technology.

Capital and operating costs have been estimated for new units. The capital cost of a 500-megawatt unit with the use of limestone is estimated at \$45 per kilowatt; a typical operating cost with limestone is

estimated at 23-25¢ per million Btu. It is not possible to generalize capital costs for retrofit units because of the special requirements for each plant. New SO₂ removal systems using lime will cost \$38 per kilowatt with typical annual operating costs of 23¢ per million Btu.

The two areas requiring further study are demonstration of long-term reliability and sludge disposal management. Long-term reliability will be evaluated and hopefully demonstrated when many of the 21 units come on stream in 1973 and 1974. To develop ecologically sound sludge disposal methods, techniques must be studied in much greater detail.

ACKNOWLEDGMENT

The author wishes to express his appreciation for contributions from the engineers of Bechtel's Scientific Development Air Quality Group. The cooperation of the SO₂ removal system suppliers is also gratefully acknowledged.

Section 1

INTRODUCTION

When the first EPA Symposium on Lime/Limestone Scrubbing was held in November 1971 in New Orleans, Louisiana, there were only three wet scrubbing systems operating. These units consisted of alkali injection into the boiler furnace followed by wet scrubbing. Today there are over 20 commercial systems being designed, constructed, or operated. We have gained much knowledge in the past 18 months, but we still have more to learn.

The lime/limestone sulfur-dioxide removal process is the most advanced system at this time. The primary reasons for this are:

- The process is more fully characterized than other processes. Approximately 20 pilot plant test programs have been conducted over the last 3 years. In addition, the EPA Test Facility has been operating for over a year, and test results will be reported at this meeting.
- The process has relatively low capital and operating costs.
- The process can achieve high sulfur-dioxide removal efficiency.

However, these systems are not without problems, which include control of scaling and erosion/corrosion and solid waste disposal.

This paper describes the commercially offered lime/limestone processes for SO_2 removal and indicates the type of alkali, capital and operating costs, types of scrubbers, and design criteria. It presents the process chemistry as it relates to system reliability and equipment selection, and it discusses the commercial systems as to boiler size, scrubber type, vendor, and status. The paper also evaluates solid waste disposal.

Section 2

CHEMISTRY OF LIME-LIMESTONE SCRUBBING OF SO_2

The chemistry of lime-limestone scrubbing is complicated because of the large number of species present in the system at equilibrium.

2.1 RAW MATERIALS AND CONSTITUENTS

The three raw materials — gas, fly ash, and limestone — each contain several constituents that affect the chemical composition of the system.

For the power plant, the gas supplies SO_2 , SO_3 , CO_2 , NO , and NO_2 ; the ash contributes Na, K, Ca, Cl, Fe, Si, and others. Limestone gives Ca, Mg, and other constituents in minor proportions — Na and K.

2.2 REACTIONS

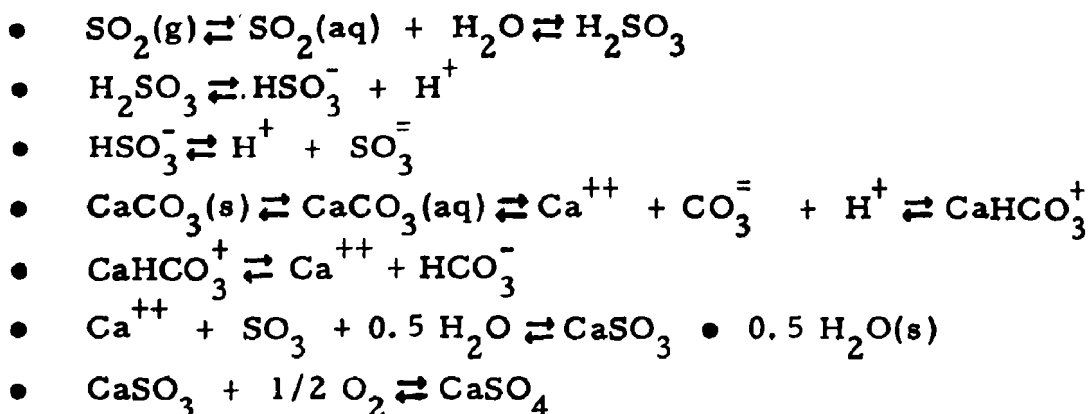
The main reactions in the scrubbers are assumed to be:

- Absorption of SO_2
- Hydrolysis to form H_2SO_3 acid
- Reaction of sulfite ion from H_2SO_3 with calcium ion from CaCO_3 or Ca(OH)_2

These reactions are affected in several ways by other constituents in the system. Detailed studies of the system chemistry have been

carried out by TVA (Ref. 1) and the Radian Corporation (Ref. 2). TVA studied the effect of supersaturation, ionic strength, and sulfite oxidation. Radian developed a computer program using 41 species and 28 equations to predict equilibrium compositions in the scrubber circuit.

The main equations in the scrubber can be written (Ref. 3):



If the system is assumed to be one of sulfurous acid formation followed by the reaction of acid with lime or limestone, then the following effects may influence the overall kinetic rate:

1. Diffusion of SO_2 to and through the gas film at the liquid surface
2. Dissolution of SO_2
3. Hydration of SO_2 to H_2SO_3 , H^+ , and HSO_3^-
4. Dissociation of HSO_3^- to form $\text{SO}_3^{=}$
5. Diffusion of H_2SO_3 and ions through the liquid film at the droplet surface and into the droplet interior
6. Hydration of CaO to $\text{Ca}(\text{OH})_2$ when CaO is used

7. Dissolution of Ca(OH)_2 or CaCO_3
8. Reaction of Ca(OH)_2 or CaCO_3 with H^+ to give Ca^{++}
9. Reaction of Ca^{++} with SO_3^- to precipitate CaSO_3

Available data indicate reactions in steps 3, 4, 8, and 9 are rapid.

The controlling mechanisms are therefore either gas diffusion, liquid diffusion, CaO hydration, or dissolution of CaCO_3 or Ca(OH)_2 . For the most used design case — introduction of CaCO_3 into the scrubber — gas phase mass transfer of SO_2 and CaCO_3 dissolution are the controlling steps. This case was studied by Boll (Ref. 4) in a three-stage scrubber, and he found that these two steps were most critical.

2.3 INFLUENCE OF PROCESS CHEMISTRY ON SO_2 REMOVAL DESIGN

In gas absorbers, one of the major criteria establishing the size of the equipment is the rate of mass transfer from the gas to the scrubbing medium. For lime or limestone scrubbing, gas-phase absorption or chemical reaction rate, or both, may be rate-controlling resistances. For optimum SO_2 mass transfer, it is necessary to maximize the surface area of the calcium-contributing reactant and to minimize the resistance of the gas-to-liquid interface — at minimum cost. Both hydrated lime, Ca(OH)_2 , and precipitated CaCO_3 [resulting from the reaction of Ca(OH)_2 with CO_2 in the flue gas] have very high specific surface area compared to ground limestone. Hence, if limestone is used, it is important to supply a large surface area per volume of SO_2 per unit of time in the scrubber to keep the solution supplied with calcium ions.

Resistance to gas phase SO_2 mass transfer can be minimized by the proper choice of scrubber type and high gas velocity. Maximizing reactant surface area can be accomplished by:

- Large liquid holdup of slurry in the scrubber
- High slurry recirculation rate
- High solids content in slurry
- Increasing feed stoichiometry
- Reducing the particle size of feed

Liquid holdup depends mainly on scrubber type, in descending order as follows: tray-type, packed-bed, floating-bed, spray tower, and venturi. Slurry recirculation rates in the order of 20 to 80 gallons per thousand cubic feet of saturated gas would be required, depending on the type of scrubber used. Solids content of 5 to 15 weight-percent are normally used in the slurry. Limestone feed stoichiometry may vary from 1.2 to 1.5 (stoichiometry being defined as the molal ratio of alkali feed to SO_2 absorbed).

Reducing the particle size of limestone is an obvious way of increasing surface area. Good results have been obtained at a particle size of 80 to 90 percent through 200 mesh.* It should also be noted that if

*U.S. Mesh No.

Typical Median Range
90% through basis, microns

100	27-66
200	14-35
300	7-18

particles are too fine, solids settling may become a problem. In addition, the mill capacity will decrease and power consumption increase for finer size reduction at a given limestone hardness.*

High slurry recirculation rate and high solids content in the slurry will not only maximize reactant surface area, but will also minimize scaling potential, if sufficient delay time (approximately 10 minutes) is provided in the recirculating tank.

2.4 WATER BALANCE AND AMBIENT QUALITY CONSIDERATIONS

It is necessary that wet scrubbing systems be operated in closed loop to minimize effects on adjacent water basins. In closed loop operation the amount of make-up water used will be equal to the amount of water evaporated to saturate the flue gas plus the amount entrained or combined with solid waste produced. The remaining liquor (i.e., pond or thickener overflow) is recycled to the process. From a process standpoint, closed loop operation requires recycling saturated solutions. Process conditions must be carefully controlled to prevent scaling.

*Limestone hardness "Work Index" - 6-10.

Section 3

COMMERCIAL SYSTEM DESIGN

3.1 PROCESS APPROACH

The development of the lime-limestone scrubbing system has taken three process routes:

- Introduction of limestone into the scrubber circuit (Figure 1)
- Introduction of limestone into the boiler to produce CaO, followed by scrubbing of the flue gas (Figure 2)
- Introduction of lime into the scrubber circuit (Figure 3)

The most used process route is introduction of limestone into the scrubber. This approach has the advantage of minimum effect on the power plant; it can achieve high SO₂ removal with minimum scaling and plugging. The disadvantage of this process is that limestone is less reactive than lime; to offset this limitation, a higher stoichiometric ratio of limestone to SO₂ must be used, more slurry must be recirculated (higher liquid-to-gas ratio), and a counter-current scrubber with several stages is required.

The second process approach of introducing limestone into the boiler furnace produces a calcined limestone. Calcium oxide (CaO) enters

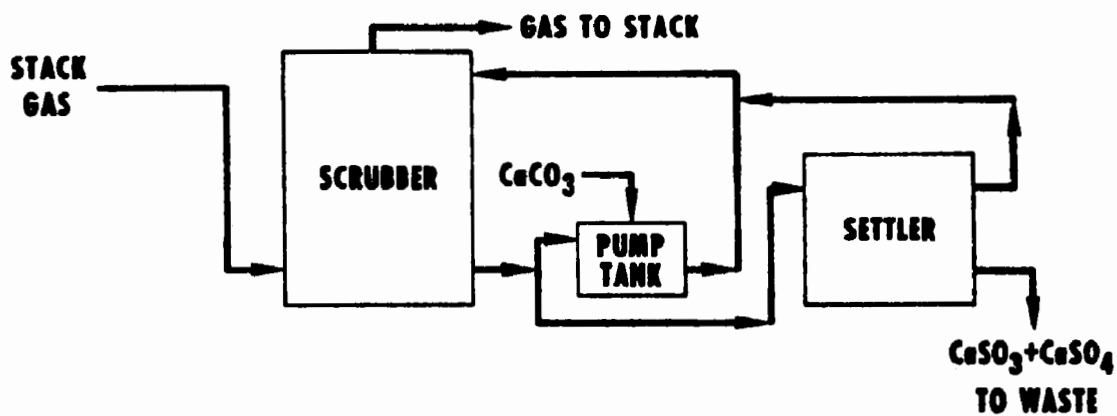


Figure 1. Scrubber Addition of Limestone - SO_2 Removal

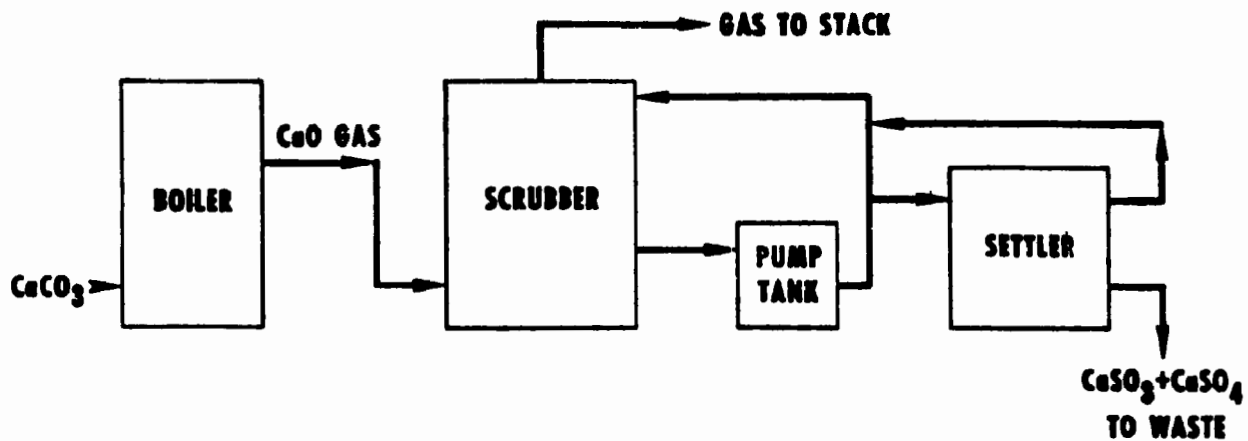


Figure 2. Boiler Injection of Limestone Followed by Wet Scrubbing

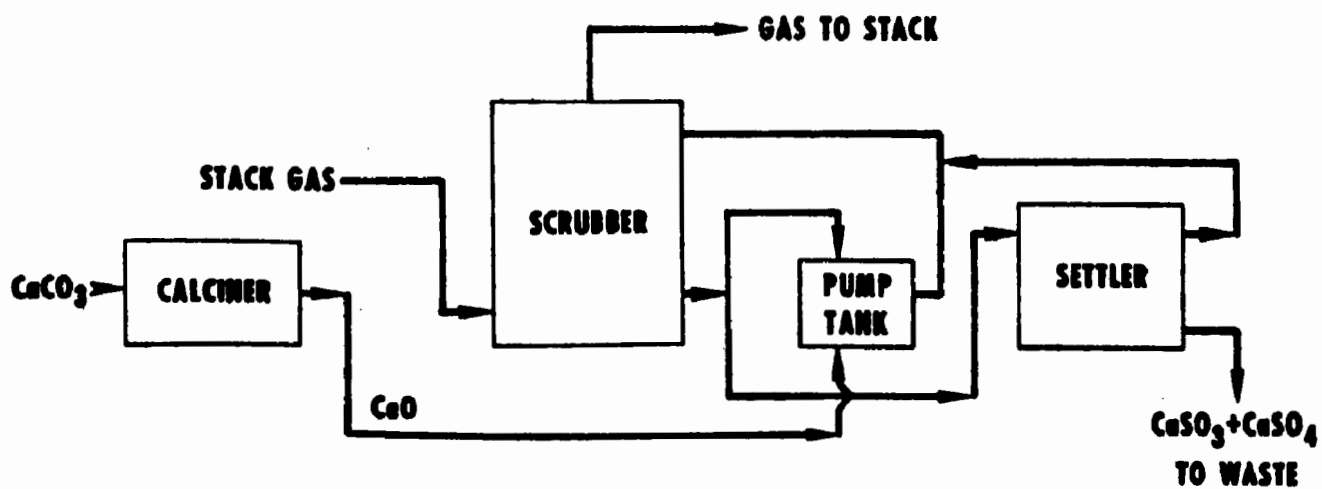


Figure 3. Scrubber Addition of Lime - SO_2 Removal

the scrubber with the flue gas. Problems with this process include boiler fouling, inactivating the lime by overburning, and increased scaling in the scrubber at the dry-wet interface. This approach is no longer offered by the SO₂ removal system supplier who originally offered it, unless requested by the customer.

Scrubbing efficiency can be increased in the third process approach by using lime in the scrubber circuit. This process has two disadvantages — the higher cost of lime over limestone and the greater potential for scaling under certain process configurations.

3.2 SCRUBBER DESIGN

In designing a scrubber system, the following main design criteria must be considered:

- Sulfur content of fuel
- Ash content of fuel (Is fly ash removed separately?)
- Percent SO₂ removal required
- Scrubber type
- System turndown
- Scrubber size and spare capacity
- Mist separators
- Gas reheat
- Waste disposal
- System power losses
- Materials of construction

3.2.1 Sulfur and Ash Content of Fuel

The sulfur content of the fuel burned in the power plant determines the required SO_2 removal to meet the new performance standards (1.2 lb SO_2 /million Btu for coal and 0.8 lb SO_2 /million Btu for oil). Three-percent sulfur coal requires approximately 80 percent removal of SO_2 from flue gas, whereas 0.8 percent sulfur coal (depending on heat value) requires 40 percent removal. Pilot plant data have shown that SO_2 removal from low sulfur flue gas is less difficult for the same liquid-to-gas ratios (40-80) because the amount of SO_2 absorbed per pass is significantly less. This can be seen by comparing inlet SO_2 values of 2400 ppm (high sulfur coal) to 600 ppm (low sulfur coal). The SO_2 absorption per pass is 1920 ppm for the high sulfur case and only 240 ppm for the low sulfur case. Control of scaling and supersaturation in the scrubbing systems is more predictable and thereby provides greater system reliability. In addition, the lime or limestone requirements are significantly less for low sulfur fuels. Waste disposal sites also require less land.

If the fly ash is removed from the flue gas before SO_2 removal is accomplished, the scrubbing system design can be different. This is particularly true as to scrubber selection. A spray column could be used to obtain 80 to 90 percent SO_2 removal with lower gas pressure drop. Waste solids disposal is also influenced by this design consideration.

If SO_2 and fly ash are removed simultaneously, a venturi followed by an afterabsorber, two stages of venturi, or turbulent contact absorber

(multistage) offer good possible choices for high removal. Waste solids requirements are higher, and process chemistry becomes more complicated.

3.2.2 Scrubber Type

The major criterion for scrubber selection is its capability to remove both sulfur dioxide and particulates with high efficiency (SO_2 removal greater than 80 percent and particulate removal greater than 99 percent). Other factors considered are ability to handle slurries without plugging, cost, control, and pressure drop.

Additional variables are:

- Liquid-to-gas ratio
- pH control
- Stoichiometric ratio of alkali to SO_2
- Percent of solids in slurry
- Limestone particle size
- Number of stages

The scrubber types that have been tested to date include the following:

- Venturi. The venturi scrubber (Figure 4) has been used when both particulate (fly ash) and sulfur dioxide must be removed. The venturi has good capability to remove fly ash down to 0.02 gr/SCF with pressure drops of 10 to 15 inches H_2O and liquid-to-gas ratios of 10 to 15 gpm per 1000 cu ft gas for typical dust loadings and particle size distributions from power plant stack gases. The

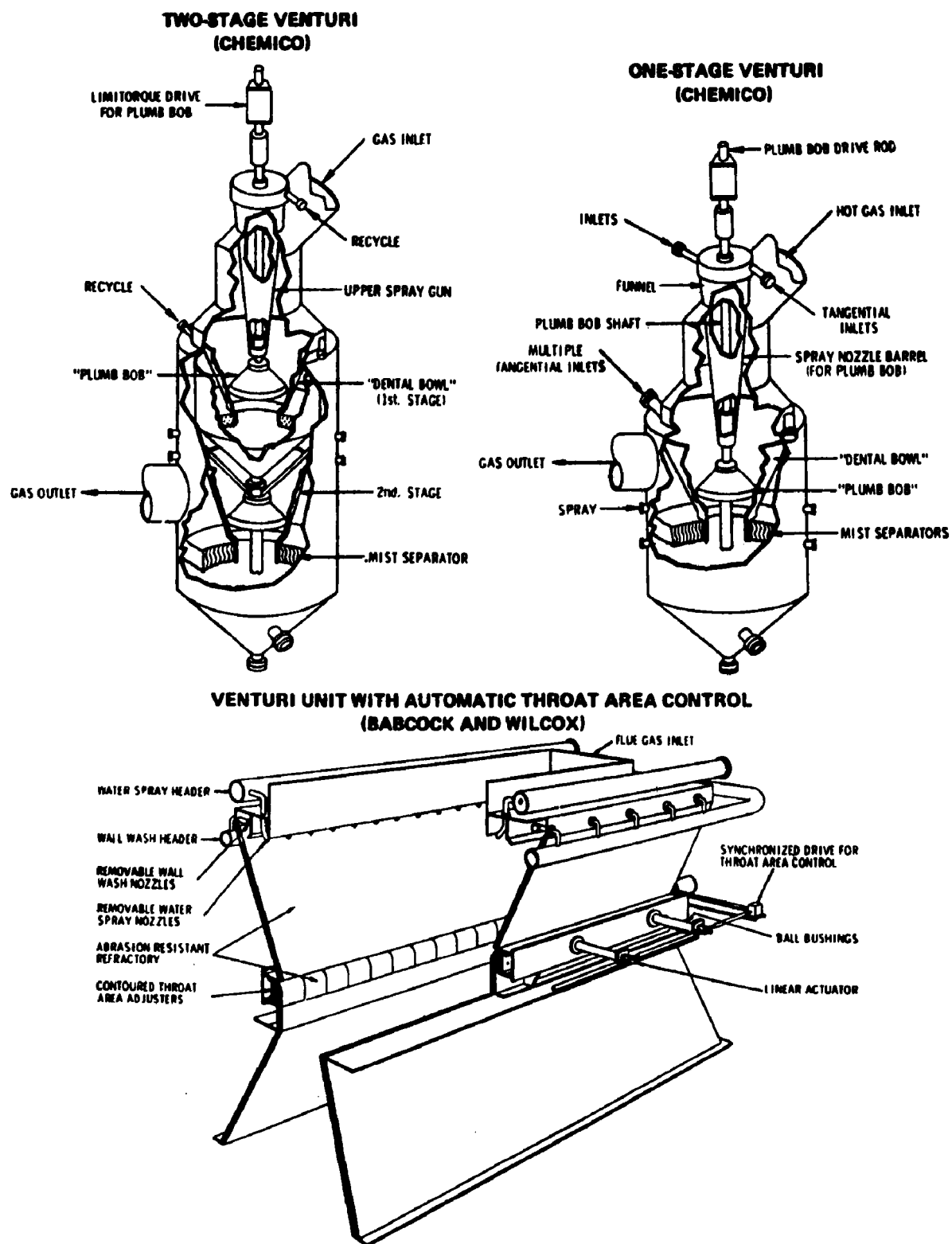


Figure 4. Venturi Scrubbers

venturi may contain an adjustable throat area that permits control of pressure drop over a wide range of flow conditions. The venturi scrubber is limited in SO_2 removal to 40 to 50 percent per stage with lime-limestone due to the short liquid residence time. It therefore requires two stages of venturis or an afterabsorber to achieve 85 to 95 percent SO_2 removal from high sulfur fuels at total liquid-to-gas ratio of 80.

- Turbulent Contact Absorber (TCA). The TCA (Figure 5) is a countercurrent multistage scrubber consisting of screens that both support and restrain the plastic spheres. The spheres move in a turbulent fashion providing good gas-liquid contact and scale removal. The number of stages generally are between two and four for high SO_2 removal with liquid-to-gas ratio of 40 to 50. The pressure drop per stage is approximately 2 to 2.5 inches H_2O .
- Marble-Bed Absorber. The marble-bed absorber (Figure 6) utilizes a 4-inch bed of packing of glass spheres (marbles) that are in slight vibratory motion. A turbulent layer of liquid and gas above the glass spheres increases mass transfer and particulate removal. This scrubber has been used mainly in the process where the limestone is added to the furnace for calcining, and the flue gases are scrubbed to remove SO_2 . Pressure drop is generally 4 to 6 inches H_2O . Liquid-to-gas ratios of 25 to 30 have been used.
- Packed-Bed Absorber. The packed-bed absorber must use open packing to prevent plugging. Packed towers have been tested in a pilot plant with high SO_2 removal and no significant scaling with low sulfur coal. Pressure drops are low - 0.4 inches H_2O per foot of packing. Scale control is extremely important in this type of scrubber, requiring liquid-to-gas ratios of 30 to 60.
- Spray Column. The spray column (Figure 7) is a counter-current type scrubber that has a low pressure drop. The spray tower requires high liquid-to-gas ratios ($\text{L/G}=80$) and several stages of sprays to achieve high SO_2 removal.

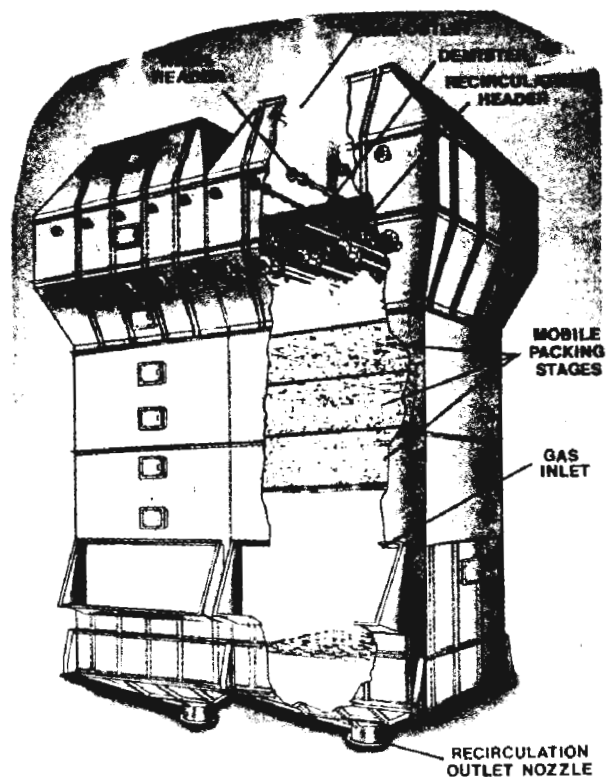


Figure 5. Turbulent Contact Absorber for SO_2 and Fly Ash Collection (UOP)

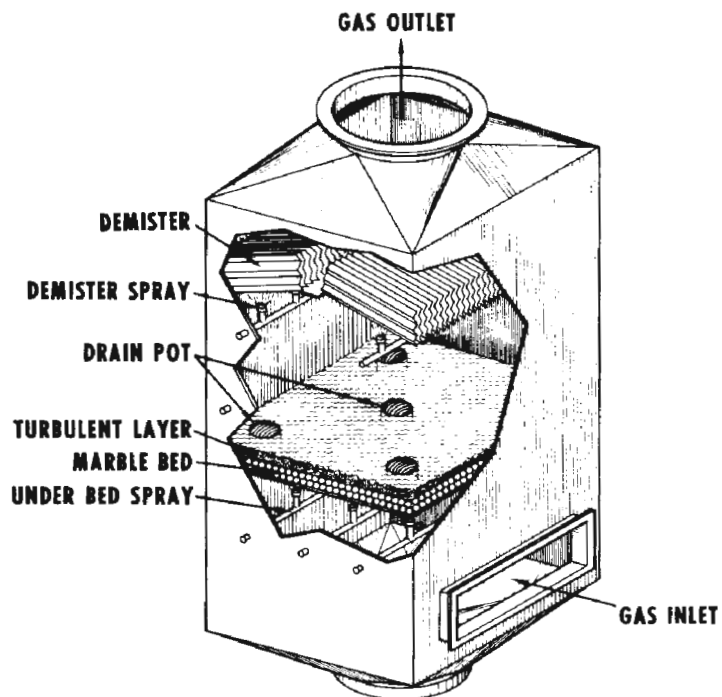


Figure 6. Marble-Bed Absorber

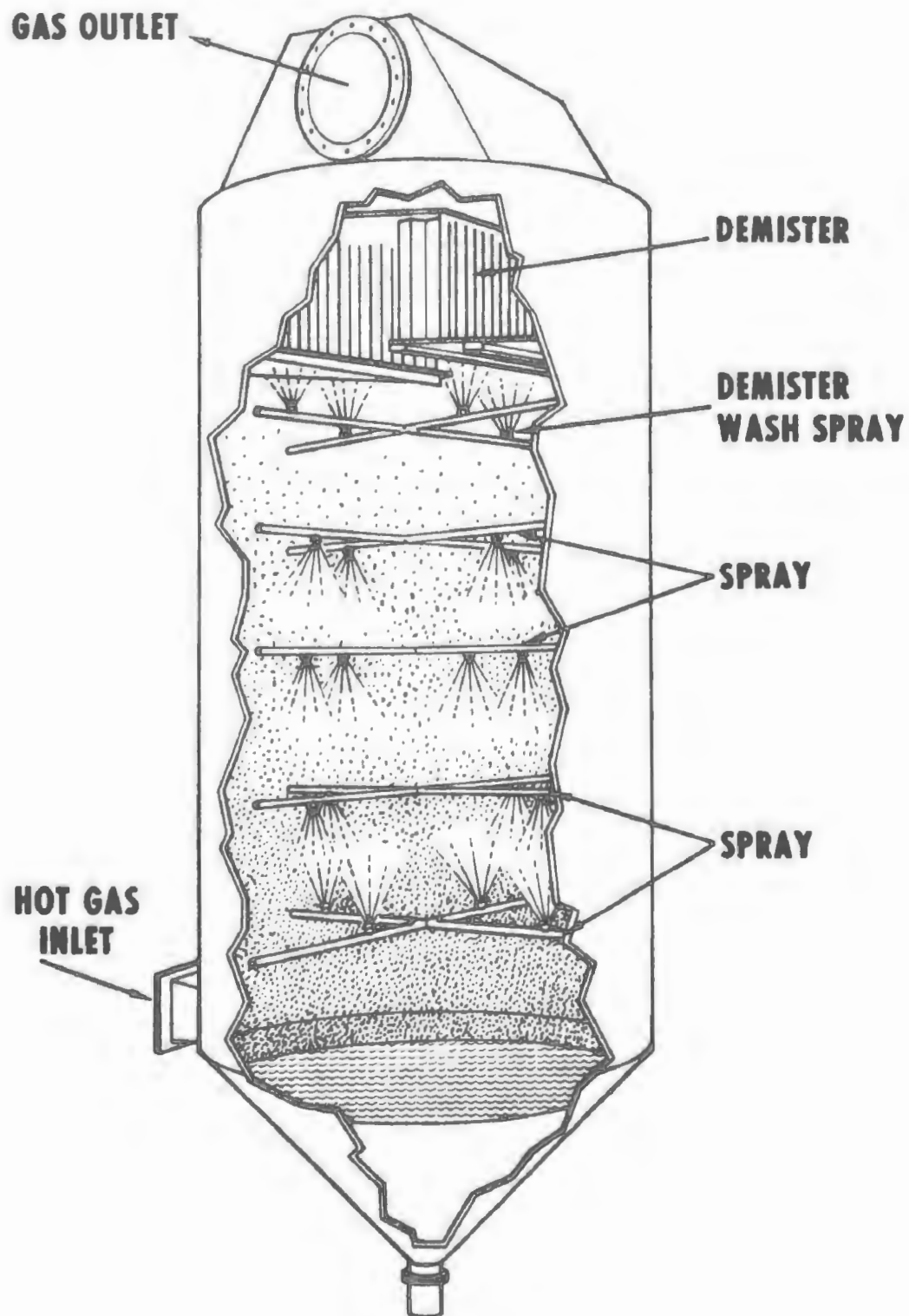


Figure 7. Spray Column

It has been tested by TVA, Peabody Engineering/Detroit Edison, and Ontario Hydro. The spray column is being tested at the EPA Test Facility, Paducah, Kentucky. Results also will be reported in a separate paper today (Ref. 5).

- Tray Column. The tray column offers high liquid hold-up and high SO_2 removal at relatively low pressure drop. The main disadvantage is the potential for scaling. High liquid-to-gas ratios ($\text{L/G} = 40$) are required. In addition, undersprays are used to wash off soft scale.
- Cross Flow Absorber. The cross flow absorber has a short gas path with the scrubber installed in a horizontal position. It has a low pressure drop and has been tested with packing or sprays. It requires a higher L/G ratio to obtain high SO_2 removal.
- Screen or Grid Scrubber. The screen or grid scrubber has been recently tested by TVA. It contains five to ten screens (7/8-inch openings). A liquid-to-gas ratio of 50 and a stoichiometric ratio of 1.5 give SO_2 removal of 75 to 80 percent. Low pressure drops were observed.

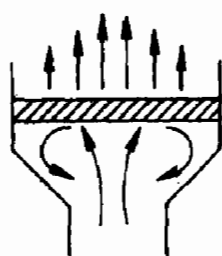
3.2.3 Scrubber Size, Turndown, and Spare Capacity

To keep the SO_2 removal system investment as low as possible, scrubber sizes of $500,000 \text{ ft}^3/\text{min}$ have been developed. This is required because the flue gas from a power plant is high — 3,000 ACFM/MW. An additional design consideration is scrubber turn-down, due to changes in boiler load. Some scrubbers can be turned down to 50 percent of design and others require compartmentalization.

In order to insure greater system reliability, spare capacity should be installed. Thus, a 500-MW unit could be designed with four modules (no spare) or five modules to insure backup capacity and system reliability. An economic analysis of a five module 500-MW unit will be presented later in this paper.

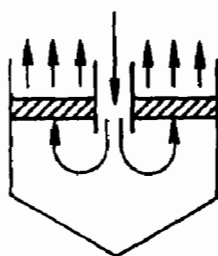
3.2.4 Mist Separators

Mist separators come in various designs, but are typically of open construction and low-flow resistance, similar to cooling tower packing. The techniques under development to control mist eliminator plugging employ such principles as:



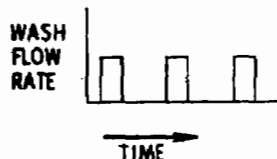
VELOCITY
REDUCTION IN
TCA

VS.

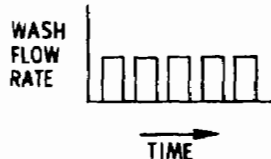


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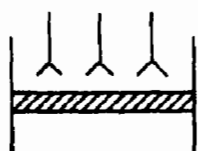
- Reduction in upward gas velocity to 8 feet per second or less, at the same time attempting not to disturb the uniformity of gas distribution



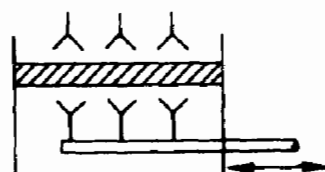
VS.



- More frequent back-washing, which may upset water balance in closed operations



VS.



- More efficient back-washing, for example employment of a traveling retractable washer similar to a conventional soot blower, in place of stationary sprays, or washing from both sides



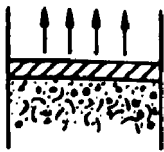
THREE - PASS

VS.

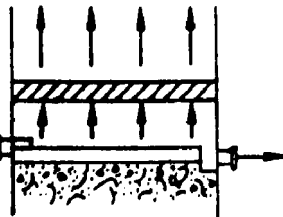


SINGLE - PASS

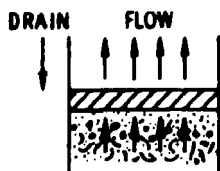
- Simplification of the mist separator design itself with possible sacrifice of entrainment removal efficiency



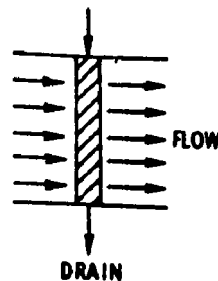
WATER
VS.



- Installation of an intermediate wash tray to lower the slurry solids entering the separator



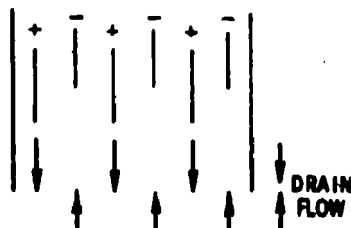
VS.



- Reorientation of the separator to "cross-flow" conditions with the gas flowing horizontally and the separators draining vertically at 90° rather than countercurrent at 180°



VS.



- Wet precipitation with a variety of configurations

It seems likely that a satisfactory answer to the problem of mist separator plugging will soon be found, and that it will consist of one or more of these measures.

3.2.5 Stack Gas Reheat

As the gas passes through a wet absorber, it will be humidified and cooled to the adiabatic saturation temperature (normally 120 to 130°F). Some water droplets may be present since the eliminator does not remove all of the mist formed in the scrubber. If the scrubber exit gas is not reheated, it will lose some of its buoyancy as a result of cooling. Thus, the effective stack height and the plume dispersion will be reduced. This should not be serious if a high degree of SO₂ removal is achieved. However, due to the low efficiency of nitrogen oxide removal, the ground level concentration of NO_x may become a serious problem, especially for existing plants where the stack height is already fixed. For new plants, this effect must be taken into consideration in stack design.

Humidification of the stack gas is also objectionable because condensation may occur and cause formation of a visible plume. This acidic plume may also create a corrosive environment around the stack area, although the stack itself is corrosion resistant.

The obvious solution is to reheat the scrubber exit gas. There is general agreement that the saturated and cooled gas should be reheated, but there is no agreement on the degree of reheating necessary or desirable. The consensus seems to be that it is not necessary to reheat it to the

original temperature (too expensive), but that it should be heated at least to a high enough temperature to minimize the water-vapor plume under most atmospheric conditions. This, of course, depends on the local meteorological conditions, but 50^oF is the most commonly used reheat design figure at present.

The methods of reheating the stack gas may be divided into direct heating and indirect heating.

Direct Heating. The major advantage of direct heating is operational reliability, because there is no heat transfer surface on which fouling can occur. Other advantages are low investment, flexibility in degree of reheat in some cases, low pressure drop, and low maintenance. There are several methods by which direct heating can be accomplished.

- Direct-Fired Reheater. Either natural gas or low-sulfur fuel oil may be used, depending on availability of fuel and cost. Natural gas is the most expensive fuel, but it is convenient and clean. Oil would be less expensive, but receiving, storing, and handling would be additional problems. Complete combustion of oil in contact with wet gas may also be a problem. The addition of sulfur dioxide and ash to the treated gas should be considered.
- Flue Gas Bypassing. Bypassing the scrubber with part of the gas stream—followed by mixing this gas with the scrubber exit gas—requires minimum investment and adds essentially no operating cost. However, this is possible only when the overall SO₂ removal requirement is low enough to allow such bypass, i. e., 50 to 60-percent removal or less. This may be possible for low-sulfur coal-fired boilers when the scrubber is preceded by a precipitator, but it is impossible for high-sulfur coal application.

- Hot Air Injection. If the air preheater is designed to produce excess hot air over the amount required for normal boiler consumption, this hot air may be used to mix with the scrubber exit gas to obtain the degree of reheat required. In doing so, the heat efficiency of the boiler will, of course, be lowered somewhat. Alternately, air can be preheated in a separate exchanger (with steam for instance), then mixed with the scrubber exit gas. This alternative gives the clean, nonfouling service expected, but it consumes more steam, because of sensible heat losses in the air, compared to direct-steam-to-stack-gas exchange. The added cost might be justified on the basis of reliability.

Indirect Heating. Indirect heating of the stack gas requires an exchanger to transfer heat from the heating medium to the gas. The advantage of this method is usually low operating cost, especially when heat from the inlet gas is transferred to the scrubber exit gas (recuperative heat exchange). The main disadvantages of this method are a higher gas pressure drop, higher investment, and possible fouling on heat transfer surfaces. If this method is chosen, finned tubes should be avoided, and devices to keep the exchanger surface clean (such as a soot blower) may be required. The following are alternative indirect reheat methods:

- Reheat with Steam. The exit gas may be heated with steam from the turbine cycle in a heat exchanger at the scrubber outlet. This method would require additional coal firing in the boiler to generate the extra steam and modification of the turbine to allow higher than normal extraction rates. In a new plant, a system could be designed to provide the steam required. The additional coal firing would still be more economical than direct-gas or oil-fired reheater.
- Recuperative Reheat System. A heat exchanger may be used for direct transfer of heat from the scrubber inlet gas to the exit gas. With this method, heat that would

be wasted is recovered. The disadvantages are the large heat exchanger required (because of low-transfer coefficient and low-temperature differential), high pressure drop, and possibility of fouling. Corrosion would also be a problem when the inlet gas is cooled to below the acid dewpoint. A cyclic-liquid heat exchange system with heat transfer from the inlet gas to water and from the water to the scrubber exit gas would permit use of smaller exchangers than those required for gas-gas exchange, and the smaller surface would reduce pressure drop. Other disadvantages remain, however.

The choice of a reheating method is not entirely an economic consideration; the system reliability must be considered as well.

3.2.6 System Power Losses

Wet scrubbing systems have significant energy requirements in terms of pumping and fan losses. When particulate removal is not required, the energy requirement is reduced substantially. Figures 8 and 9 show the order of magnitude to expect for fan and pumping losses from these systems. To these must be added an allowance for discharge pumps, small auxiliaries, lighting, and instrumentation.

Certain assumptions are incorporated in these figures, and the user is cautioned to consider results obtained from them as preliminary estimates only. The assumptions made in their construction are as follows:

- Compressibility effects for the fan are negligible.
- Fan efficiency is 60 percent.
- Motor efficiencies are 93 percent.

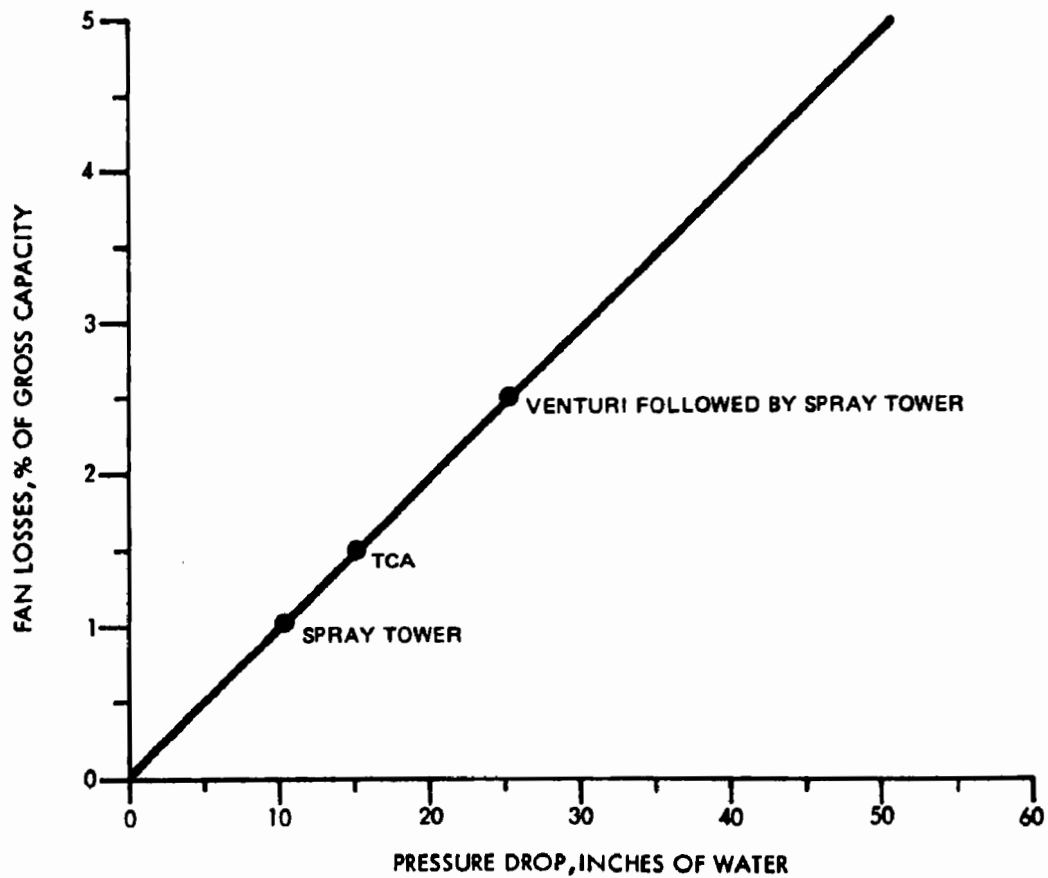


Figure 8. Station Electrical Loss as a Function of Draft Requirements

- Pump efficiencies are 85 percent.
- Scrubbing liquor solids are 10 percent.
- Liquid flow is turbulent. The sum of potential and friction losses is 80 velocity-heads. (This is typical of 80-foot elevation, plus pipe and fitting losses, with an allowance for control-throttling losses.)
- There is single-stage absorption.
- Flue gas generation was assumed to be 3000 actual cubic feet per minute per megawatt.

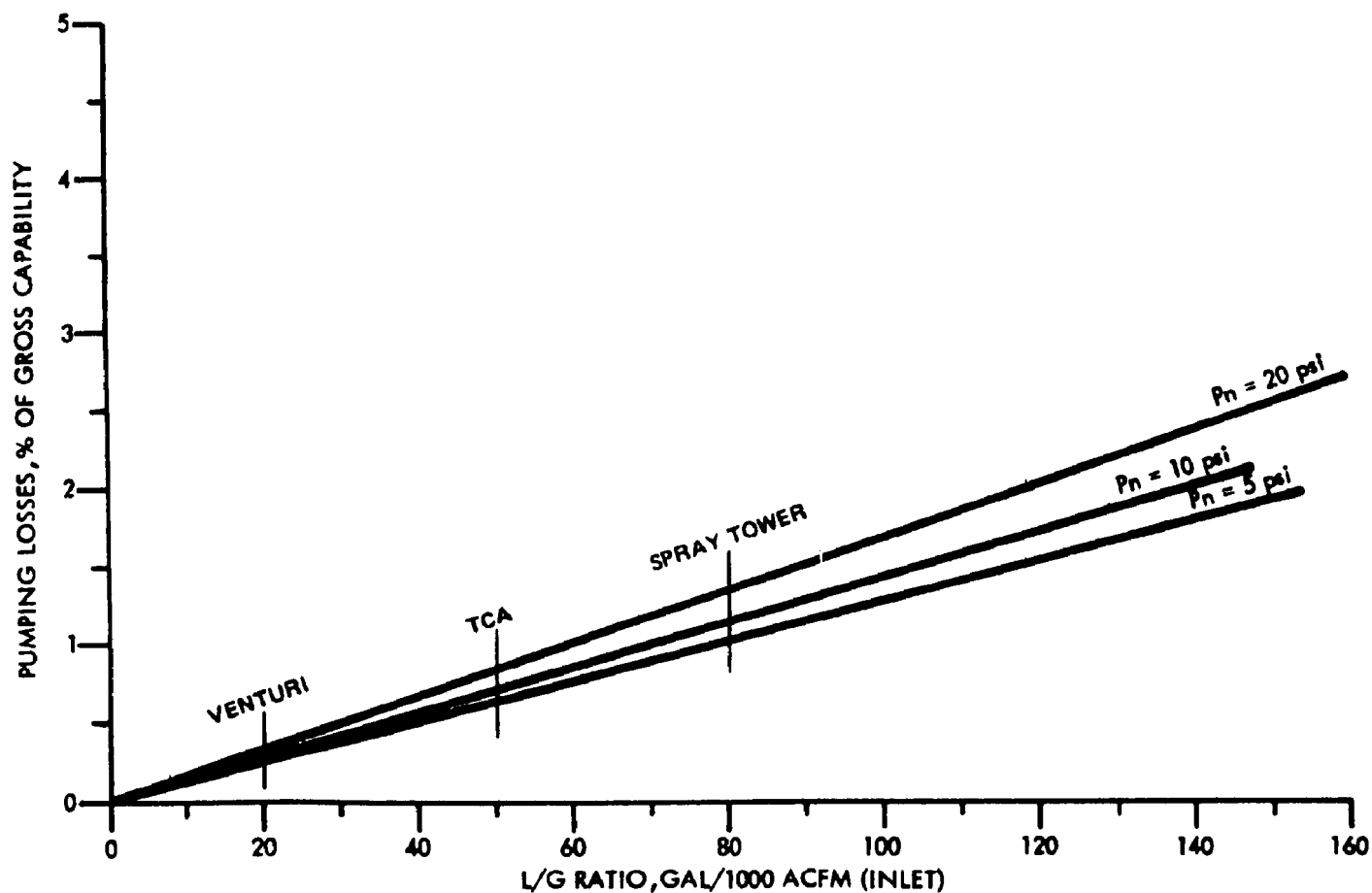


Figure 9. Station Electrical Loss as a Function of L/G Ratio and Nozzle Pressure

3.2.7 Materials of Construction

Any part of a wet scrubbing system that is in contact with wet SO₂ gas or acidic scrubbing liquor should be constructed of acid-resistant material. If solids are also present in the system, abrasion-resistant material should be used. The material specified should be able to withstand the highest temperatures encountered during normal operation and upset conditions.

Stainless steel 316L is sometimes used for scrubber construction. However, if chloride is present, stress corrosion will be a problem. Chloride stress corrosion is frequently characterized by so massive a failure that the affected metallic part must be totally replaced. A common form of prevention is to provide an upgraded alloy (e. g., Alloy 20, Incoloy, or Inconel), but an alloy demands a premium cost consistent with its higher nickel content.

Elastomer-lined (soft rubber or neoprene) carbon steel can be effective under abrasive conditions and temperatures up to about 175^oF. The temperature must be well controlled to protect the lining. Field rubber lining costs roughly four dollars per square foot. A further advantage of these linings is the lower maintenance costs in descaling. The scale-substrate bond is more readily broken than in the case of stainless steel or alloy metals.

Rubber-linings applied in the shop have relatively strong vulcanized bonds because they are autoclave cured. Field linings employ chemical curing agents rather than heat, and their quality is not always comparable. Ambient temperatures must not fall below 70^oF during the curing period. Vessel components with short-axis dimensions exceeding 10 to 12 feet cannot be shipped by rail, hence, they must be field-lined.

A serious problem area inside scrubbers is the zone where hot gases first contact the liquor medium, because temperature control is sometimes difficult. An acid-proof gunite is now being offered by Pennwalt for protection of these areas. The gunite is bonded directly to the steel with thickness from 0.5 to 1.5 inches. The gunite will withstand tem-

peratures up to 750°F, and the applied cost is \$4 to \$10 per square foot. Gunite can also be used for duct and stack lining. In using gunite, the added weights and stresses must be considered.

Another lining material of promise is glass-flake reinforced-polyester resin, such as the Ceilcote 100 and 200 series and Carboglass 1601. This material is trowel-applied at 40 to 80 mils thickness on carbon steel and can withstand temperatures up to 200°F under conditions of continuous operation. The applied cost is \$3 to \$4 per square foot. Its abrasion resistance improves when well wetted, and it can be field-patched with relative ease, compared to elastomeric linings.

3.3 WASTE DISPOSAL

The nature of calcium sulfite and calcium sulfate solids leaving the system has created a problem that remains incompletely defined. Judging from the experience at Mitsui Aluminum and at Will County Station No. 1, there seems to be some indication that the solids from limestone systems may not settle as completely in the pond as those from lime systems.

The limestone solids at Will County have been observed to settle only to 35 percent. Under such conditions they have no bearing strength, but behave like quicksand. This not only increases the acreage requirements, but it also creates a possible hazard to stray animals and wildlife.

One possible solution is to install supplemental mechanical dewatering equipment. Another is to use lime in place of limestone, although at greater cost. Also, the use of coagulants to improve settling is a possibility. Furthermore, it is not clear whether the lack of consolidation originates from the use of calcium carbonate (as opposed to calcium hydroxide), or whether it can be primarily attributed to excessive size reduction of the limestone feed. Until this is established, limestone systems should have built-in turndown on their size reduction circuits. The determining factor in size reduction is the classifier circuit, comprised of liquid cyclones. These return the oversized material to the ball mill, but reject the material of requisite fineness so that it passes on to the process.

It has been found very difficult to reliably simulate the properties of these solids on a laboratory scale. The reasons for this appear related to ionic strength — i. e., the slow buildup of minor soluble salts in the circulation slurry that alters a solubility relationship of its principal constituents. Invariably laboratory slurries turn out to be faster settling than encountered at full scale. Further detailed studies based on pilot operation are required.

The waste sludge produced in the lime/limestone scrubbing process requires special study for proper management. The sludge consists primarily of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 or Ca(OH)_2 , and fly ash. The quantities are significant, 500,000 tons/yr, 50-percent solids for a 500 MW power plant burning 3-percent sulfur coal. The principal method for most of the 20 full-size installations is disposal in a pond located on the power plant site. However, there are many plants that have insufficient land and therefore must condition the solids for disposal some distance from the plant.

Suitable areas that are ecologically sound must be found. Studies should be carried out to determine the feasibility of disposing of these solids in the mines where the coal was produced. The unit trains that transport the coal to the power plant could logically carry the sludge back to the mines. The sludge must be dewatered so that it can be transferred easily to and from the trains. Studies should be funded to evaluate this concept. Other sites that should be studied are old limestone quarries and salt domes. These should be acceptable from an ecology point of view. The large disposal sites might be operated by state agency and a fee be charged for disposal.

Another important disposal technique used where land is not available at the plant site involves dewatering the sludge and transporting it by truck or barge to a suitable landfill. Further studies are necessary to better understand this technique.

Chemical fixation processes are also being developed. These processes generally involve pozzolanic (cementitious) chemical reactions requiring the presence of lime. Such reactions lead to the formation of dry solids with potential landfill and reclamation applications. This technique requires additional study to define optimum conditions.

Limited research on the use of fly ash and limestone-modified fly ash has been performed. Additional research is required to explore the utilization of lime/limestone sludge to perhaps 25 percent of the quantity produced. In Japan, the sulfite is usually oxidized to sulfate and the gypsum produced is used for construction. This potential market should be further explored in the United States.

The Coal Research Bureau of West Virginia University has been performing research under partial support from the Environmental Protection Agency to develop and evaluate utilization of such a solid-waste fly-ash mixture. As a result of this research, several possible areas of utilization have emerged. These include production of autoclaved materials such as calcium-silicate brick or block, aerated or foamed concrete, and cement materials.

Based on the above comments, it is evident that further study is critically needed to define a sound plan of solid waste management.

Section 4

STATUS OF FULL-SIZE INSTALLATIONS

Although process development for SO_2 removal using lime/limestone scrubbing continues at an intensive rate, the U.S. industry has decided to install full-size units to meet air quality regulations and to accelerate technology. To date, there are 21 commercial-size installations using lime or limestone scrubbing (see Table 1). There are also four scrubber systems for particulate removal only (not listed in Table 1) that have contributed to the state of the art. Table 1 gives the operational status and design criteria of 21 installations; 11 units were retrofits and 10 installations are planned for new power stations. The largest facilities are the Mansfield plant of Ohio Edison (two 900 MW - 3 percent S coal), and the Navajo plant of Salt River Project (three 750 MW - 0.5 to 0.8 percent S coal). These units are designed for alkali addition into the scrubber circuits.

Other points that should be emphasized are:

- Units Operating - 8
 - Alkali furnace injection - 3
 - Alkali into scrubber circuit - 5
 - Total MW installed - 1900

- Units being engineered and constructed — 12
 - Alkali furnace injection — 0
 - Alkali into scrubber circuit — 12
 - Total MW to be installed — 9600

In 1968 and 1969 at Union Electric's Meramec Station and Kansas Power & Light's Lawrence Station, the first full-size units were installed. Both employed finely pulverized limestone injected into the boiler furnace followed by wet scrubbing utilizing a marble bed scrubber. Operating experience revealed a number of problems that included scaling and corrosion. A typical flow diagram for this process approach is shown in Figure 10. The system at Meramec has been abandoned, and the Lawrence Unit has been substantially modified. A second unit at Lawrence Station was installed and started up in December 1971. Reported SO_2 removal is 70 percent at a stoichiometry of 0.7.

The first full-size limestone scrubbing system in this country utilizing alkali addition into the scrubber liquor circuit was installed as a retrofit unit at the Will County Station of Commonwealth Edison. The unit involved is a 180-MW cyclone boiler with a two-stage venturi/absorber to remove fly ash, followed by SO_2 . More has probably been learned from this installation about practical operating problems with limestone during its one year of operation than from any other pilot plant to date. The major problems experienced are maintaining clean demisters, system reliability due to mechanical problems, and disposal of waste solids. SO_2 removal efficiencies reported were 75 to 85 percent. A typical flow diagram for this process is shown in Figure 11. Table 2 presents preliminary test data for 1972 (Ref. 7).

**Table 1. OPERATING AND PLANNED FULL-SIZE LIME/LIMESTONE DESULFURIZATION
FACILITIES IN THE UNITED STATES**

	Utility Company/Plant	Absorbent	Megawatts	New or Retro.	Scheduled Startup	Fuel	Supplier
1.	Union Electric Co. (St. Louis)/ Meramec No. 2	CaO	140	R	September 1968	3.0-% S coal	C-E
2.	Kansas Power & Light/ Lawrence Station No. 4	CaO	125	R	December 1968	3.5-% S coal	C-E
3.	Kansas Power & Light/ Lawrence Station No. 5	CaO	430	N	December 1971	3.5-% S coal	C-E
4.	Commonwealth Edison/ Will County Station No. 1	CaCO ₃	175	R	February 1972	3.5-% S coal	Babcock & Wilcox
5.	City of Key West/Stock Island	CaCO ₃	37	N	June 1972	2.75-% S fuel oil	Zurn
6.	Kansas City Power & Light/ Hawthorne Station No. 3	CaO	130	R	Mid-Late 1972	3.5-% S coal	C-E
7.	Kansas City Power & Light/ Hawthorne Station No. 4	CaO	140	R	Mid-Late 1972	3.5-% S coal	C-E
8.	Louisville Gas & Electric Co./ Paddy's Run Station No. 6	Ca(OH) ₂	70	R	Mid-Late 1972	3.0-% S coal	C-E
9.	Kansas City Power & Light/ La Cygne Station	CaCO ₃	840	N	Late 1972	3.2-% S coal	Babcock & Wilcox
10.	Arizona Public Service Co./ Cholla Station	CaCO ₃	115	R	Early 1973	0.4-1-% S coal	Research Cottrell
11.	Duquesne Light Co. (Pittsburgh)/ Phillips Station	CaO	100	R	May 1973	2.3-% S coal	Chemico
12.	Detroit Edison Co./ St. Clair Station No. 6	CaCO ₃	180	R	December 1973	2.5-4.5-% S coal	Peabody
13.	Ohio Edison/Mansfield Station	CaO	1800 (2 boilers)	N	Late 1974- Early 1975	coal - 3-%	Chemico
14.	Tennessee Valley Authority/ Widow's Creek Station No. 8	CaCO ₃	550	R	April 1975	3.7-% S coal	TVA
15.	The Montana Power Co./ Colstrip Units 1 & 2	Fly Ash + CaO	720 (2 boilers)	N	May 1975	0.8-% S coal	CEA
16.	Northern States Power Co. (Minnesota)/ Sherburne County Station No. 1 & 2	CaCO ₃	Total 1360	N	May 1976 (No. 1, 700Mw)	0.8-% S coal	C-E
17.	Northern Indiana Public Service Co./ Kankakee 14	CaO or CaCO ₃	500	N	June 1975	3.0-% S coal	Not selected
18.	Mohave-Navajo/ Mohave Module (Vertical*)	CaCO ₃ /CaO	160	N	March 1974	0.5-0.8-% S coal	Procon/UOP/ Bechtel
19.	Mohave-Navajo/ Mohave Module (Horizontal*)	CaCO ₃ /CaO	160	N	December 1973	0.5-0.8-% S coal	Southern California Edison/Stearns Roger
20.	Salt River Project/ Navajo Station	CaCO ₃	2250 (3 boilers)	N	July 1977	0.5-0.8-% S coal	Procon/UOP/ Bechtel
21.	Southern California Edison/ Mohave Station (Horiz/Vert)	CaCO ₃ /CaO	1500 (2 boilers)	R	December 1976	0.5-0.8-% S coal	Not selected

*Southern California Edison is program manager.

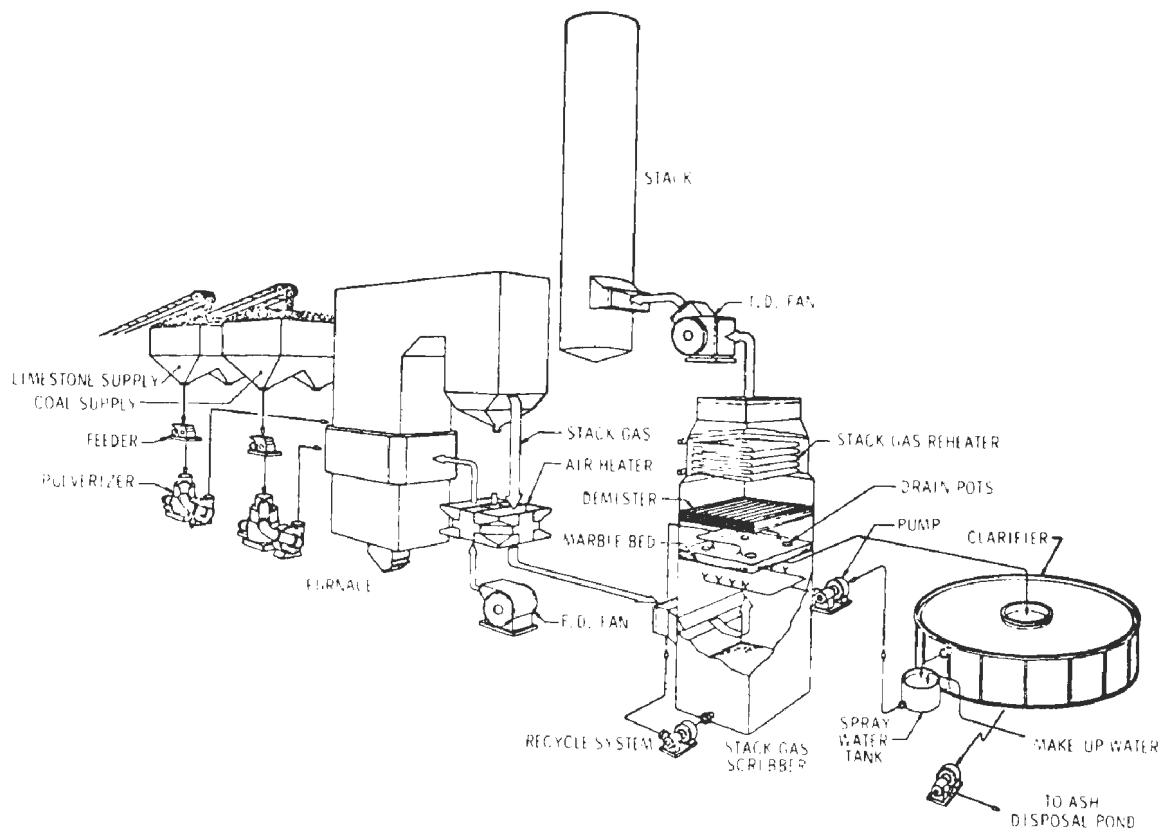


Figure 10. Particulate and SO₂ Removal System Employing Marble Bed with Limestone Calcining in the Boiler
(Source: Combustion Engineering)

Table 2. WILL COUNTY UNIT 1 WET SCRUBBER TEST DATA ("A" SCRUBBER, MAY 1972)

Test Number	1	2	3	4	5	6	7	8	9	10	11	12
Date	5-18	5-18	5-19	5-19	5-20	5-20	5-21	5-21	5-22	5-22	5-23	5-23
Load, MW	113	113	114	115	111	112	113	115	110	111	—	58
Gas Flow, 10 ³ CFM	335	335	335	340	335	320	315	310	315	335	205	215
Scrubber System, Pressure Difference, Inches H ₂ O	24.5	29	21	25	24	25.5	22.5	22.0	23.2	23.0	16.0	18.0
Dust Inlet, gr/SCFD	—	.0944	.1440	.1470	.1105	.1790	—	—	.3060	.2580	—	—
Dust Outlet, gr/SCFD	.0232	.0079	.0073	.0298	.0261	.0255	—	—	.0205	.0334	—	—
SO ₂ Inlet, ppm	1145	1140	890	930	1130	1000	640	910	1000	545	1200	1150
SO ₂ Outlet, ppm	67	75	294	35	285	118	18	45	223	180	45	50
SO ₂ Removal Efficiency, %	94	93	67	96	75	88	97	95	81	67	96	96
Absorber Slurry Density, %	3.4	5.2	5.5	5.2	2.5	4.3	5.0	—	2.9	2.2	—	1.5
Absorber pH	6.5	6.3	7.4	6.3	5.7	5.8	7.2	5.7	5.9	5.4	6.1	6.1

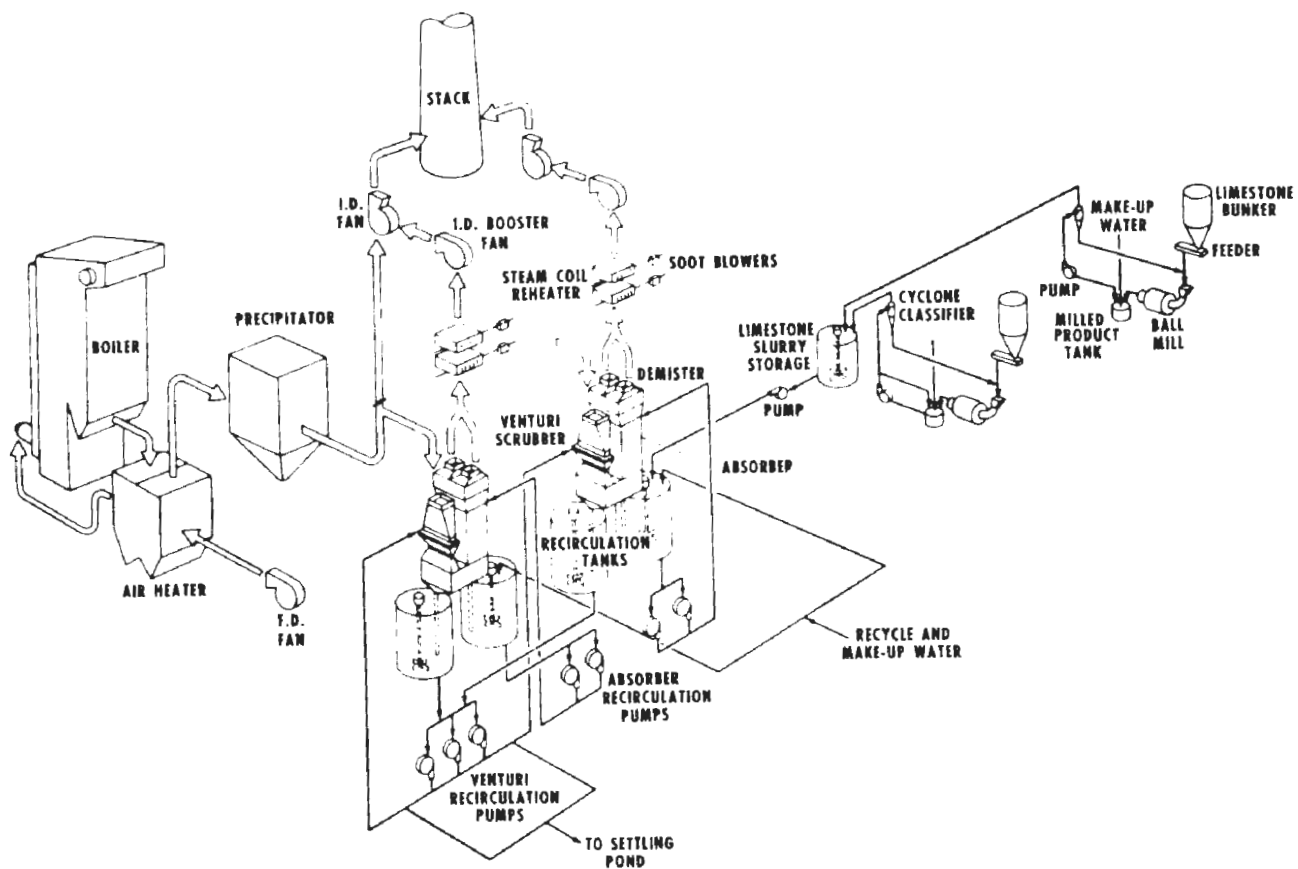


Figure 11. Will County Station Unit No. 1 (Limestone Added to Scrubber – Venturi plus TCA Absorber)

The first scrubbing system utilizing lime introduced into the scrubber circuit has been installed at the Phillips Station of Duquesne Power and Light. It is presently going through startup and should supply valuable information when in full operation later in 1973. This unit is reported to be designed based on the Mitsui Aluminum unit in Japan, which uses a calcium hydroxide scrubber (Ref. 8). To date the Japanese system is the most successful operating unit based on a throwaway process. It has been operating since March 29, 1972 without any significant downtime. SO_2 removal efficiencies have been reported to be 80 to 90 percent. A typical flow diagram for this process is shown in Figure 12.

The Hawthorne Units 3 and 4 of Kansas City Power & Light are presently in the first stages of operation. One uses alkali injection into the boiler furnace and the second has been modified to inject lime into the scrubber.

The Paddy's Run Station of Louisville Gas & Electric is the first plant to test carbide sludge [$\text{Ca}(\text{OH})_2$]. Test results based on a relatively short period of operation indicate high removal of SO_2 .

Kansas City Power & Light's LaCygne plant is presently in startup and should be in full operation during the next 60 days.

When most of the 20 units are operating, significant progress toward commercial demonstration will be realized.

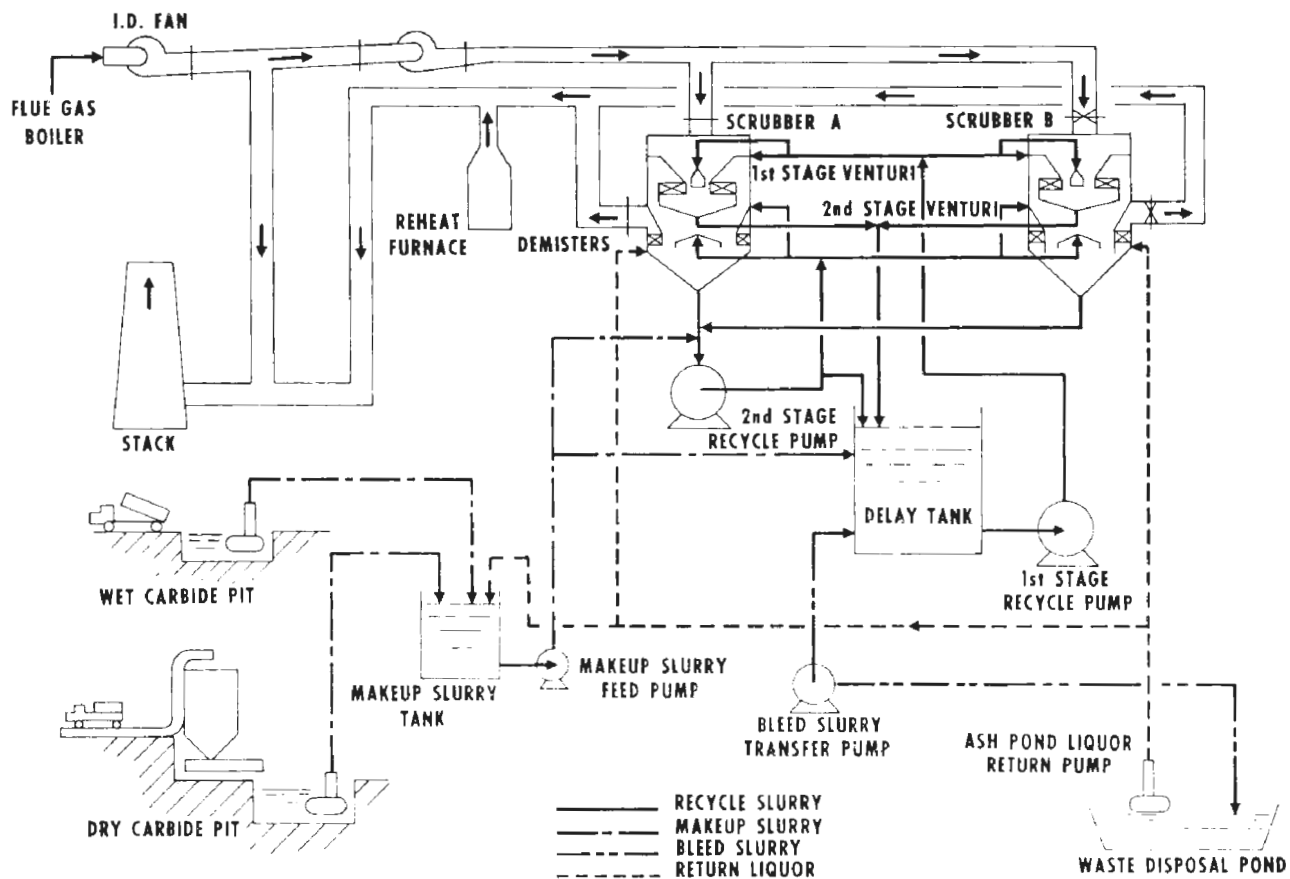


Figure 12. Chemico/Mitsui Flue Gas Desulfurization System (Lime Added to Scrubber)

Section 5

LIME/LIMESTONE COMMERCIAL OPERATING CONDITIONS OFFERED BY SO₂ REMOVAL SYSTEM SUPPLIERS

Suppliers for SO₂ removal systems are growing steadily. A review of the market reveals seven suppliers with full-scale experience. There are five other companies that have just recently entered the market.

The seven companies with full-scale experience were contacted to obtain design information concerning SO₂ removal guarantees related to percent sulfur fuel, scrubber type, liquid-to-gas ratio, stoichiometry, percent solids in slurry, alkali type, hold tank residence time, and any qualifications concerning system design. The results of this study are presented in Table 3.

It is interesting to note most companies will supply systems using lime or limestone as the alkali and provide SO₂ removal guarantees that vary from 70 to 90 percent, respectively, or as required to meet performance standards. Important operating parameters such as liquid-to-gas ratio and stoichiometry have changed in design range. Liquid-to-gas ratio has increased from 20 to as high as 100, the average being 60. Stoichiometry has decreased from 1.75 to as low as 1.0 based on SO₂ absorbed, the average being 1.2. There appears little restriction on the percent sulfur in the fuel as it relates to guarantees or size of units.

Module designs, as large as 150 megawatts each, for units up to 800 megawatts, are provided by U.S. suppliers. All process designs are based on alkali addition to the scrubber circuit.

When schedule was discussed, most suppliers stated a minimum time schedule of 24 months from purchase order to startup. A preferred time period would be 30 months, depending on backlog. The time required for a bidder to respond to a functional specification ranges from 4 to 10 weeks, with 8 weeks being typical. An additional period of 8 weeks is required to review proposals, select supplier, and conduct preaward negotiations. Based on the above requirements, the total time period is approximately 36 months. In addition, pilot plant testing to evaluate limestone reactivity is desirable.

Table 3. OPERATING CONDITIONS OFFERED BY SO₂ REMOVAL SYSTEM SUPPLIERS

Supplier	Scrubber	Alkali	Liquid to Gas Ratio, gal/MCF	% Sulphur Fuel	Stoichiometry	% Solids	Hold Tank Res. Time, min.	Pilot Plant Capability	SO ₂ Removal Guarantee, %	Full Size Experience
Chemical Construction Co.	Venturi 2 stage spray column	Lime Limestone	40-80 80	0.5-4	0.8-1.3 1.3-1.5	12 10-12	3 3	Yes	90 75	Yes
Combustion Engineering	1 or 2 marble beds ^(a) (bottom spray only)	Lime Limestone Carbide sludge	25-30 25-30 25-30	0.5-4 0.5-4 0.5-4	1.0 1.2-1.3 1.0	7-10 7-10 7-10	15 15 15	Yes	Meet performance standards	
Babcock & Wilcox	Low pressure drop quencher plus tray absorber	Lime Limestone Carbide sludge	40-50 40-50 40-50	0.5-4 0.5-4 0.5-4	1.1 1.2-1.3 1.1	5-8 5-8 5-8	4-6 4-6 4-6	Yes	90 80 90	Yes
Peabody Engineering	Venturi plus spray column	Lime Limestone	(b) (c)	0.5-4 0.5-4	1.1 1.2-1.3	15 15	8-10 8-10	Yes	90 85	Yes
UOP - Air Correction	Turbulent Contact Absorber (3 stages)	Lime Limestone	40 40	0.5-4 0.5-4	1.25 1.50	10 10	5 5	Yes	90 85	Yes
Combustion Equipment Assoc.	Venturi (if particulate included) (2 stage) spray column (SO ₂ only)	Lime Limestone	60 80	0.5-4 0.5-4	1.1-1.3 1.2-1.4	8-12 8-12	3-5 10-12	Yes	90 80-85	Yes Yes
Research Cottrell	Multicontact absorber Bahco system ^(f)	Limestone Lime	(d) 	0.5-2 3-4	1.1-1.3	10-15	5-10	Yes	90 ^(e) 90 ^(f)	Yes

a. Furnace injection of alkali not offered unless requested.

b. L/G = 20 for venturi, 50-60 for spray column with lime.

c. L/G = 80 for spray column with limestone.

d. L/G (1st stage) = 50-60; L/G (2nd stage) = 15-30.

e. Research Cottrell has no restriction on system design or guarantee for units using fuel with 2 percent or less sulfur. For fuel with greater than 2 percent sulfur, they require a 100-MW demonstration unit before building a full-size (i.e., 800 MW) installation.

f. Bahco is limited to 100,000 CFM, or 35 MW, and offers limestone systems.

Section 6

CAPITAL AND OPERATING COSTS OF FULL-SIZE SO₂ REMOVAL SYSTEMS

In order to develop capital and operating costs, Bechtel cost estimates were used as a basis. The basis for design of lime/limestone scrubbing systems was a "typical" new 520-megawatt boiler burning high sulfur coal (3 percent S). SO₂ removal required is approximately 80 percent. Particulate removal preceded the SO₂ removal. A spare train was provided for system reliability, and a pond is available for disposal of the waste solids.

It has generally been the practice to cite capital costs on a "per kw" basis, whereas a "per CFM" cost basis is more meaningful across the range of combustion conditions encountered. Economics of scale provide unit savings for scrubbers up to 500,000 CFM. Above this size, duplication of scrubber trains is necessary, and cost savings cease to apply.

A common reason for high "per kw" cost is the installation of a complete scrubber train with isolation dampening so as to make on-stream maintenance. For a five-train system, this is equivalent to 25 percent of installed cost. This practice is not always necessary, being dependent on utility load balancing as well as on reliability and proven

maintenance record for the particular system employed. Other reasons for "high" costs per kw are due to high contingencies for system modifications and high escalation rates.

It should be noted that no costs were shown for real estate deeded over to sludge ponding. Instead, a flat charge of \$2 per ton of wet sludge (40-percent solids) was allowed. A slight advantage was given to lime sludges in that it was assumed the solids would settle to 50-percent solids. In addition, it should be emphasized that disposal costs are highly site-sensitive. If the sludge must be treated for disposal off site, the charge per ton could double to \$4.00 and thus increase operating costs by 15 percent.

Capital costs have been divided into direct costs and indirect costs. Direct costs include yard facilities, raw material handling, scrubber system, and sludge handling. Indirect costs include field costs, engineering, home office, escalation, and fee. Estimated capital cost for a "typical" new 520-megawatt unit using limestone scrubbing is \$23,400,000 or \$45 per kw. The total installed cost is \$10.70 per ACFM. The estimated cost per kwh is 2.26 mills, based on limestone at \$5.00 per ton delivered (stoichiometry at 1.5 and a sludge charge of \$2.00 per ton). If limestone can be purchased at \$3.00 per ton, the annual cost would be 2.15 mills/kwh. Based on 10,000 Btu/lb coal, the cost per million Btu is estimated to be 23¢. If sludge disposal cost is \$4.00 per ton, the annual operating cost would be 26¢ per million Btu. Tables 4 and 5 summarize these costs and give the basis for the estimate.

The estimated capital cost for a "new" 520-megawatt lime scrubbing system is \$19,600,000 or \$38/kw. This is equivalent to \$9/ACFM.

The estimated cost per kwh is 2.16 mills based on lime at \$20 per ton delivered. Sludge disposal costs are reduced due to less sludge produced because of lower stoichiometry and better settling of solids to 50 percent by weight. Annual cost for SO₂ removal is estimated to be 23¢ per million Btu. Tables 6 and 7 summarize these costs

Retrofit costs for SO₂ removal are greatly affected by specific plant conditions. Therefore, no effort has been made to present costs for retrofit units. More detailed information on cost considerations can be found in a paper presented by Burchard (Ref. 9).

Table 4

CAPITAL COST - LIMESTONE SCRUBBING^(a)

Cost Item	Thousands of Dollars	Dollars/kw	Dollars/ACFM Installed
Yard facilities	648		
Raw material handling	2,347		
Scrubber system	7,427		
Sludge handling (on-site)	<u>755</u>		
Direct costs, subtotal	11,177		
Field costs, engineering and home office, escalation, contingency, and fee	12,253		
Total installed	23,430	45.05	10.70

a. 520-MW gross output; 3.1-percent S coal; 81-percent SO₂ removal; particulate matter removed by others; 80-percent load factor; with ponding; spare train

Table 5

ANNUAL OPERATING COST - LIMESTONE SCRUBBING^(a)

Cost Item	Total Requirement	Range of Unit Cost Experience	Unit Cost, This Study	Annual Cost, \$Thousand	Cost per kwh, mills
Basic alkali, tons	205,000	\$ 3.00-9.00	\$ 5.00	1,025	0.293
Process water, gal x 10 ³	461,000	\$ 0.02-0.15	\$ 0.02	9	0.003
Power, demand, kw	7,940	\$15.00-40.00	\$35.00	278	0.078
Power, energy, kwh x 10 ³	53,400	\$ 0.90-5.00	\$ 5.00	267	0.076
Steam, demand, annual Btu x 10 ⁶	800,000	\$ 0.08-0.25	\$ 0.20	160	0.046
Steam, energy, Btu x 10 ⁶	615,000	\$ 0.10-0.55	\$ 0.55	338	0.097
Operating labor, 3/shift	25,200	—	\$ 6.25	158	0.045
Operating labor overhead at 75%				118	0.034
Maintenance at 5% of direct cost				557	0.159
Maintenance overhead at 30%				167	0.048
Capital recovery, 15 yr, 7-1/2% (.1315 multiplier)				3,081	0.881
Insurance and property taxes at 1.9%				444	0.127
Sludge disposal, tons	659,000	\$ 0.75-5.00	\$ 2.00 ^(b)	1,318	0.377
Total Cost				7,920	2.26

a. 520-MW gross output; 3.1-percent S coal; 81-percent SO₂ removal; particulate removal by others; 80-percent load factor; with ponding; spare train

b. Waste solids are assumed to be 40 percent by weight dry solids. At \$4 per ton for sludge disposal, annual cost increases to \$9,238,000 or 2.64 mills per kwh

Table 6
CAPITAL COST – LIME SCRUBBING^(a)

Cost Item	Thousands of Dollars	Dollars/kw	Dollars/ACFM Installed
Yard facilities	555		
Raw material handling	592		
Scrubber system	7.427		
Sludge handling (on-site)	<u>755</u>		
Direct costs, subtotal	9,329		
Field costs, engineering and home office, escalation, contingency, and fee	10,262		
Total installed	19,591	37.68	8.96

- a. 520-MW gross output; 3.1-percent S coal; 81-percent SO₂ removal; particulate removal by others; 80-percent load factor; with ponding; spare train

Table 7

ANNUAL OPERATING COST — LIME SCRUBBING^(a)

Cost Item	Total Requirement	Range of Unit Cost Experience	Unit Cost This Study	Annual Cost, \$ Thousand	Cost per kwh, mills
Basic alkali, tons	94,000	\$15-25	\$20.00	1,880	.537
Process water, gal x 10 ³	1,754,000	\$.02-.15	\$00.02	35	.010
Power, demand, kw	12,109	\$15-40	\$35.00	424	.121
Power, energy, kwh x 10 ³	81,500	\$.90-5.00	\$ 5.00	407	.116
Steam, demand, annual Btu x 10 ⁶	800,000	\$.08-.25	\$00.20	160	.046
Steam, energy, Btu x 10 ⁶	615,000	\$.10-.55	\$00.55	338	.097
Operating labor, 3/shift	25,200	—	\$ 6.25	158	.045
Operating labor overhead @ 75%	—	—	—	118	.034
Maintenance @ 5% of direct cost	—	—	—	466	.133
Maintenance overhead @ 30%	—	—	—	140	.040
Capital recovery, 15 yr, 7-1/2% (.1315 multiplier)	—	—	—	2,576	.736
Insurance and property taxes at 1.9%	—	—	—	372	.106
Sludge disposal, tons	416,000	\$.75-5.00	\$ 2.00 ^(b)	832	.238
Total Cost				<u>7,906</u>	<u>2.260</u>

a. 520-MW gross output; 3.1-percent S coal; 81-percent SO₂ removal; particulate removal by others; 80-percent load factor; with ponding; spare train

b. Waste solids are assumed to be 50-percent by weight dry solids. At \$4 per ton for sludge disposal, annual cost increases to \$8,738,000 or 2.5 mills per kwh

Section 7

CONCLUSIONS

1. Commercial technology has advanced to the point where system suppliers offer guarantees of 80 to 90 percent SO₂ removal for limestone and lime, respectively.
2. Process design has become more conservative with higher liquid-to-gas and lower stoichiometric ratios. Both should give greater system reliability.
3. Twenty-one full-size lime/limestone scrubbing units for SO₂ removal are being engineered, constructed, or operated.
4. Capital cost for new 500-megawatt SO₂-removal limestone units burning 3 percent sulfur coal is \$45 per kw. Operating cost is 23 to 25 cents per million Btu (including capital).
5. Capital cost for lime scrubbing units under the same conditions as for the previous conclusion is \$38 per kw. Operating cost is 23 cents per million Btu.
6. Two areas requiring further study and evaluation are reliability and solid waste disposal.

Section 8

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WASTE PRODUCTS FROM THROWAWAY
FLUE GAS CLEANING PROCESSES -
ECOLOGICALLY SOUND TREATMENT AND DISPOSAL

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NOTES

1. The mention of company names or products is not to be considered as endorsement or recommendation for use by the U. S. Environmental Protection Agency.
2. EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice results in difficulty in clarity, NERC-RTP provides conversion factors for the particular non-metric units used in the document. For this paper these factors are:

<u>British</u>	<u>Metric</u>
1 acre	4047 meters ²
1 acre-ft	1233.6192 meters ³
5/9 (°F-32)	°C
1 ft	0.3048 meter
1 ft ²	0.0929 meters ²
1 ft ³	0.0283 meters ³
1 ft ³ /short ton	0.0312 cubic meters per metric ton
1b/in. ²	70.31 grams per centimeter ²
1 mile ²	2.59 kilometers ²
1 mile ² -ft	0.7894 square kilometer-meter
1 ton (short)	0.9072 metric tons

ABSTRACT

Extensive application of lime/limestone throwaway processes will create large quantities of wet sludge. The sludge solids consist primarily of flyash or oil soot plus sulfonated and unsulfonated calcium salts and contain many impurities and trace elements associated with the raw materials involved. In addition, neutralization of unmarketable abatement sulfuric acid can potentially create large quantities of similar sludge. Based on current and projected utilization of lime/limestone throwaway processes, the sludge problem is quantified. Results of a preliminary assessment of current technical approaches and techniques for treatment and disposal of sludge are discussed, including potential for ground and surface water degradation. An EPA program to determine ecologically and economically acceptable methods for disposal of lime/limestone sludge is described. The program includes the physical and chemical characterization of sludge materials from: representative sorbent/fuel combinations; an evaluation of potential water pollution or other problems associated with disposal of both untreated and treated (subject to dewatering, oxidation, chemical fixation, etc.) sludge; and a study of the economics of various disposal/treatment combinations. Preliminary data and analyses are presented.

1.0 INTRODUCTION

A major problem inherent in any flue gas desulfurization system is the necessity of disposing of or utilizing large quantities of a sulfur product. The sulfur compounds produced are either saleable (sulfuric acid, sulfur dioxide, or elemental sulfur) or throwaway (calcium-sulfur compound sludge materials). The technology of processes producing abatement sulfuric acid is currently more advanced than for those producing the other saleable products. To date, however, most utilities have favored utilization of lime or limestone scrubbing throwaway processes.

Although research and development is currently underway in a number of processes with saleable sulfur products, most will not be commercially available until the late 1973-1975 period. Allowing 2 years for retrofit to an existing plant and 5 years for a new installation including a control system, the earliest application of these processes could be late 1975 and 1978, respectively. It is significant to note that of 23 full-size desulfurization control processes for power plants in design, construction, or operation, 17 are lime/limestone scrubbing throwaway systems. This majority, undoubtedly based on a higher degree of confidence in understanding, process characterization, and current commercial availability, and the timing indicated above, suggests that throwaway processes will comprise a very significant percentage of flue gas cleaning installations in the near term at least to 1980. (It should be noted that the double alkali process--soluble alkali scrubbing, lime/limestone regeneration of soluble alkali--is

currently regarded by many to be an attractive alternative to lime/limestone slurry scrubbing. However, this process results in a very similar throwaway product.) The majority of the remaining installations will very likely be comprised of processes producing sulfuric acid since these processes appear to be further advanced than those producing other saleable sulfur products.

Extensive application of the throwaway processes will create large quantities of wet sludge with solids consisting primarily of flyash or oil soot plus $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, CaCO_3 , and possibly some Ca(OH)_2 from lime scrubbing processes, and $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, and CaCO_3 from limestone scrubbing processes. In addition, neutralization of unmarketable abatement sulfuric acid can potentially create large quantities of sludge consisting primarily of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Typically, the water in equilibrium with these sludges will not only contain varying amounts of these materials as dissolved solids in the 3,000-15,000 ppm range (primarily Ca^{++} , SO_4^- , Mg^{++} , and SO_3^-), but also many impurities and trace elements found in the applicable raw materials such as the alkali sorbent, the fuel material, and the process water.

For a number of years the Environmental Protection Agency has been engaged in research and development concerned with utilization of lime/limestone-modified pulverized flyash resulting from lime/limestone based desulfurization processes. Acknowledging the potential solid waste and water pollution problems associated with these processes, the prime objective was that an air pollution problem should not be transferred to these other areas. A study of the utilization of

flyash^(1,2) indicated that only about 7-10 percent of flyash is currently utilized and that under current technology and economic conditions, utilization would probably not exceed about 25 percent in the near term. Similar limiting conditions are expected to apply to sludge materials. Additionally, analysis of dry-collected limestone-modified flyash indicated the presence of potentially toxic elements.

On the basis of these results, the rapid emergence of lime/limestone wet scrubbing as the dominant desulfurization process, and a lack of knowledge regarding potential heavy metal and toxic element involvement in the scrubber chemistry, EPA reoriented its activities toward ecologically sound and "safe" treatment/disposal of the waste products from these throwaway processes. Techniques for treatment and disposition may be applicable to sludges produced by neutralization processes.

This paper quantifies the problem of lime/limestone throwaway process generated sludge, examines and assesses potential treatment and disposal alternatives, identifies problem areas, and presents the EPA program, including results to date.

2.0 QUANTIFICATION OF THE PROBLEM

Typical quantities of throwaway sulfur products, potential saleable products, and coal ash production for a typical 1000 Mw coal-fired boiler are presented in Table 1. From this table rough comparisons between the production rate and storage volumes* for typical throwaway sulfur products may be compared to typical saleable products and to coal ash, the normal waste product for a coal-fueled plant. The following are important observations which can be made:

1. The production rates (dry basis) of throwaway sulfur product are approximately 45-80 percent larger (dry) than those of ash normally produced; this leads to a total (sludge plus ash) throwaway requirement about 2.5-3.0 times the normal coal ash disposal rate. The ranges reflect lime and limestone sludges, respectively.

2. Large storage volumes are required for ultimate disposition of the sludges. For example, for a 1000 Mw coal-fired unit over a 20-year lifetime, about 860-1100 acres** (1.3-1.7 square miles) of disposal land would be required for a wet sludge (50 percent solids) ponded to a 10-foot depth. The ash alone would require about 250 acres (0.4 square miles) ponded to the same depth. Thus, the volume required for the throwaway sulfur product is approximately 275 percent greater than

*It should be noted that rough estimates for solids packing specific volume were used to calculate potential storage volumes required for 20 years of boiler operation; depending on the process, lime sludges can be allowed to settle in a storage pond to a maximum of about 50 percent solids slurry, or can be dewatered to about 70 percent or more solids by various techniques.

**Factors for converting these and other English units to their metric equivalents may be found on page iii.

Table 1. TYPICAL QUANTITIES OF ASH AND SULFUR
PRODUCTS FROM A 1000 MW COAL-FIRED BOILER CONTROLLED WITH
A LIME OR LIMESTONE SCRUBBING FLUE GAS DESULFURIZATION SYSTEM

	Yearly Production, 1000 MW (tons/yr)	Assumed Packing Volume (ft ³ /ton of dry material)	Approximate Volume Required for Storage 1000 MW for 20 Years (acre-feet)
Coal Ash	288,000 (dry)	19 (wet; 20% water)	2510
Lime Sludge (dry)		22	4210
73% CaSO ₃ ·1/2H ₂ O	304,000		
11% Ca(OH) ₂	47,000		
11% CaSO ₄ ·2H ₂ O	45,000		
5% CaCO ₃	21,000		
	<u>417,000</u>		
Lime Sludge (wet; 50% solids)	834,000	45	8600
Limestone Sludge (dry)		22	5225
58% CaSO ₃ ·1/2H ₂ O	305,000		
9% CaSO ₄ ·2H ₂ O	45,000		
33% CaCO ₃	170,000		
	<u>520,000</u>		
Limestone Sludge (wet; 50% solids)	1,040,000	45 (assumed same as for wet lime sludge)	10,800
Sulfuric Acid (95% conc)	243,000	17.6	1960
Sulfur (dry)	75,600	23 (80% packing)	800

Assumptions: Coal - 3.5 percent S content, 12 percent ash content.

Coal Rate - 2,400,000 tons/yr for 1000 Mw on stream for 6400 hours/yr (0.75 lb/Kwh).

Lime Sludge - Based on performance of Chemico Ca(OH)₂ scrubbing unit in Japan (Mitsui Aluminum Co.)
at 1.28 Ca(OH)₂/SO₂ mole ratio and 85 percent utilization.

Limestone Sludge - Based on preliminary EPA/Bechtel/TVA data from the TVA Shawnee Power Plant at
1.65 CaCO₃/SO₂ mole ratio and 85 percent utilization.

Removals - 90 percent of SO₂ in flue gas converted to sulfur product, 100 percent of ash collected.

for ash normally produced and the total volume requirement is about 4 times that for ash alone. The ranges reflect lime and limestone sludges, respectively.

3. Potentially large quantities of sulfuric acid can be produced by certain flue gas desulfurization processes such as Catalytic Oxidation, Wellman-Lord, and magnesium oxide scrubbing. Approximately 24 million tons per year of concentrated sulfuric acid can be produced per 100,000 Mw of flue gas desulfurization capability. This is close to the total U.S. sulfuric acid production rate, which was 29.3 million tons in 1971. Additionally, the use of a sulfuric acid plant and neutralization as a control strategy in the smelting industry has the potential for producing large quantities of sludge. Assuming stoichiometric quantities, for each ton of sulfuric acid neutralized, approximately 1.75 tons of dry sludge would result.

4. Elemental sulfur appears the most attractive product in terms of production rates and potential storage volume. Only about 76,000 tons per year of sulfur would be produced per 1000 Mw of flue gas desulfurization; this leads to a storage area of about 80 acres (0.12 square miles) over a 20-year lifetime, assuming a 10-foot depth.

The numbers of Table 1 become significant when one considers that in the foreseeable future, probably through 1980, U. S. electric utilities will likely continue the current pattern of ordering wet scrubbing systems; a majority of these orders will probably be for wet lime/limestone processes producing a throwaway sludge. Forecasts based on a government interagency Sulfur Oxide Control Technology Assessment Panel (SOCTAP) report⁽³⁾ indicate that for coal:

1. Over 20,000 Mw of generating capacity could be equipped with SO₂ scrubbing systems by 1975, but the equipped capacity is estimated to be closer to 10,000 Mw.

2. By 1977, the equipped capacity may be 48,000-80,000 Mw, but the lower end of the range is considered a more realistic estimate; i.e., approximately 50,000 Mw.

3. By 1980, at least 75 percent of the coal-fired capacity could be equipped with stack gas scrubbers. This is equivalent to about 144,000 Mw. Assuming 75 percent of the total stack gas scrubbing installations utilize a lime/limestone throwaway process results in 108,000 Mw controlled in this way.

Known commitments for lime/limestone scrubbing systems indicate control of approximately 1900 Mw in 1972, 6700 Mw by 1975, and 9000 Mw by 1977.

The above data were used to prepare Figure 1 which presents the growth of coal-fired generating capacity and a comparison with known committed and forecast utilization of lime/limestone scrubbing processes for flue gas cleaning. Although a function of plant size, sulfur content, and other factors, the total waste sludge generated to 1980 was roughly estimated using the data from Table 1. The results are shown in Figure 2. In addition, an estimate of limestone sludge production rates and disposal area requirements as a function of plant size and coal sulfur content was also determined. These are shown in Figure 3.

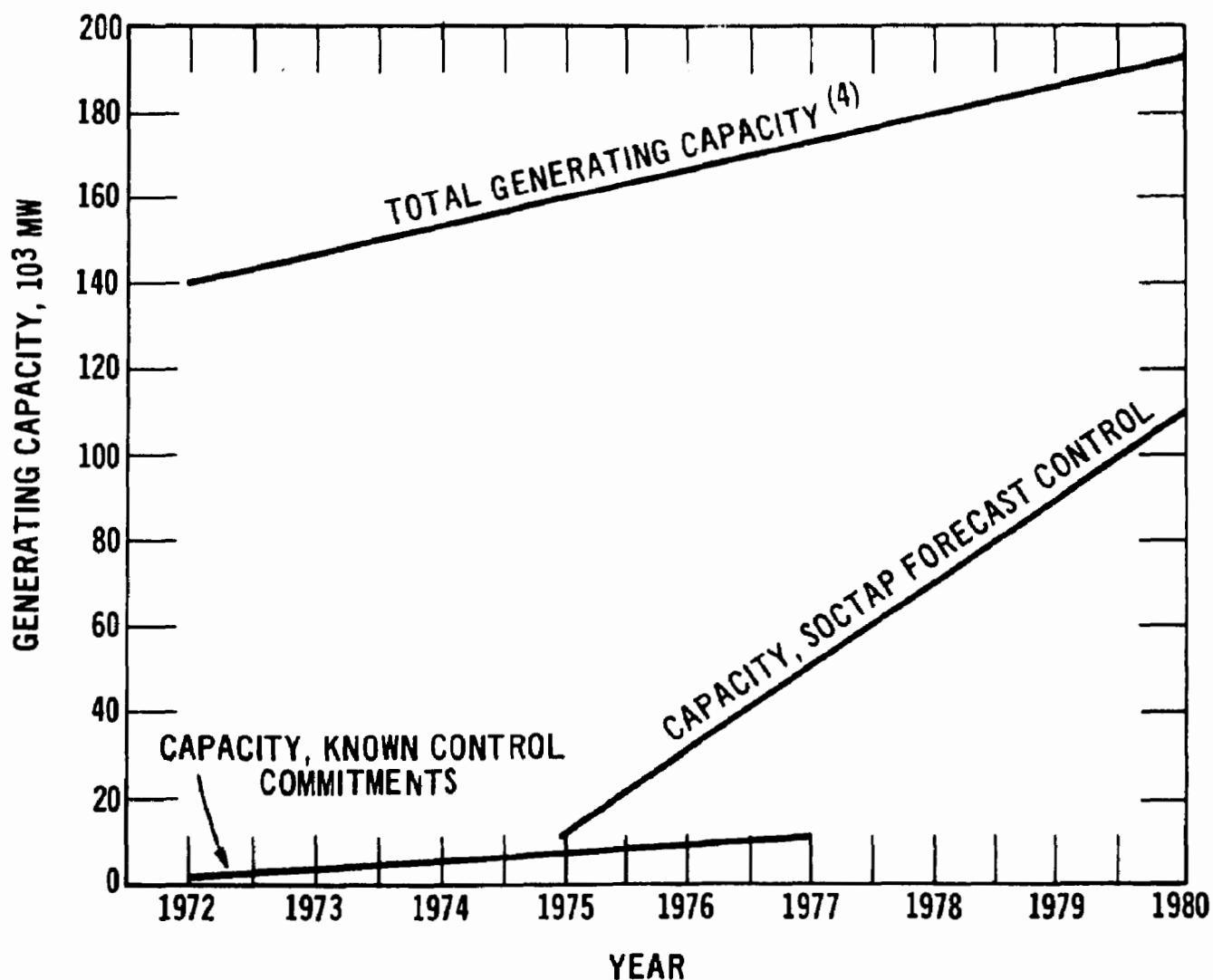


Figure 1. Comparison of estimated electric utility coal generation capacity with current and forecast control by lime/limestone scrubbing.

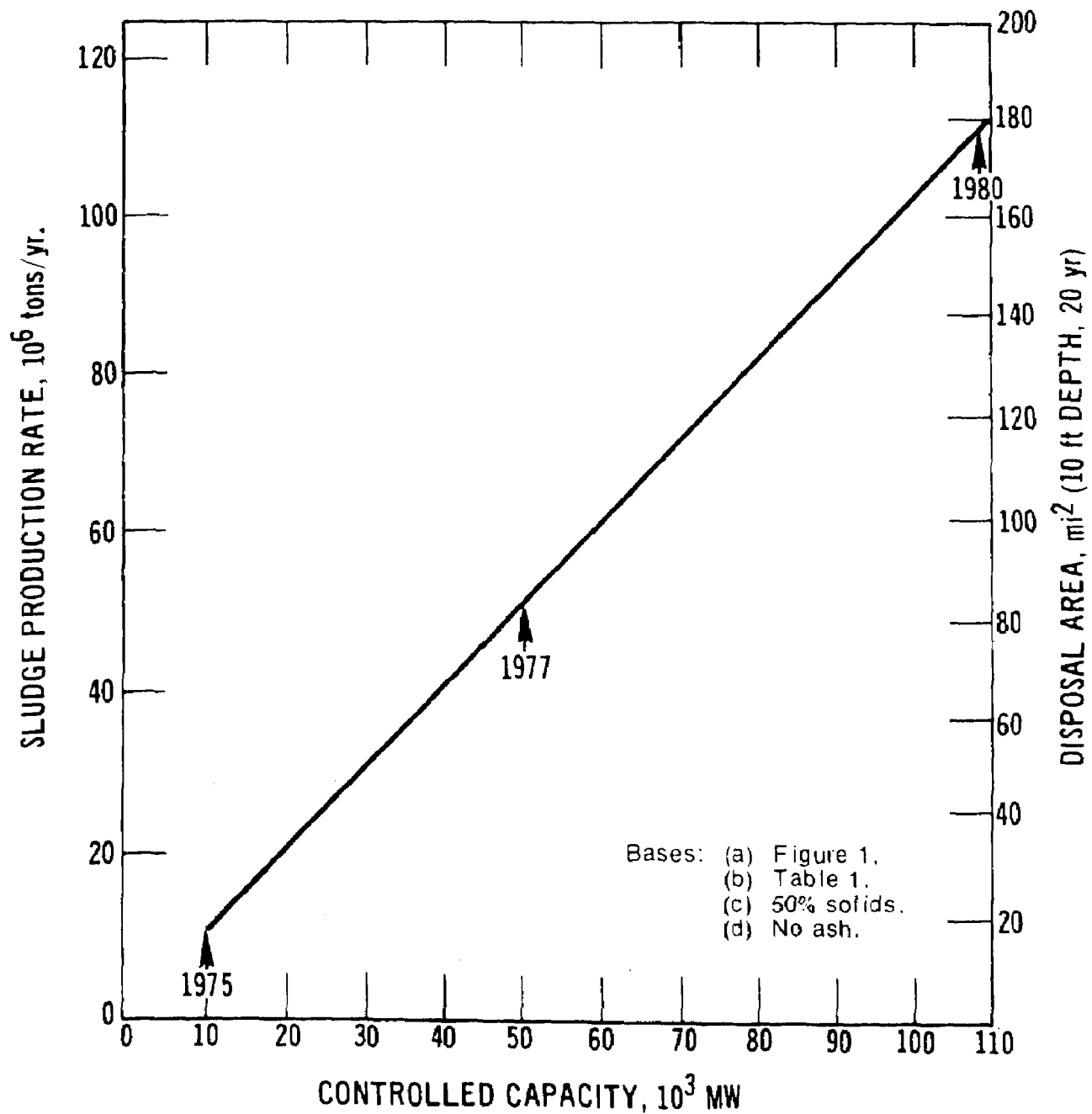


Figure 2. Estimated production rate and disposal area requirements for limestone sludge through 1980.

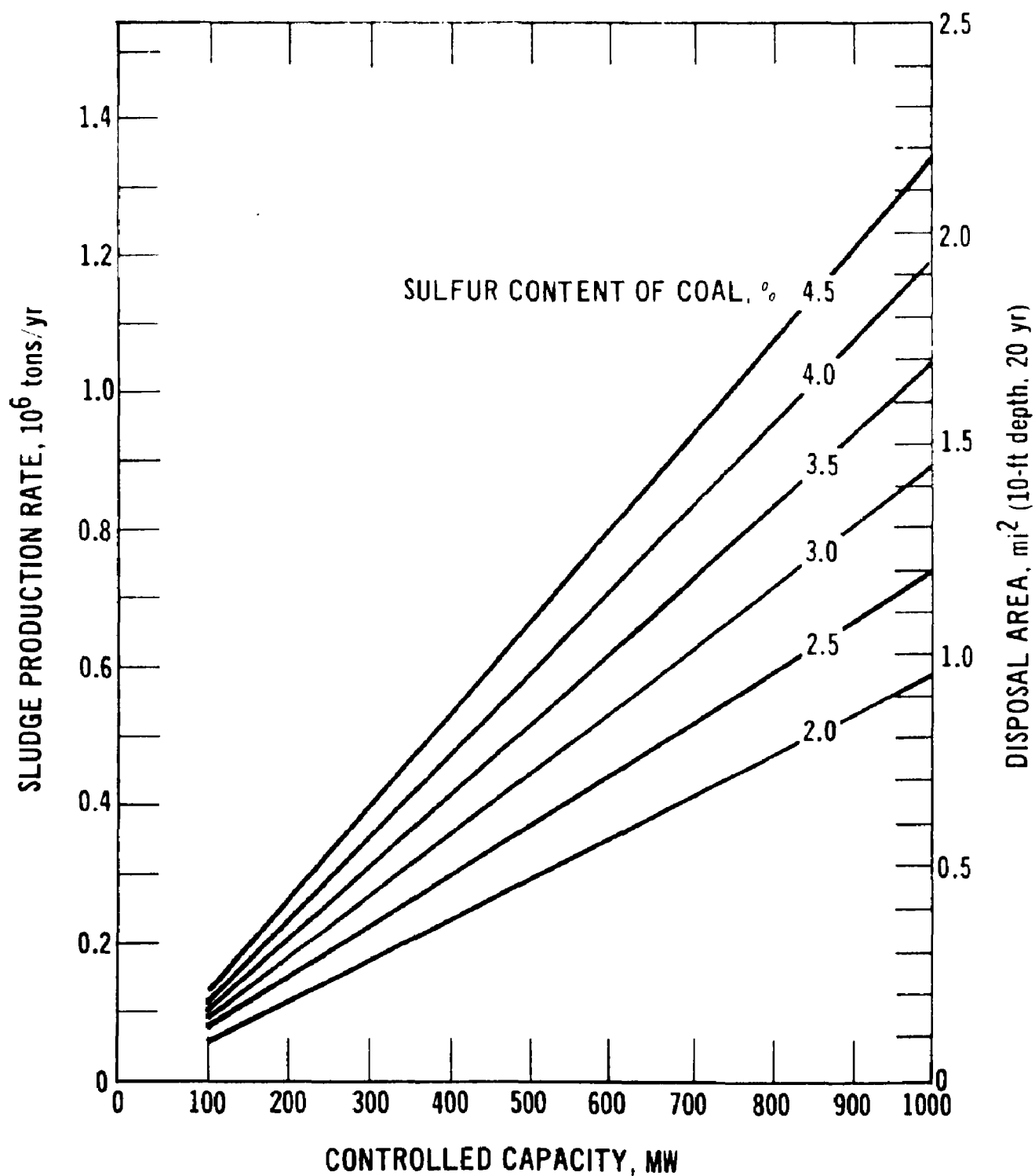


Figure 3. Estimated production rate and disposal area requirements for limestone sludge (50% solids) from flue-gas desulfurization. (Basis: Table 1).

The magnitude of the 1980 estimates of Figure 2 appears significant from the following comparisons:

1. Strip and Surface Mining - The estimated 1800 square mile-feet* required to be committed for sludge disposal (50 percent solids) by 1980 is:

- a. About 89 percent of the total land disturbed by strip and surface mining of coal as of January 1965.⁽⁵⁾
- b. About 3.5 times the square mile-feet which will be utilized in strip and contour mining of coal from 1973 to 1980. The strip and contour mining utilization is estimated at 73.5 square-mile feet per year based on 1967 Bureau of Mines reports.^(5,6) This rate is undoubtedly lower than the present and forecast rate, but the comparative order of magnitude is obvious.

2. Coal and Ash Production - The estimated 112 million tons/year production rate of wet sludge by 1980 is:

- a. Approximately 25 percent of the weight of all the coal (450 million tons) estimated to be required for electric power generation in 1980.⁽⁴⁾
- b. Approximately 175 percent of the weight of all the wet ash (approximately 20 percent moisture) from all the coal required for power generation in 1980. An ash content of 12 percent was assumed for the coal.

*Square miles X ft(depth); e.g., 180 mi² X 10 ft = 1800 mi²-ft.

3.0 PRELIMINARY ASSESSMENT OF TREATMENT/DISPOSAL TECHNOLOGY

Currently, all of the existing or planned lime/limestone scrubbing facilities for power plants in the United States employ the two major ash disposal techniques, ponding and landfill, for lime/limestone waste sludge disposal. Disposal of the sludge has been chosen because of unknown technical and economic factors and the lack of a readily available market for large-scale utilization of the waste material, although research and development has shown at least limited use is feasible in some structural applications. This section discusses the results of a preliminary assessment of treatment/disposal technology made in late 1972, to assist in formulation of the EPA program.

3.1 Ponding

Since ponds are widely used by electric utilities for the disposal of ash, it is not surprising that ponding is considered to be a prime means of sludge disposal. In fact, ponds are employed for disposal of sludge in about 60 percent of existing or planned U. S. power plant locations of lime/limestone scrubbing facilities. In addition, small ponds are used for partial dewatering and temporary storage of the sludge in almost all locations where other methods are being employed. In general, ponds are used where a large area of inexpensive land is available near the power plant. If sufficient land is available, the pond is designed to eventually store wet sludge material over the lifetime of the power plant.

The production rates (tons/year, dry basis) of sulfur product waste material are approximately 50 percent larger than the ash normally

produced. This leads to a total (sludge plus ash) waste disposal requirement about 2.5 times the normal coal ash disposal rate. In addition, since some sludge materials retain up to 60 percent moisture even after an extended period of settling time, pond volumes several times the size of normal ash ponds are required for sludge disposal.

This moisture-retaining tendency, or tendency for the solids not to compact well upon settling, has been attributed to the thin platelet-like crystal structure of calcium sulfite ($\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$), which usually represents the majority of the sulfur in the sludge. The calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) crystals, on the other hand, are "blocky," and tend to compact well. This situation has created interest in means of oxidizing the sulfite in the pond to sulfate. Oxidation of the sulfite could reduce the pond volume requirements, as well as make the pond area more easily reclaimable, rather than the possibility of indefinitely remaining a wet "bog." Oxidation can also reduce the potential oxygen demand of the sulfite in solution. However, oxygen consumption by the sulfite does not appear to be a major problem because of the slowness of the reaction under normal pond conditions.

Oxidation of the sulfite could lead to other problems, however. Over an ambient temperature range, the calcium sulfate is on the order of 50 to 100 times more soluble than the sulfite, so the pond water pollution potential would be greatly increased. This solubility could cause problems with reclaimed pond areas through sub-surface dissolution. An alternative to oxidation might be dewatering using filtration, centrifugation, etc. prior to ponding. Solids with approximately

30 percent moisture have been generated by filtration in limestone scrubbing pilot tests at EPA. Unfortunately, it is not currently known whether the dewatered material will "set-up" permanently; i.e., will harden or remain dewatered after exposure to rainfall. (See Section 5.2.2.)

With either a lime or limestone scrubbing system, ponding creates the potential for water pollution. Lime sludge solids consist primarily of $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, CaCO_3 , and possibly some Ca(OH)_2 , and flyash; limestone sludge solids consist primarily of the same compounds, excluding Ca(OH)_2 . Both sludges contain liquor which is, in all likelihood, saturated in calcium sulfite and sulfate. In fact, pilot and full-scale operating data have shown that it may be super-saturated in calcium sulfate. Magnesium, a normal impurity in lime and limestone, is also contained in the sludge. Because of the high solubility of magnesium sulfite and sulfate, magnesium is a serious potential pollutant in the liquor associated with the sludge. It is anticipated that in most applications, a relatively low limit may have to be put on the magnesium contained in the lime or limestone, possibly rendering dolomitic limestones unsuitable.

A variety of additional chemicals from sources other than lime and limestone are also present in the sludge. The chlorides in the coal, for example, are given off in the combustion process as HCl. The HCl is removed in the scrubber and, through internal recycle of scrubber liquor, the concentration of soluble chlorides builds up in the liquor. The concentration levels reached are dependent on: the quantity of chlorine in the coal, the solubilities of the chlorides formed, and the

quantity of liquor associated with the waste sludge. The dissolved solids level in the scrubber liquor is greatly affected by this chloride build up, which presents another potential water pollution problem.

It is generally recognized that flyash contains trace quantities of potentially toxic elements, although usually in extremely insoluble form. For example, limited analysis of dry-collected limestone-modified flyash from EPA's dry limestone injection program indicated 50-200 ppm As, about 200 ppm each of Ba and V, and 200-500 ppm Pb. It is also recognized that trace quantities of toxic elements present in coal and oil are volatilized in the combustion process and are potentially removed from the flue gas in a wet scrubbing process, subsequently ending up in the waste sludge. In addition, lime and limestone can contain trace impurities which will be present to some extent in the process streams. Any trace chemicals in the makeup water will also be present. Because of the internal recycle of scrubber slurry, and the recycle of water from the pond back to the scrubber circuit, it is possible that trace chemicals from all of the above sources will build up in concentration with time. Similar to the chloride problem, the concentration levels reached are dependent on: quantities in the above sources, their solubilities, and the quantity of liquor associated with the sludge. Potential exists, therefore, for trace chemical contamination of both surface and groundwaters unless proper precautions are taken.

To prevent unintentional seepage of liquor through the dikes and floor of the pond into groundwater, it may be necessary to use a

sealant material. The pond diking should also be carefully designed to avoid overflow and run-off of sludge liquor into surface water. In addition, the system must be operated in a closed- or nearly-closed-loop mode of operation. This means that all liquor entering the pond is recycled to the scrubber circuit; no sludge liquor is released to any watercourse.

In the majority of full-scale installations currently in operation, attempts have been made to operate in a closed-loop mode. However, in most of these facilities, seepage, run-off, and other mechanisms could be postulated which would allow liquor to be released into surface or groundwater, at least periodically. It should be noted that ash ponds which have been used for many years have similar potential water pollution problems, although there are little available data related to water contamination by ash liquors. However, soil amendment studies using flyash have shown trace element ingestion by plant life, suggesting the possibility of leaching from flyash ponds.

In summary, although ponding is currently widely used, the following potential problems are evident:

1. Volumes several times the size of normal ash ponds, because of high moisture content in solids containing a significant percentage of calcium sulfite.
2. Potential sulfite oxygen demand.
3. Potential dissolution of calcium sulfate, with resultant water pollution potential.

4. Potential reslurry of dewatered solids when exposed to rainfall.
5. Impurities and trace chemicals in the sludge, with inherent water pollution potential.
6. Seepage, run-off, and/or overflow of liquor from the pond.

3.2 Landfill

Although landfill operations are included in less than 40 percent of existing or planned lime/limestone scrubber locations, ash disposal has involved techniques other than ponding in these locations. (Actually, in most cases ponding ultimately results in a landfill-type operation; to reclaim the land when the pond is filled, the "pond" must be covered with earth, similar to a landfill.)

Since the sludge material contains large quantities of liquor and therefore is difficult to handle, dewatering of the material for transportation is likely although not absolutely necessary. Clarification alone will probably result in not more than 50 percent solids, so further dewatering by either filtering or centrifuging will likely be necessary. The filtered or centrifuged material can then be transported to a suitable landfill site. As mentioned in the previous sub-section, it is not currently known whether the dewatered material will remain dewatered after exposure to rainfall. (See Section 5.2.2.) If it does not, a fixation or stabilization technique must be applied.

Chemical fixation processes are currently being developed by many companies, including IU Conversion Systems, Dravo, Chicago FlyAsh, Chemfix, and others. Such processes generally involve pozzolanic* chemical reactions between flyash and lime. In most lime processes, the hydrated lime in the scrubber and the slurry recycle tank is almost completely converted to calcium carbonate. Therefore, although the percentage of unreacted calcium carbonate in a lime process sludge is less than that in sludge from a limestone process, the sludge components are identical. This means that lime must be added to the sludge to generate the pozzolanic process, possibly along with an accelerating agent to decrease the curing time. Reaction of the lime and flyash leads to the formation of a relatively dry solid in which the sludge components are physically, and possibly chemically, bound up. This is desirable because it decreases the potential dissolution of these components and thus the possibility of groundwater contamination through leaching or nearby surface water contamination through run-off.

Binding up the sludge components through a chemical fixation process is currently being applied at the limestone scrubbing facility at Commonwealth Edison's Will County Station. It is also planned for the lime scrubbing facility at Duquesne Light's Phillips Station, to be

*Pozzolan: Generic name for cementitious material which is based on original use of volcanic rock or ash containing silica, alumina, lime, etc. as a material of construction in ancient aqueducts. Named after Pozzuoli, Italy, where it was first found.

started up in mid-1973. It is not currently known whether fixation techniques will be applied to additional projects, although it is known that the techniques are being considered for a large new coal-fired facility.

In summary, problems similar to those of ponding exist with landfill operations, for example:

1. Potential reslurry of dewatered solids when exposed to rainfall.
2. Dissolution of calcium compounds and trace chemicals in the sludge material, with resultant water pollution potential.

Fixation processes may alleviate the problems associated with landfill, but these require further evaluation.

3.3 Utilization

As development activity in limestone scrubbing has increased during the past few years, investigations in the utilization of flyash and limestone waste sludge material have been undertaken. Private companies involved in this area have included Combustion Engineering, IU Conversion Systems (formerly G&WH Corson), and others. In Japan, oxidation of the sulfur products to gypsum for construction use is underway. EPA has sponsored work at West Virginia University's Coal Research Bureau⁽⁷⁾ and at Aerospace Corporation.⁽¹⁾

The approach taken in the EPA programs was to determine current and potential utilization of flyash, assess applicability of limestone waste sludge material and, based on its properties, assess its potential for

new applications. However, it was found that in 1970, only about 7 percent of all the flyash produced by coal-burning power plants was actually utilized - primarily for concrete, structural fill, lightweight aggregate, raw material for cement, filler for bituminous products, and road base material. It was estimated that the maximum practical potential usage under current technology and associated market conditions would only be about 25 percent. Thus, approximately 75 percent of the flyash produced in the United States was not considered marketable in the near term because of: expected variation in the composition of the flyash due to coal composition changes during operation, unfamiliarity with this material, and the general inability to readily compete economically with conventionally used materials. Because of similar limitations there is not expected to be widespread utilization of limestone sludge material in the United States, at least not in the near future.

It can be concluded, therefore, that although utilization is desirable in the long run, near-term treatment/disposal solutions to the sludge problem must occupy a higher priority for EPA research and development. However, promising utilization approaches which result in materials which can be disposed of as "waste," to be utilized at some time in the future, are considered applicable to the current problem.

3.4 Conclusions

This preliminary assessment of treatment/disposal technology, made in late 1972, indicated a considerable number of potential problem areas, all described earlier in this paper. Some efforts are being expended by private industry, but these seem to be directed toward

solving the problems of a specific application, and are in many instances quite limited in scope. Because of the wide variety of scrubber systems, sorbent/fuel combinations, power plant land use considerations, etc., there is quite an apparent need for a program with a broad, national scope which will encompass as many situations as possible. This broad-based program would take into account currently available information, generate new information, and disseminate findings to all electric utilities, private industry, and the general public. It also would have the advantage of reducing the cost of specific application-oriented development by, among other things, avoiding duplication of effort.

EPA has initiated a program with the objective of meeting as many of these requirements as practicable. Due to fiscal and other constraints, the program, although broad in scope, includes neither the full range of sorbent/fuel combinations, nor their associated treatment disposal techniques. In addition, demonstration of the most promising treatment/disposal technology is yet to be undertaken. However, the EPA program described in Section 4.0 is considered a major first step.

4.0 THE EPA PROGRAM

An EPA contract, "Wet Collected Limestone-Modified Fly Ash Characterization and Evaluation of Potentially Toxic Hazards" was formalized late in 1972 with the Aerospace Corporation. The contract provides for a detailed characterization of wet collected limestone-modified flyash and an evaluation of the potential toxic hazards posed in processes that may be performed in subsequent handling, disposal, or utilization of the sludge. The need for this study was based on the results of previous programs conducted by EPA which indicated the following:

1. Analyses performed on dry collected limestone-modified flyash identified the presence of heavy metal trace elements that could pose a toxic hazard, depending upon their chemical/physical state.
2. The wet collected limestone-modified ash may contain even greater quantities of the heavy metal elements as a consequence of the wet scrubbing of the ash and flue gases, and poses a potential hazard in its disposal or utilization.
3. Water-soluble elements pose an additional health hazard in the disposal of waste waters because of the large quantities of water required for the process scrubbing.

However, when procurement for the current contract was initiated, potential utility sources to obtain representative sample types were limited; disposal was essentially limited to ponding; and commercial acceptability of throwaway processes and the corresponding quantity of material requiring disposal was unknown. These factors led to a

program of limited scope with prime ecological emphasis on toxicity. Since that time, additional utility sources using different sorbent/fuel combinations and applying other treatment/disposal techniques have become operative. These additional combinations with their different elemental compositions and treatment/disposal techniques needed to be taken into consideration. Although toxicity is still important, toxic element concentrations are expected to represent only a very small percentage of the total quantities to be disposed of. Based on the above and the current and projected magnitude of the sludge problem, EPA now plans an expanded program to allow a more complete assessment of ecological acceptability, technical state of the art, and economics for the various treatment/disposal techniques.

The objective of the expanded program is to determine ecologically and economically acceptable methods for treatment/disposal of lime/limestone sludge and to provide pertinent input for the establishment of realistic water and solid waste regulations and standards. Sample materials, representative of as many situations of lime/limestone wet scrubbing process applications as practicable, will be obtained. In addition, test, operational and economics data from a wide variety of sources will be taken into consideration.

The basic elements of the program are as follows:

1. An inventory of sludge components, including chemical analysis of various types of sludge and the raw materials from which they are formed (lime or limestone, coal or oil,

process water). Sorbent/fuel combinations to be studied are limestone/Eastern and Western coals, lime/Eastern coal, and double alkali/Eastern or Western coal.

2. An evaluation of the potential water pollution and solid waste problems associated with disposal of the sludge, including consideration of existing or proposed water effluent, water quality and solid waste standards or guidelines. The information would also assist in the evaluation of potential treatment/disposal techniques described below.
3. An evaluation of treatment/disposal techniques with emphasis on ponding and "fixed" and "unfixed" landfill (and related land use applications). Physical analyses and tests of various sludges will be conducted, including determination of the effects of dewatering, oxidation, chemical fixation, aging, etc., on stability, compactibility, leachability of solubles, potential pond seepage, potential run-off problems, and other disposal considerations. The economics of various treatment/disposal combinations will also be studied.
4. A recommendation of the best available technology for sludge treatment/disposal based on the evaluation described above. Pertinent input for the establishment of realistic water and solid waste regulations and standards may also be provided.

The approach taken by the EPA in undertaking this program is to utilize EPA funded or co-funded scrubber sources, the cooperation of several utilities who have installed scrubber systems and (as much as possible) the knowledge and technical expertise of EPA water and solid waste organizations. EPA personnel conducted a survey of potential electric utility participants for the planned program. Factors in the study included facility availability, additive/fuel combination, facility size, treatment techniques (dewatering, oxidation, chemical fixation, etc.), and final sludge disposition (ponding, landfill, other). Table 2 presents the results in order of facility availability to support the EPA program.

Upon completion of the survey, contacts were made with several of the utilities to determine their willingness to provide sludge and raw material samples, as well as information concerning their sludge treatment and disposal activities. In addition, discussions were held with several scrubber system companies, waste treatment/utilization/disposal companies, and EPA water and solid waste personnel regarding review and integration of activities and information.

Aerospace Corporation efforts have been limited to the scope of the current EPA contract. However, these efforts have been conducted and coordinated to the maximum extent possible with EPA efforts toward meeting the objectives of the planned program expansion. Surveys of current treatment, disposal, and utilization technology, as well as chemical analyses and physical testing of samples from the TVA Shawnee facility, have been conducted. Progress of Aerospace and EPA efforts are discussed in Section 5.0.

Table 2. POTENTIAL SLUDGE TREATMENT/DISPOSAL PROGRAM UTILITY PARTICIPANTS

(X = Current; P = Possible Additions)

Facility (Availability Status)	Sorbent Fuel	Scale	Dewatering Technique					Final Disposition		
			Clari- fier	Filter	Centri- fuge	Dryer	Pond	Ponding	Landfill	Other
TVA-Shawnee (Current)	Limestone now, lime later Eastern coal	Proto- type	X	X	X			X		
City of Key West-Stock Island (Current)	Limestone (coral marl) Residual oil	Full					X		X (Unfixed)	
Commonwealth Edison Co.-Will County (Current)	Limestone Eastern coal	Full	X	P		P	X (Well points)		X (Sealed) (Fixed)	
Southern California Edison-Mohave	Limestone & lime Western coal	Pilot		X	P			X		
Kansas City Power & Light- Hawthorn (Current)	Boiler injected limestone Coal (possible E&W blend)	Full	X				X (Well points)	X		
Kansas Power & Light- Lawrence (Current)	Boiler injected limestone Eastern coal	Full					X	X		
Louisville Gas & Electric- Paddy's Run (Current)	Carbide sludge (Ca(OH) ₂) Eastern coal	Full	X	X					X	

Table 2 (Continued). POTENTIAL SLUDGE TREATMENT/DISPOSAL PROGRAM UTILITY PARTICIPANTS

(X = Current; P = Possible Additions)

Facility (Availability Status)	Sorbent		Scale	Dewatering Technique					Final Disposition		
	Fuel			Clari- fier	Filter	Centri- fuge	Dryer	Pond	Ponding	Landfill	Other
Northern States Power- Black Dog (Current)	Limestone		Pilot	X					X		
	Western coal										
Kansas City Power & Light- LaCygne (Current)	Limestone		Full						X		
	Eastern coal										
Arizona Public Service- Cholla (Approx mid-1973)	Limestone		Full						X (Solar evap)		
	Western coal										
Duquesne Light- Phillips (Approx mid-1973)	Lime		Full	X				X (Curing)		X (Fixed)	
	Eastern coal										
Detroit Edison- St. Clair (Late 1973)	Limestone		Full					X		X (Unfixed)	
	Eastern coal										

5.0 PROGRAM PROGRESS

5.1 Industry and Intra-EPA Coordination

The information highlights discussed here are based on an initial survey conducted as part of the EPA program via informal meetings and/or recent publications. The information generally falls into the categories of general, technical, and economic.

5.1.1 General - Leachate pollution of groundwater or water courses appears to be the primary concern for sludge disposal. Results of various studies have shown a cause for this concern. For example, greenhouse studies have shown that application of selected samples of flyash to soil increases the availability of boron, molybdenum, zinc, phosphorus, and potassium to plants by supplying soluble forms of these elements and/or modifying the soil pH.⁽⁸⁾ These results add credibility to the implication that these elements and others can leach from flyash even though the ash consists primarily of glassy silicates considered relatively insoluble in aqueous environments. While leaching in this particular application is undoubtedly a function of surface area exposed to permeating moisture, it provides additional evidence that water quality may be sacrificed by unsuitable disposal of flyash/sulfur sludges. Further, at least one state has preliminarily disapproved disposal of a particular sulfur sludge on the basis that potentially toxic materials in the sludge were in excess of potable water standards.

Coordination with EPA water personnel indicated that because of a lack of detailed information, there are presently no Federal water

effluent, water quality, or groundwater standards* which take into account power plants with on-site desulfurization systems. As a result, State and local regulatory agencies are applying available water standards dealing with receiving stream quality and potable water. The Federal Water Pollution Control Act Amendments of 1972 require the setting of standards applicable to effluents and groundwater, and also establish a goal of zero pollution discharge by 1985.

Based on the above, a study on recycle, reuse, or treatment of effluent waters related to flue gas lime/limestone wet scrubbing processes is under consideration by EPA water personnel. This study would be closely coordinated with the program discussed in this paper and represents additional broadening of the overall EPA program. The study, directed toward determining the implications of open-loop or partially open-loop systems, would involve analyzing effluent liquor downstream of the scrubber system. In addition, the study would include the potential for treatment of the water after scrubbing and/or dewatering. Noxious effects as well as toxic hazards would be considered, with technology and economics determined for all cases.

Coordination with EPA solid waste personnel also indicated that there are no specific Federal standards* related to power plant sludge disposal. However, considering the current lack of information concerning sludge properties, disposal of sludge in sanitary landfills is not expected to be permitted.

*Current and proposed State and Federal guidelines, standards, etc., are being compiled for correlation with EPA program results.

For these and other reasons, there is considerable interest in treatment of the sludge to combine primary and trace elements into new crystalline phases and also to reduce the leaching rate. One such treatment technique under development results in the production of synthetic aggregate, which would be used immediately or stored for subsequent use. This lime/flyash/sulfur sludge aggregate would be used in load-bearing applications in place of natural aggregate with either conventional cement binder material or with lime/flyash/sulfur sludge binder material. Synthetic aggregate production was advanced as a means of raw material (limestone aggregate) conservation as well as ecologically sound disposition of sludge. This would free limestone supplies for scrubbing and other uses. Without this approach, local limestone availability in sufficient quantity to supply sorbent materials for large scale wet scrubbing installations has been questioned.

On-site flyash availability in sufficient quantity for some treatment formulations may be questionable. In other words, even with all the plant flyash available, some utilities may need additional flyash or a substitute, depending on final disposition of the treated sludge. For utilities which currently market their flyash, the problem is even greater. In fact, one such utility is currently looking for a flyash substitute for their sludge disposal process. Although optimum formulations are not presently known, applications such as structural or non-structural landfill, base course materials, and synthetic aggregate are expected to require different mix proportions.

Additional information related to sludge disposal has been generated through EPA efforts in mine drainage pollution control and solid waste disposal. EPA mine drainage activities have resulted in numerous reports dealing with sludge produced by neutralization of acid mine drainage. This type of sludge was one of those tested at Transpo '72. (See Section 5.1.2, below.) The reports cover areas such as in-situ sludge precipitation, sludge supernatant treatment, thickening and dewatering, use of latex as a soil sealant, and technical and economic feasibility of bulk transport.

Although primarily concerned with municipal sludge, many EPA solid waste activities relate to the EPA sludge program under discussion.

Examples include the following:

1. Methods of removing pollutants from leachate water.
2. Determination of organic and metal characteristics of leachate from selected landfills.
3. Evaluation of landfill liners.
4. Development of mathematical models to determine effects of landfill leachate on groundwaters.
5. Leachate pollutant attenuation in soils.
6. Moisture movement in landfill cover material.

The EPA reports and other results of continuing coordination will be taken into account under the current program.

5.1.2 Technical - A wide divergence in physical properties between untreated sludges has been reported. Settling rates varied considerably and thickener design parameters have shown large spreads

from source to source and even within the same source.⁽⁹⁾ Although the large variations observed in sludge behavior are currently not completely explained, it is known that sulfite/sulfate ratio, percent flyash, and other measures of chemical composition have a definite effect. However, the operating conditions which result in the difference in sludge properties (or its chemical composition) are not as well defined.

As mentioned earlier, there is considerable interest in treatment of sludges in pozzolanic fixation processes using lime. The production of the sulfur sludge pozzolan is based on:

1. The reaction of lime with soluble sulfates originating in either the flyash or the sludge water to form calcium sulfate and tie up water.
2. The reaction of lime, sulfate, iron oxide, and/or alumina to form complex crystalline sulfoferrites or sulfoaluminates such as ettringite ($\text{Al}_2\text{O}_3 \cdot 3 \text{CaSO}_4 \cdot 31 \text{H}_2\text{O}$).
3. The reaction of lime with the glassy silica of the flyash resulting in the well-known pozzolanic reaction proceeding slowly to form the calcium silicate, tobermorite.

These reactions reportedly result in significant changes in physical and chemical properties of the sludge. A reduction in permeability, an important property directly related to ecological disposal, has been reported. This is based on falling head permeability tests indicating a decrease by about 2 orders of magnitude between raw sludge and treated sludge

after a week.^(10,11) It has also been reported that the trace element concentration in leachate from a sulfur sludge pozzolan produced from acid mine waste sludge was also reduced by about 2 orders of magnitude. Considering these results, the availability of soluble contaminants to groundwaters could be reduced on the order of 10,000 times.

It is postulated that the expansive nature of ettringite crystallization during hardening seals the mass and prevents shrinkage cracks, thereby reducing permeability. Thus, dimensional stability appears to be another important property of the sulfur sludge pozzolan especially when compared to untreated sludge.

There is also some evidence that inclusion of sulfur sludges improves the properties of conventional (lime/flyash/aggregate) pozzolans. The mix containing sulfur sludge is reported to develop superior early strength; greater final strengths appear possible. For example, compressive strengths of up to 350, 750, and 1100 psi have been reported for sulfur sludge pozzolan samples cured at 100°F for 2, 7, and 28 days, respectively.⁽¹⁰⁾ With unspecified formulations and cure conditions, unconfined compressive strengths of 800 and 1600 psi after 14 days and 1550 and 2700 psi after 28 days were also reported.⁽¹¹⁾ It is postulated that these properties are also the result of the ettringite crystallization.

Transpo '72 results,⁽¹²⁾ on the other hand, indicated paving material compressive strengths of about 100 and 225 psi for an acid mine drainage sludge pozzolan and an SO₂ scrubber sludge pozzolan, respectively, after 28 days at 73°F. However, this is a single test

result and time did not permit optimization of the formulation. In addition, it is reported that inadequate compaction, sealing and curing time due to inclement weather and other factors may have compromised performance. Cube compressive strengths of synthetic aggregate made from acid mine drainage sludge and SO₂ scrubber sludge and cured at 73°F were approximately 3500 and 3300 psi, respectively, after 28 days; and approximately 6500 and 6000 psi, respectively, after 90 days. Synthetic aggregate used directly as a crushed aggregate in conventional binder material and as an aggregate in the sludge/flyash/lime paving mixture was reported to perform adequately, with no evidence of failure.

5.1.3 Economics - The cost of local (within 20 miles) disposal of wet (50 percent solids) lime/limestone sludge, including an additive for pozzolanic fixation, has been estimated by one source to be as low as \$2.50 and by another to be as high as \$10/ton.⁽¹³⁾ However, the bases for these estimates are not completely known and may be significantly different from each other. The cost of the additive (primarily lime) has been estimated at from less than \$18 up to \$20/ton; a 3 percent by weight addition for sludge treatment would result in a cost of \$0.50 to \$0.60/ton of wet (50 percent solids) sludge.

The cost of aggregate formation from the sludge has been estimated from about \$5 to \$8/ton. This compares to a cost of from \$1.50 to \$8/ton for naturally occurring aggregate; this cost depends on local supply, transportation, etc. A typical average cost is reportedly about \$2.50/ton.

The choice between disposal by landfill and synthetic aggregate production depends on many factors, such as natural aggregate availability and costs, transportation costs, land availability, and plant size. Because of the many variations in these factors from one power plant to another, it is difficult to select a single overriding consideration. However, it has been estimated that the break-even point for synthetic aggregate production (versus disposal cost) is approximately 200,000 tons/year wet sludge production. Below this sludge production rate, the economics reportedly favor direct disposal. The bases for this break-even point is unknown. However, the plant size for 200,000 tons/year of wet sludge can be estimated from Figure 3, Section 2.0.

5.2 EPA/Aerospace Corporation Contract

Initial results of analytical and physical property tests on limestone scrubbing sludge and process materials from the TVA Shawnee power plant burning Eastern coal are discussed below. It should be noted that these results are of a very preliminary nature and are based on a single sample from one source. As such, these results may or may not be representative of those from other samples from the same source or from different sources.

5.2.1 Chemical Analysis - Emission spectrographic analysis of clarifier underflow liquor and solids (separated by centrifugation) and of the limestone indicated:

1. Liquor - No toxic components; dissolved solids content representative of equilibrium calcium sulfate concentration.

2. Solids - Presence of several heavy metals, including lead, gallium, chromium and titanium. In this specific case, based on the above results of analysis of liquor which had been in equilibrium with the solids, these elements do not appear to present a toxic hazard. However, the specific compounds and their solubilities under other conditions are presently unknown.
3. Limestone - Presence of strontium in addition to carbon, sodium, magnesium, aluminum, silicon, potassium and calcium. All other elements found are constituents of tramp clay minerals in the limestone. No other mineral phases were found. The limestone showed few major impurities that could cause potentially toxic effects.

Ion microprobe mass analyzer (IMMA) results have shown good agreement with the emission spectrographic analysis. More precise analyses of solids by spark source mass spectrometry (SSMS) and liquors by atomic absorption (AA) are in progress. Available physiological concentration effects data and toxic and hazardous element standards are being compiled for correlation with analyses of untreated and treated sludge materials and run-off, overflow, and leachate liquors.

Tests to determine whether potentially toxic components may sublime from a pond surface subjected to drying by solar heating indicated that this was not a problem up to 650°F.

5.2.2 Physical Properties Testing - Testing of unconditioned (raw) sludge from the clarifier underflow produced the following preliminary results:

1. Drainability and Water Retention - In a falling head column, a naturally settled sludge of approximately 50 percent solids showed steady state drainage of 7.5×10^{-5} cm/sec. After air drying to less than 15-20 percent moisture, the column was found to be virtually impervious until several days later. At that time, initial drainage was noted, but at a rate about half that indicated above. At intermediate column dryness, initial rate and delay in drainage were intermediate. In each case the final drainage rate was approximately equivalent to the steady state rate with the 50 percent solids sludge. In the experiments with sludge dried above 50 percent solids, the column appeared to regain sufficient water to return to the initial water content (about 50 percent) and permeability. The effects of extended time, and other dewatering and compaction techniques on this sludge behavior are not currently known.
2. Corrosion - Sample specimens of 1100 aluminum and 1010 mild steel have been exposed to sludge solids and supernatant liquor. The aluminum specimens have shown no degradation. The effect on steel specimens differs between that portion suspended within the solids and that immersed within the liquor. After 1 month, the area in contact with the solids appeared dull black, and a weight loss of about 1 percent was measured. After 2 months, the area within the solids was heavily encrusted with corrosion products and bound

sludge particles and a net weight gain of more than 10 percent was measured. The area in the liquor displayed rust ($\text{Fe}(\text{OH})_3$) which was non-adhering and easily rinsed from the specimen.

3. Viscosity - The viscosity of sludge samples with solids contents varying from 50 to 60 percent was measured with a viscometer which uses a rotating cylindrical cup immersed in the fluid being measured. Peak viscosities of 120 poises for 60 percent solids and 20 poises for 50 percent solids were measured. Thixotropic behavior was exhibited by all samples.
4. Bulk Density - Bulk density was determined for sludge with water content from zero to 100 percent. Normally settled and dried sludge bulk density was 1.2 g/cm^3 (75 lb/ft^3). With increasing water content, the bulk density increased to a maximum of about 1.7 g/cm^3 (106 lb/ft^3) for a water content of about 30 percent.
5. Shrinkage - Sludge cast into a known volume and allowed to air dry exhibited linear shrinkage of about 4 percent. Shrinkage of this magnitude could produce cracks in dried ponds, providing paths for subsequent leaching.

5.3 Concluding Remarks

The authors were concerned with presenting results obtained so early in the EPA program. However, the overriding consideration in presenting these results was to transfer information in this important area as soon as possible.

Additional information and details pertaining to industrial activities and EPA program progress related to sludge treatment and disposal can be found in other papers presented at this symposium.

6.0 PRELIMINARY CONCLUSIONS

In addition to the obvious conclusion that much extensive research and development remains to be done, the following preliminary conclusions, based on initial progress, are drawn.

6.1 Untreated Sludge

1. Based on reported sludge variability and divergence of properties between and within sources, there is a definite need to thoroughly characterize sludge materials before a disposal/utilization scheme can be determined.
2. Sublimation of potentially toxic components does not appear to be a problem at upper extremes in ambient temperature.
3. Air-dried, naturally settled sludge exhibits a tendency to regain moisture back to its equilibrium moisture content and initial permeability. Effects of other treatments and extended time are currently unknown.
4. Mild steel does not appear to be a satisfactory material for use in storage or handling of untreated sludge.
5. Sludge pumpability appears to be significantly reduced as solids content increases from 50 to 60 percent solids.
6. Air-dried sludge exhibits a tendency to shrink enough to produce cracks which could serve as paths for leaching to occur.

6.2 Treated Sludge

1. The treatment of sludge in a pozzolanic fixation process appears to significantly reduce the permeability of the

material; the leachability of trace elements from within the material is not clearly established.

2. The extent to which lime, flyash, and sulfur sludge proportions influence permeability, leachability, and strength development is not clearly established.
3. The inclusion of sulfur sludge in conventional (lime/flyash/aggregate) pozzolans, for load-bearing applications, produces a material which appears to develop superior early strength and (possibly) greater final strength.
4. Pozzolanic mixtures of lime, flyash, aggregate and sulfur sludge may be useful for road basecourse construction; they do not appear useful for wearing surfaces.
5. Synthetic aggregate produced from lime, flyash, and sulfur sludge may be suitable for basecourse construction either directly as crushed aggregate with conventional binder materials or as aggregate with a lime/flyash/sulfur sludge binder material. Substitution of synthetic aggregate for all or part of the natural aggregate required in a construction mixture could significantly increase the use of the waste sludge input.
6. Optimum formulations for the various disposal/utilization techniques are not clearly established.

6.3 General

The reader is reminded of the nature of the results on which these preliminary conclusions are based. Much more data and information must be obtained and interpreted before firm conclusions can be reached.

The attainment of these firm conclusions in the shortest possible time will require a high degree of cooperation between industry and governmental agencies to assess, develop, and apply the sludge treatment, disposal, and utilization technologies.

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TEST RESULTS FROM THE EPA
LIME/LIMESTONE SCRUBBING TEST FACILITY

by

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Section 1

INTRODUCTION

In June 1968, a three phase program was initiated whose aim was the testing of a large, versatile prototype system to fully characterize wet lime and limestone scrubbing for removal of sulfur dioxide and particulates from boiler flue gas. The Office of Research and Monitoring (OR&M) of the Environmental Protection Agency (EPA) is sponsoring this program, with Bechtel Corporation of San Francisco as the major contractor and test director, and the Tennessee Valley Authority (TVA) as the constructor and facility operator.

Phase I of the test program consisted of preliminary engineering, equipment evaluation and site selection. Phase II involved the detailed design and construction of the facility and the development of the test plan and mathematical models for predicting system performance. Phase III, the testing portion of the program, began in March 1972.

The test facility consists of three parallel scrubber systems each capable of treating approximately 30,000 acfm (10 Mw equivalent) of flue gas, which are integrated into the flue gas ductwork of an existing coal-fired boiler at the TVA Shawnee Power Station, Paducah, Kentucky.

This paper will cover, primarily, the test results for wet limestone scrubbing from September 1972 to April 1973 at the test facility. The operability and reliability of the facility during the limestone testing will be covered in a second paper at this symposium (Ref. 1). The results of air-water and sodium carbonate testing from May 1972 to August 1972 have been presented in Ref. 2.

Section 2

TEST PROGRAM OBJECTIVES

The overall objectives of this program are to evaluate the performance, reliability and economics of closed-loop limestone and lime wet scrubbing processes. The following are specific goals of the program:

- Investigate and solve operating and design problems, such as scaling, demister plugging, corrosion and erosion (see Ref. 1).
- Generate test data to characterize scrubber and system performances as a function of the important process variables.
- Study various sludge disposal methods.
- Develop mathematical models to allow economic scale-up of attractive operating configurations to full-size scrubber facilities and to estimate capital and operating costs for the scaled-up system designs.
- Determine operating conditions for optimum SO₂ and particulate removal, consistent with operating cost considerations.
- Perform long-term reliability testing.

Section 3

TEST FACILITY

The test facility has been described in detail in Ref. 3. It consists of three parallel scrubber systems, each with its own slurry handling system. Scrubbers are of prototype size, each capable of treating approximately 30,000 acfm of flue gas from the TVA Shawnee coal-fired boiler No. 10. Therefore, each circuit is handling the equivalent of approximately 10 Mw of power plant generation capacity. The equipment selected was sized for minimum cost consistent with the ability to extrapolate results to commercial scale. The 30,000 acfm scrubber train was judged to meet these requirements. Boiler No. 10 burns a high-sulfur bituminous coal leading to SO₂ concentrations of 2300-3300 ppm and inlet grain loadings of about 2 to 6 grains/scf in the flue gas.

Based on their ability to handle slurries without plugging or excessive pressure drop and on their reasonable cost and maintenance, the following scrubbers were selected for testing:

- (1) Venturi followed by a spray-tower (after absorber)
- (2) Turbulent contact absorber (TCA).
- (3) Marble-bed absorber (Hydro-Filter)

Figures 1, 2, and 3 depict, approximately to scale, the three scrubber types along with the demisters (and demister wash sprays) selected for de-entraining liquor in the gas streams. Note that, for the TCA scrubber (Figure 2), a Koch wash tray has been installed between the uppermost stage and the demister, in order to provide a liquid barrier to prevent the bulk of the entrained slurry from impinging directly onto the demister.

Typical system configurations for the venturi, TCA and Hydro-Filter systems are shown in Figures 4, 5, and 6, respectively. Such process details as flue gas slurry saturation sprays and demister or Koch tray wash sprays are not shown.

FIGURE 1
**SCHEMATIC OF VENTURI SCRUBBER
AND AFTER-SCRUBBER**

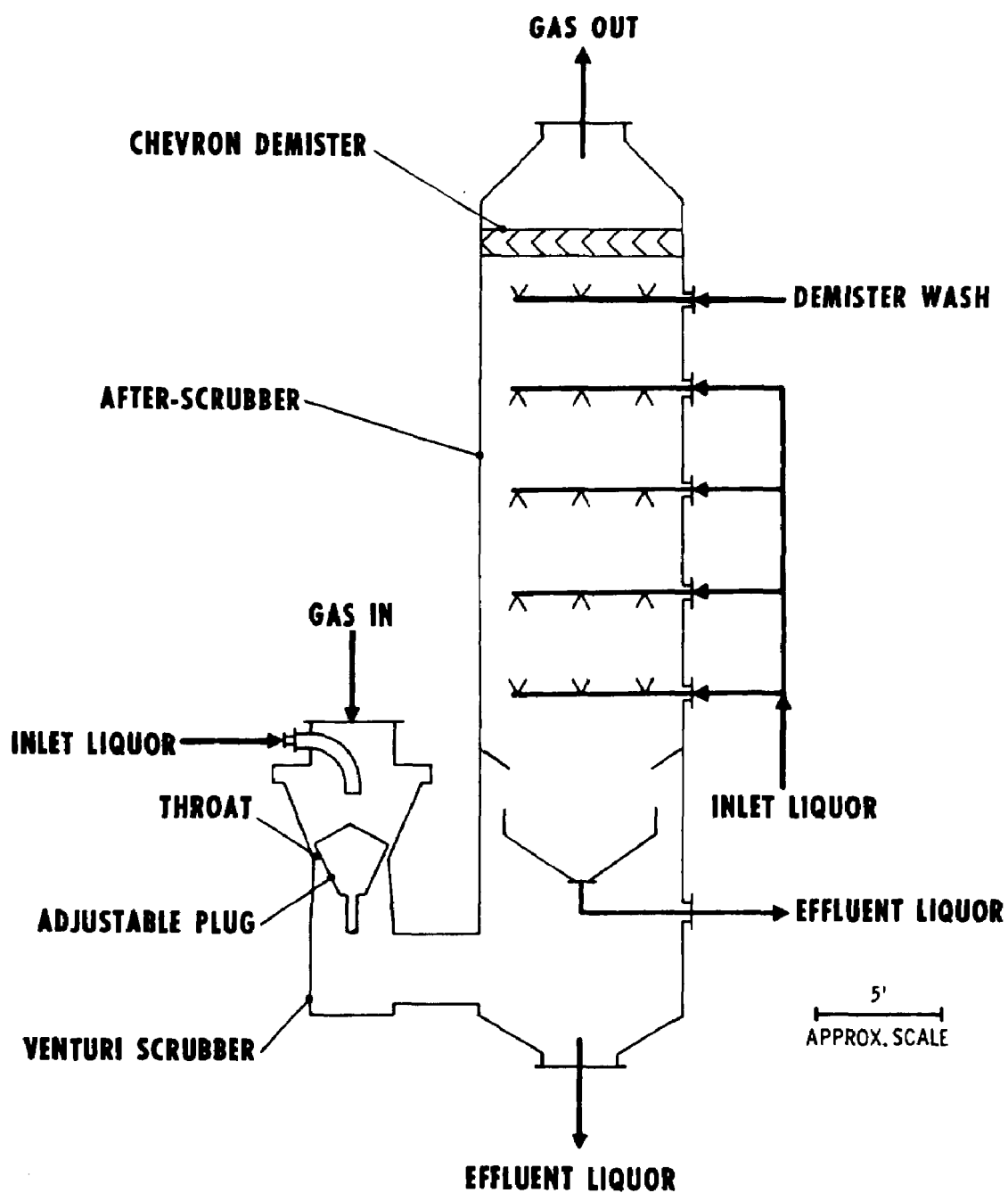


FIGURE 2
SCHEMATIC OF THREE-STAGE TCA SCRUBBER
WITHOUT TRAP-OUT TRAY

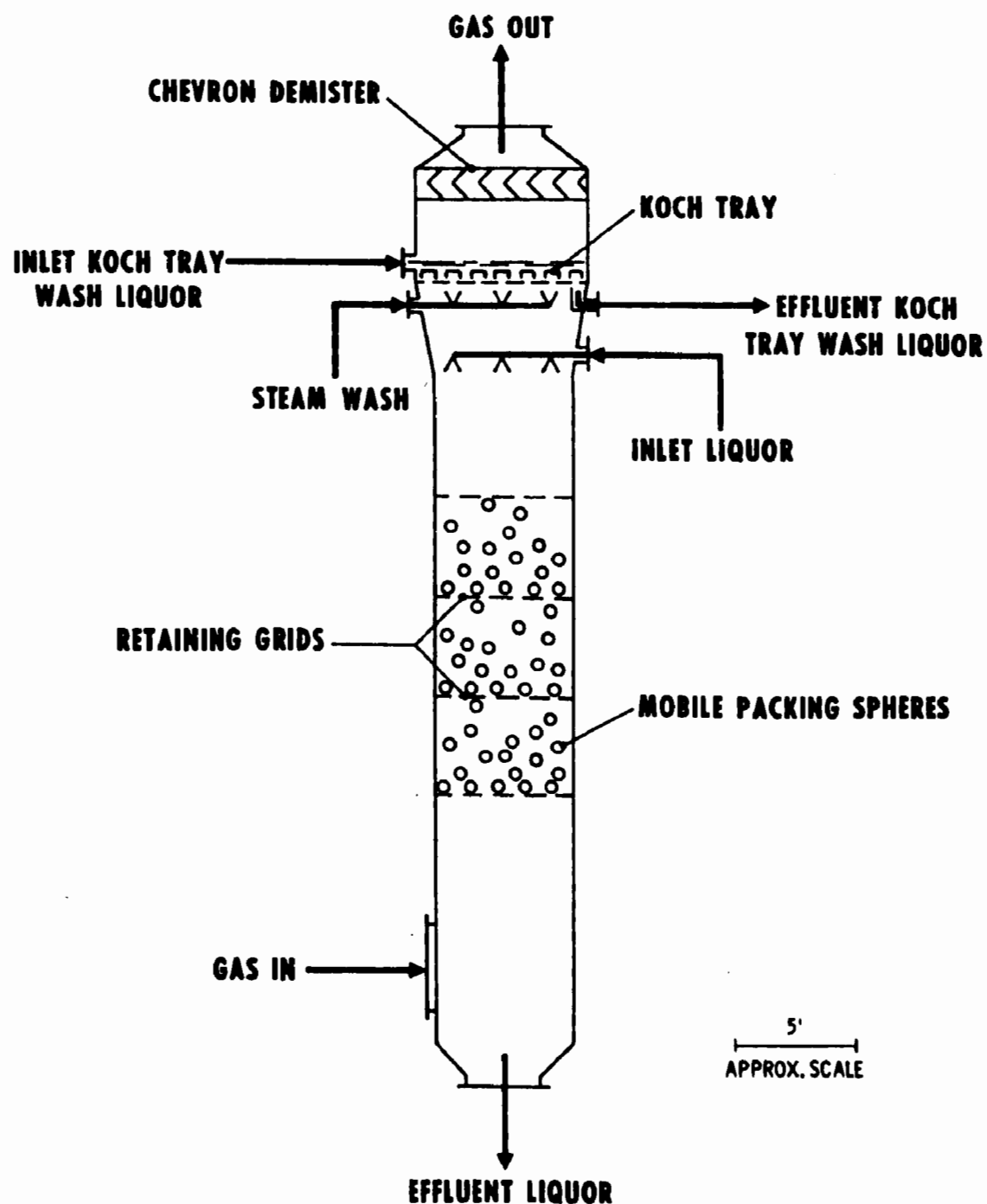


FIGURE 3
SCHEMATIC OF HYDRO-FILTER SCRUBBER

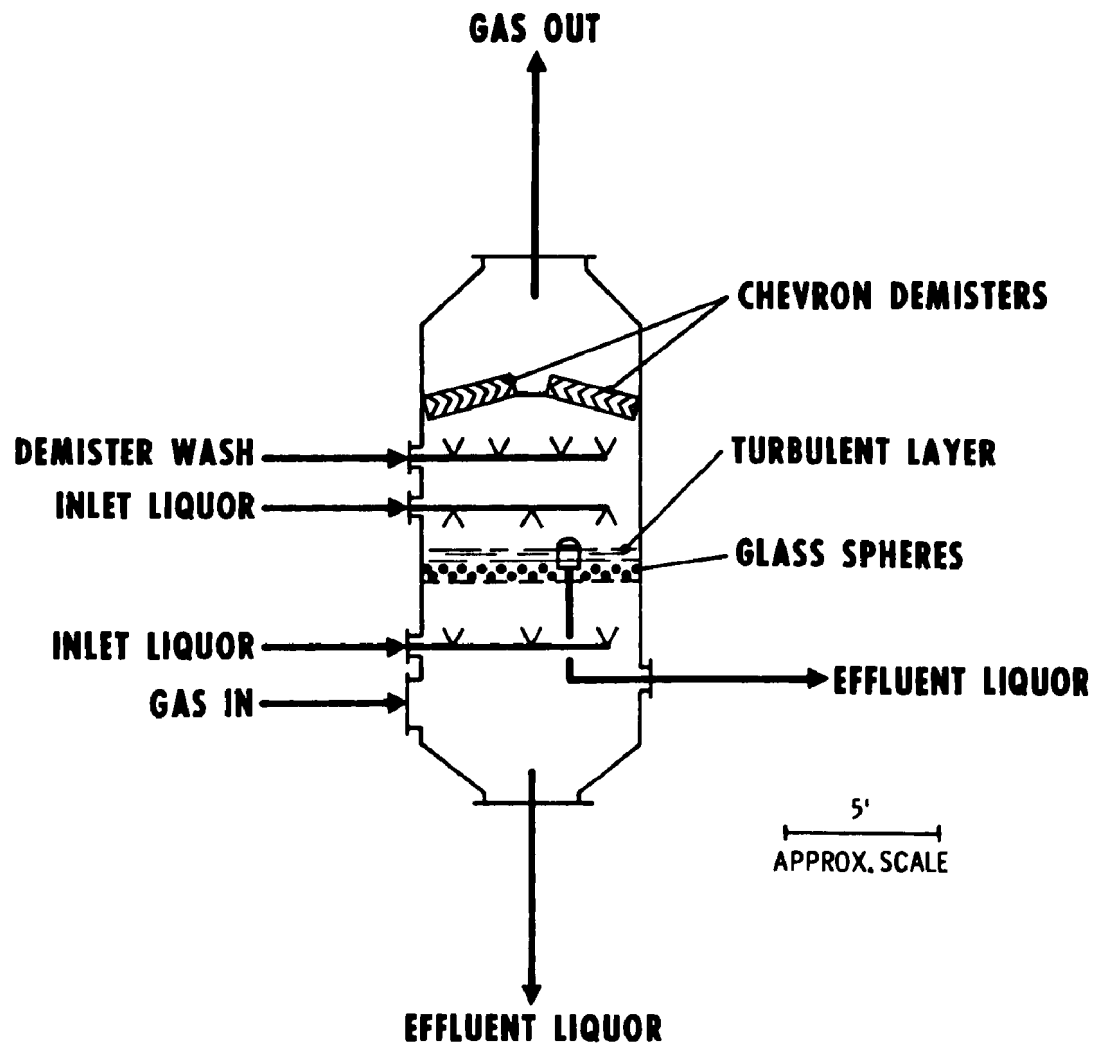


FIGURE 4
EPA TEST FACILITY
TYPICAL PROCESS FLOW DIAGRAM
FOR VENTURI SYSTEM

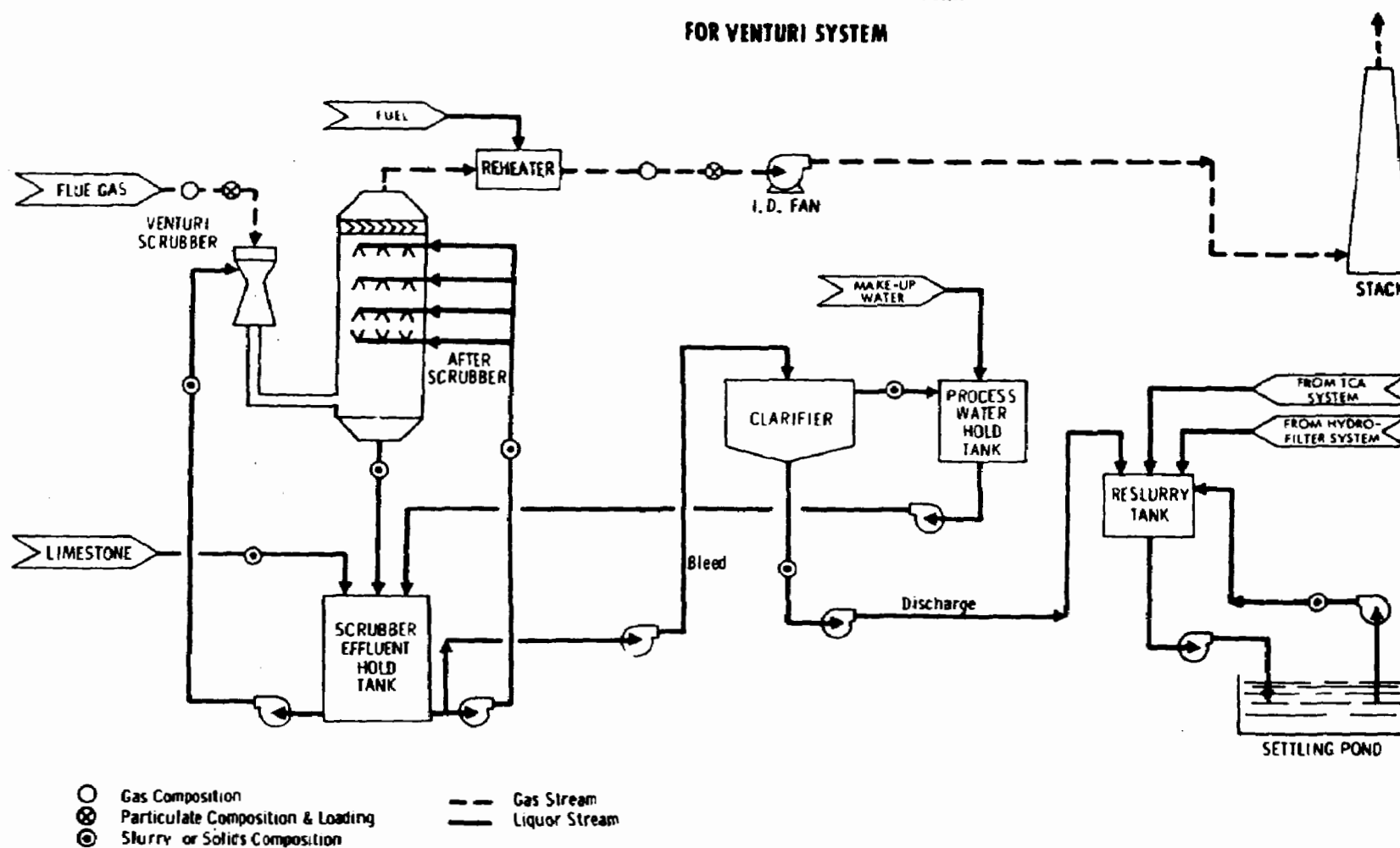


FIGURE 5
EPA TEST FACILITY
TYPICAL PROCESS FLOW DIAGRAM
FOR TCA SYSTEM

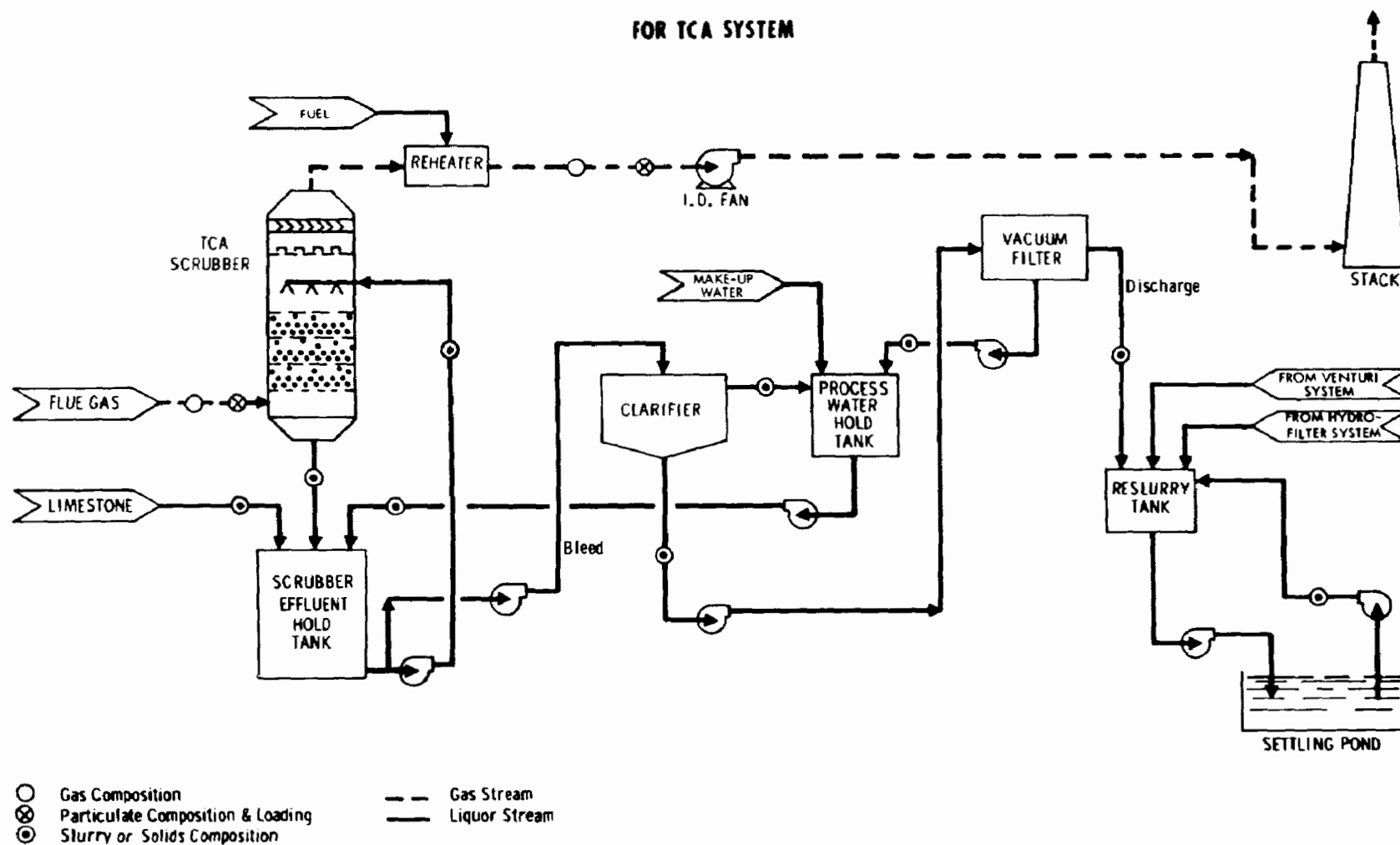
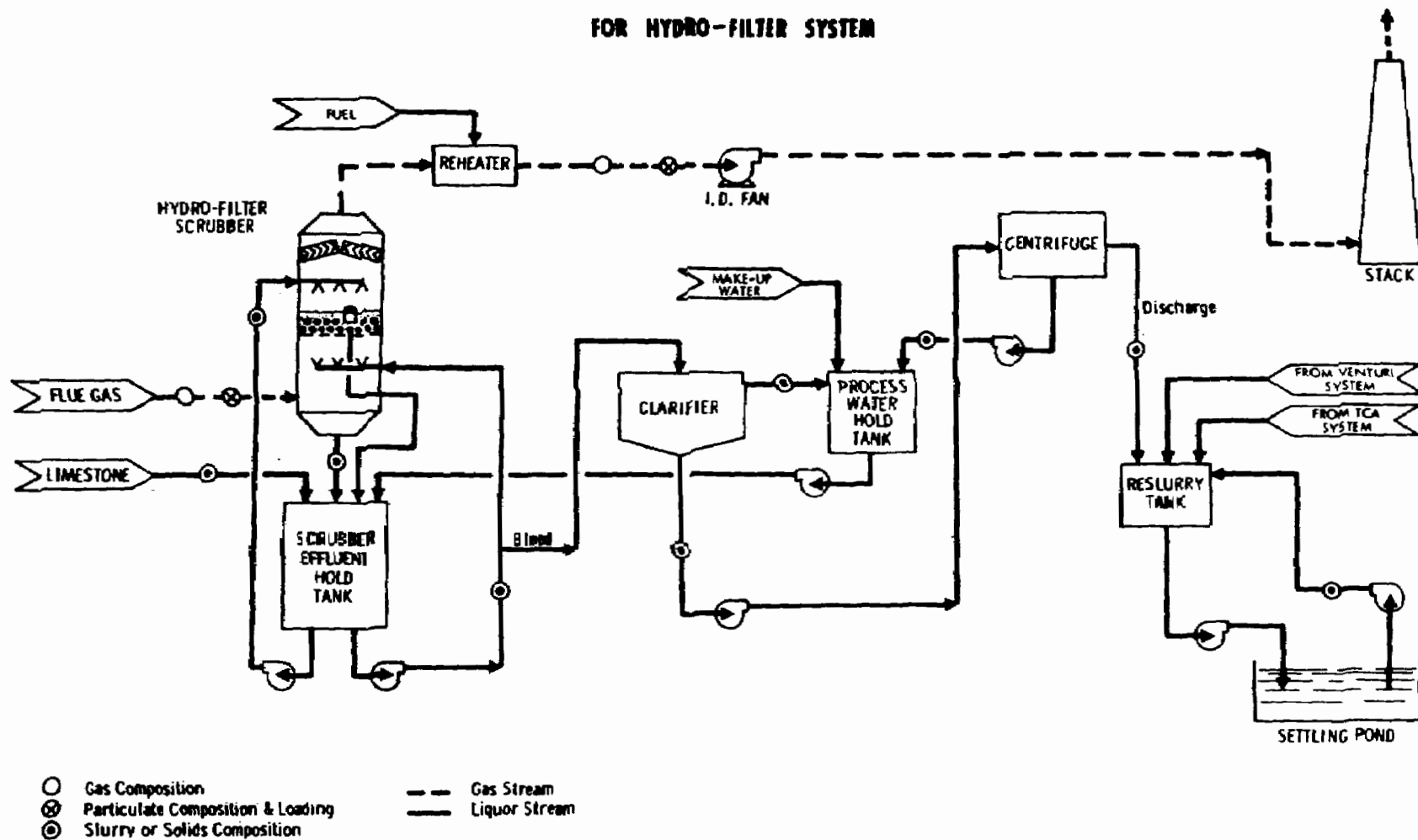


FIGURE 6
EPA TEST FACILITY
TYPICAL PROCESS FLOW DIAGRAM
FOR HYDRO-FILTER SYSTEM



Section 4

TEST PROGRAM

The following contains a brief description of the test program. A more detailed description has been presented in Refs. 2 and 3. In Table 1, a description of the reports which are presently scheduled for general distribution is presented.

4.1 TEST PERIODS AND TEST PROGRAM SCHEDULE

The following sequential test blocks have been defined for the test program.

- (1) Air-Water Testing
- (2) Sodium Carbonate Testing
- (3) Limestone Wet Scrubbing Testing
- (4) Lime Wet Scrubbing Testing

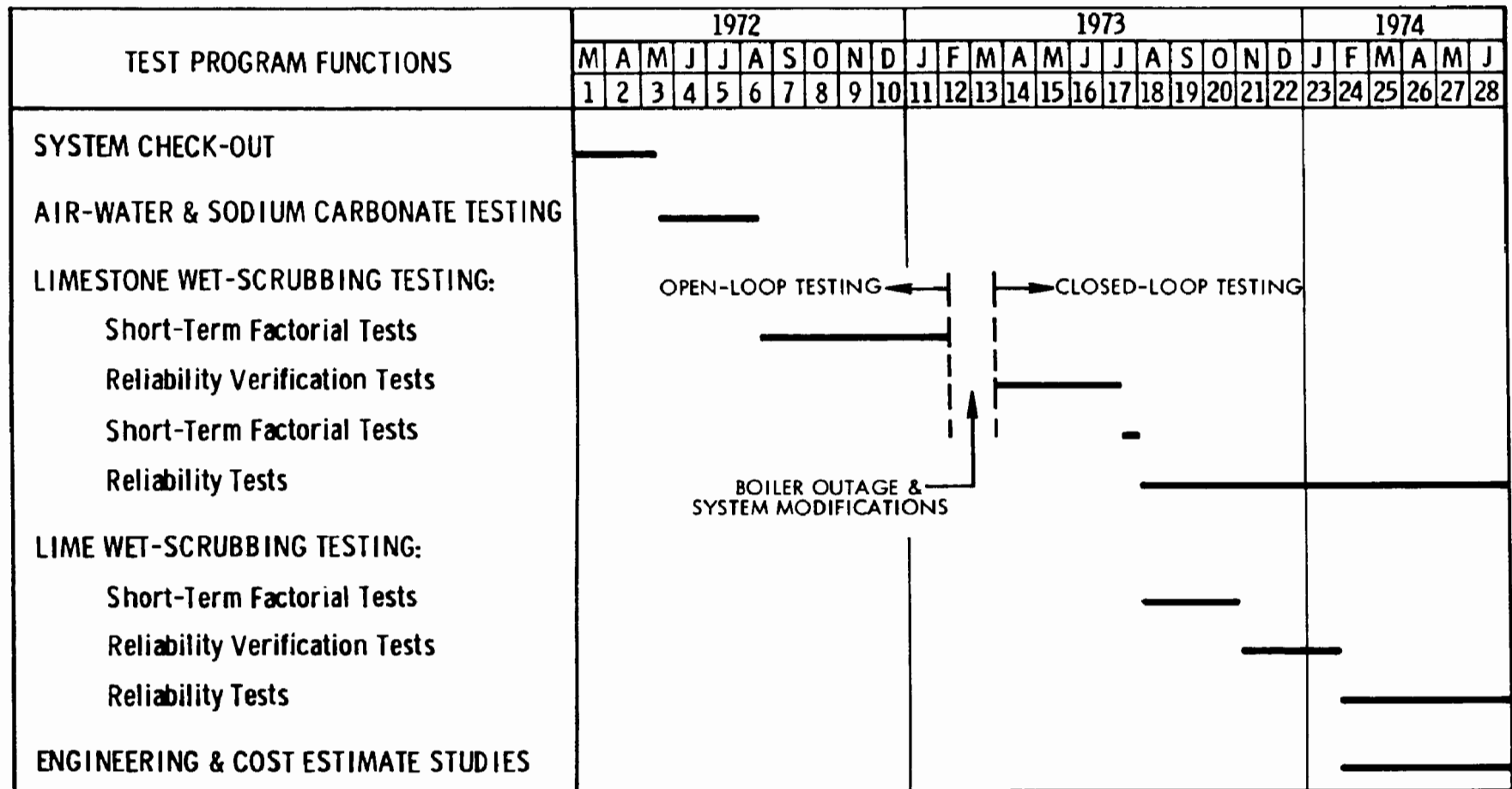
The test program schedule is presented in Figure 7. As can be seen, the air-water and sodium carbonate tests have been completed. As of mid April 1973, limestone wet scrubbing short-term factorial tests were approximately 90% complete and longer-term reliability verification tests were approximately 25% complete.

Table 1

TOPICAL AND FINAL REPORT DESCRIPTION

<u>Report Title</u>	<u>Information to be Included</u>	<u>Estimated General Publication Date</u>
1. Air-water, Sodium Carbonate and Open-Loop Limestone Test Results	Summary of operational problems and resolutions, planned and actual test designs, results of air-water and Na_2CO_3 testing, utilization of data for model development, results of open-loop limestone testing with interpretation of data.	June, 1973
249 2. Limestone Wet-Scrubbing Test Results	Summary of operating problems and resolutions associated with reliability verification testing, planned and actual test design, results of closed-loop factorial tests, interpretation of data, status of process model development and selection of parameters for limestone long-term reliability testing.	September, 1973
3. Lime Wet-Scrubbing Test Results/Limestone Reliability Test Results Status	Summary of operational problems and resolutions associated with lime reliability verification testing, planned and actual test designs, results of factorial lime testing, status of process model development, interpretation of data and status of limestone reliability testing.	February, 1974
4. Final Report	Summary of total test program with particular emphasis on lime and limestone reliability test results, mathematical models, scale-up design and economic studies.	July, 1974

FIGURE 7
PHASE III
SHAWNEE TEST SCHEDULE



4.1.1 Air-Water Testing

These experiments, which use air to simulate flue gas and water to simulate alkali slurry, are designed to determine pressure drop model coefficients and observe fluid hydrodynamics (e.g. Hydro-Filter turbulent layer) for all three scrubbers in clean systems.

4.1.2 Sodium Carbonate Testing

Two series of sodium carbonate tests have been designed. The first, or high concentration series, utilizes concentrated (~ 1 wt. % sodium ion) water solutions of sodium carbonate to absorb SO_2 from flue gas and from a synthetic flue gas composed of air and SO_2 . These tests are designed to determine uncertain model coefficients for the case where gas-side mass transfer is rate controlling. The second, or low concentration series, uses dilute (~ 0.125 wt. % sodium ion) sodium carbonate solutions to absorb SO_2 from flue gas and synthetic flue gas. For this series, gas-side mass transfer is not rate controlling and liquid-side mass transfer uncertain coefficients can be calculated using relationships for gas-side coefficients developed from the high concentration tests. These runs also help ascertain the absorption capability of liquors associated with some variations of the Double Alkali scrubbing process (see Ref. 4) over a range of operating conditions.

4.1.3 Limestone Wet-Scrubbing Testing

The primary objectives of these test sequences for closed liquor loop* operation, are:

- (1) To characterize, as completely as practicable, the effect of important independent variables on particulate removal and SO₂ removal.
- (2) To identify and resolve operating problems, such as scaling and demister plugging.
- (3) To identify areas or regions for reliable operation of the three scrubber systems, consistent with reasonable SO₂ removal, and to choose attractive (economic) operating configurations from within these regions.
- (4) To determine long-term operating reliability with attractive configurations for one or more of the scrubber systems and to develop more definitive process economics data and scale-up factors.

In order to accomplish the first objective, it will be necessary to make a large number of "short-term factorial tests" for each scrubber system. Based on tests performed to date, it appears that meaningful data on SO₂ and particulate removal can be obtained during tests lasting from 4 hours to one day.

In order to accomplish the second and third objectives, a relatively small number of longer-term (2+ week) "reliability verification tests" will be made on each scrubber system. These longer-term tests will also be useful to:

* Closed vs. open liquor loop operation will be discussed subsequently.

- Obtain more reliable material balances.
- Quantify any variations in SO_2 and particulate removal and system slurry compositions with time.

The fourth objective will be accomplished by running "reliability tests," lasting from 4 to 10 months, on attractive operating configurations for one or more of the scrubber systems. During these tests, the systems will be carefully monitored for potential long-term reliability problems, such as erosion and corrosion of system components. The ability to effectively operate such systems under varying load and SO_2 inlet conditions will also be studied during this test period.

Early during the short-term factorial test period (see Figure 7) it became apparent that it was not feasible to operate the test facility in a totally closed liquor loop, without facility modifications.* A closed-loop test is a test wherein the raw water input to the system is nearly equal to the water normally exiting the system from the humidified flue gas and the waste sludge transferred to the pond. In an open loop system, raw water input is significantly greater than the water outflow in the exit gas and sludge. Therefore, process liquor must be discharged from the system to maintain an overall

* These modifications were completed during a five-week boiler-outage in February and March, 1973 (see Figure 7). The major modifications included: eliminating pump sealing water on the Allen-Sherman-Hoff pumps by changing from Hydroseals to Centriseals; humidifying the hot inlet flue gases with slurry instead of with raw water; and washing demisters with process liquor diluted with raw water instead of with raw water only. Other major modifications to the systems during the boiler outage, not necessarily effecting the water balance, are discussed in Ref. 1.

water balance. In a commercial system such discharge may not be acceptable due to potential water pollution problems. Also, during open-loop operation reliability may be unintentionally enhanced since the additional raw water added tends to desaturate liquors returning to the scrubber, thereby tending to reduce scaling and plugging. It is expected, however, that important SO_2 removal data has been obtained during the short-term open-loop factorial testing, since other pilot-scale testing has indicated that SO_2 removal is relatively independent of liquor composition for limestone scrubbing systems.

To date, therefore, the order of limestone testing has been (see Figure 7):

- (1) Open-loop short-term factorial testing.
- (2) Closed-loop long-term reliability verification testing.

4.1.4 Lime Wet Scrubbing Testing

This test series, which involves introduction of hydrated lime (calcium hydroxide) directly in the scrubber circuit, will resemble the limestone wet scrubbing test program. The major difference will be the absence of any open-loop tests. Again, tests will be divided into three general categories (see Figure 7): short-term factorial tests, longer-term reliability verification tests and long-term reliability tests.

4.2. LIMESTONE WET SCRUBBING TEST DESIGNS

4.2.1 Short-Term Factorial Testing

The test sequences for the short-term factorial experiments are all full or partial factorial designs (with centerpoint replicates included) based upon the chosen independent variables, their levels and the restraints of time as outlined in Figure 7. The choice of the independent variables and their levels was based upon pilot plant test results, the restraints of the systems and results from mathematical models which relate the dependent and independent variables.

Table 2 shows the independent variables and levels which are to be investigated during limestone factorial testing for the three scrubber systems. These variables and levels are always tentative, since the experimental test program is continuously reviewed and up-dated, as information is generated. Intermediate variable levels for centerpoint replicate runs (e.g., stoichiometric ratio = 1.5) have not been included in Table 2.

The results, to date, of short-term (open-loop) factorial testing for the three scrubber systems are presented in Section 5.

4.2.2 Reliability Verification Testing

Assuming that each reliability verification test will last about 2^+ weeks, and assuming 1/3 downtime for each system (for inspections, cleanings, etc.), only about six tests can be made for each scrubber system,

TABLE 2
INDEPENDENT VARIABLES AND LEVELS FOR LIMESTONE FACTORIAL EXPERIMENTS

Venturi System			TCA System			Hydro-Filter System		
Variable	Levels		Variable	Levels		Variable	Levels	
Scrubber configuration	1	Venturi alone	Number of Stages	1	1 stage	Marble-Bed Height	1	3 inches
	2	Spray tower alone		2	3 stages		2	5
	3	Venturi and Spray tower						
Gas Flow Rate	1	15,000 acfm	Gas Flow Rate	1	15,000 acfm	Gas Flow Rate	1	20,000 acfm
	2	30,000		2	30,000		2	30,000
Liquor Flow Rate to Venturi and to Spray Tower*	1	300 gpm	Liquor Flow Rate	1	600 gpm	Total Liquor Flow Rate	1	400 gpm
	2	600		2	1200		2	800
Stoichiometric Ratio**	1	1.00 mole/mole	Stoichiometric Ratio	1	1.00 mole/mole	Stoichiometric Ratio	1	1.00 mole/mole
	2	1.75		2	1.75		2	1.75
Percent Solids Recirculated	1	6%	Percent Solids Recirculated	1	6%	Percent Solids Recirculated	1	6%
	2	15		2	15		2	15
Effluent Hold Tank Residence Time	1	2.3 min	Effluent Hold Tank Residence Time	1	4.6 min			
	2	4.6		2	30			
	3	40						
	4	60						
Venturi Pressure Drop	1	6 in. H ₂ O						
	2	9						
	3	12						
Number of Spray Headers in Spray Tower	1	2 headers						
	2	4						

* After Mid-May 1973, the maximum liquor flow to the spray tower will be 1200 gpm.

** Stoichiometric ratio is defined as moles CaCO₃/mole SO₂ inlet.

given the restraints of time outlined in Figure 7. Obviously, not all variables which are assumed to affect system reliability can be comprehensively studied within the six-run limitation.*

Earlier open-loop factorial runs were all made at high stoichiometries (greater than 1.75 moles CaCO_3 /mole SO_2 abosrbed) and had scrubber inlet liquor pH's ranging from 6.0 to 6.3. It is planned that a majority of the reliability verification tests will be made at reduced scrubber inlet liquor pH's (5.7-5.9), reduced stoichiometries (1.1-1.5 moles CaCO_3 /mole SO_2 absorbed) and, of course, slightly reduced SO_2 removals. These "reduced-pH" runs should result in improved overall system reliability, because of larger oxidation rates at the lower pH's and, of course, increased limestone utilizations (less CaCO_3 added/mole SO_2 absorbed).

The higher oxidation rates at reduced pH's will result in improved clarifier operation and in a larger percentage of "seed" CaSO_4 crystals within the process slurry**. An increase in the percentage of CaSO_4 crystals will probably result in reliable operation at lower percent solids recirculated and/or in smaller effluent hold tank sizes (residence times), which is economically desirable. The increase in limestone utilization results, of course, in a reduction in waste mass solids handling and in limestone requirements. These improvements may be offset, however, by the need for larger scrubbers in order to obtain the specified removals.

* These tests will be supplemented with reliability verification tests with the EPA pilot TCA scrubbers at Research Triangle Park, N. C. (see Section 4.4).

** Oxidation of sulfite to sulfate in the E. H. T. can also be increased by air-sparging (Ref. 5).

On Tables 3, 4, and 5, the proposed limestone reliability verification test plans for the venturi, TCA, and Hydro-Filter systems are shown. For the venturi system, the effect of percent solids and gas rate on reliability, with two different demister types, will be tested. For the TCA system, the effect on reliability of percent solids, residence time, air sparging, and gas rates are tested. For the Hydro-Filter system, the effect on reliability of percent solids, gas rate, and scrubber inlet pH (at 10% solids) are tested. Solids separation tests for the clarifier, filter, and centrifuge will be made on the three systems throughout the entire test period.

The runs listed in Tables 3, 4, and 5 have been listed in the expected order in which they will be made. An attempt has been made to start the testing on each system at conditions which are expected to give high probability for reliable operation (e.g. high L/G, high effluent residence time).

As of late April 1973, the initial runs on Tables 3, 4, and 5 for the three scrubber systems have been in progress for about 20 days each (see Section 7).

4.3 ANALYTICAL SCHEDULE

Samples of slurry, flue gas and limestone are taken during each test run for chemical analyses, particulate size sampling and limestone reactivity tests. Batch samples of coal are taken periodically for chemical analysis. Locations of sample points are shown on Figures 4, 5, and 6. In addition, clarifier settling tests, filter leaf tests, and filter and centrifuge "operational tests" are also being

Table 3

PROPOSED TEST PLAN FOR RELIABILITY VERIFICATION
TESTS WITH VENTURI SYSTEM

Venturi and Spray Tower

Venturi pressure drop = 9 in. H₂O

Liquor rate to venturi = 600 gpm

Residence time = 20 min

Stoichiometric ratio = 1.3-1.5 moles CaCO₃/moles SO₂ absorbed (expected)

Inlet liquor pH = 5.7-5.9

<u>Run</u> <u>No.</u>	<u>Percent</u> <u>Solids</u> <u>Recirculated</u>	<u>Spray Tower</u> <u>Liquor Rate, gpm</u>	<u>Gas Rate,</u> <u>acfm</u>	<u>Demister</u> <u>Type</u>	<u>Expected</u> <u>Percent</u> <u>SO₂ Removal</u>
1	15	600	20,000	A	60-70 ^(b)
2	8	600	20,000	A	60-70
3	15	600	20,000	B	60-70
4	8	600	20,000	B	60-70
5	(a)	1200	20,000	(a)	70-80
6	(a)	1200	30,000	(a)	65-75

(a) To be determined from runs 1 - 4.

(b) Expected SO₂ removal at high-pH (6.0-6.3) is from 70-80%.

Table 4

PROPOSED TEST PLAN FOR RELIABILITY VERIFICATION
TESTS WITH TCA SYSTEM

Three stages of TCA spheres, 5" per stage

Liquor rate = 1200 gpm

Stoichiometric ratio = 1.3 - 1.5 moles CaCO_3 /moles SO_2 absorbed (expected)

Inlet liquor pH = 5.7 - 5.9

Expected SO_2 removal = 80 - 90%. For high stoichiometry (> 1.5) and high pH (6.0 - 6.3) expected SO_2 removal is from 90 - 95%.

<u>Run No.</u>	<u>Percent Solids Recirculated</u>	<u>Residence Time, min.</u>	<u>Air-Sparging</u>	<u>Gas Rate, acfm</u>
1	15	20 (EHT)	No	20,000
2	8	20 (EHT)	No	20,000
3	(a)	20 (EHT)	Yes	20,000
4	15	5-6 (EHT)	Yes	20,000
5	8	5-6 (EHT)	Yes	20,000
6	15	5-6 (EHT)	Yes	30,000
7(b)	15	4.6 (RT)	No	20,000

(a) To be determined from results of runs 1 and 2.

(b) Will be run if time permits.

Note: "EHT" stands for effluent hold tank and "RT" stands for recirculation tank.

Table 5

**PROPOSED TEST PLAN FOR RELIABILITY
VERIFICATION TESTS WITH
HYDRO-FILTER SYSTEM**

Height of marble-bed = 3-1/2 inches

Liquor rate = 800 gpm (total)

Residence time = 30 min

Stoichiometric ratio = adjusted to give desired pH or SO₂ removal
(expected between 1.3 and 1.6 moles CaCO₃/moles SO₂ absorbed)

<u>Run No.</u>	<u>Percent Solids Recirculated</u>	<u>Approximate pH to Scrubber</u>	<u>Gas Rate, acfm</u>	<u>Expected SO₂ Removal, %</u>
1	10	5.7	20,000	70
2	10	6.2	20,000	80
3	15	5.7	20,000	70
4	6	5.7	20,000	70
5	15	5.7	30,000	70
6	6	5.7	30,000	70

conducted periodically. A typical analytical schedule for a limestone wet-scrubbing test and a summary of the analytical methods for determining important species in slurry, coal and alkali are presented in Ref. 2.

4.4 EPA PILOT PLANT SUPPORT

In support of the Shawnee prototype testing activities, two smaller scrubbing systems (300 acfm each), which are capable of operating over a wide range of operating conditions, have been installed at EPA's Research Triangle Park, N.C. facility. The small pilot scale units are capable of simulating the TCA scrubber circuit and have already generated large quantities of closed-loop data on certain TCA configurations.

Section 5

SHORT-TERM FACTORIAL LIMESTONE TEST RESULTS

5.1 SO₂ REMOVAL RESULTS

In this section, the significant SO₂ removal results from the open-loop limestone factorial test sequences are presented graphically. The complete listing of all pertinent data, in tabular form, for all of the open-loop runs made prior to the boiler outage (see Figure 7), will be presented in the first interim report (see Table 1).

The SO₂ removals during open-loop testing have all been corrected for the dilution effect of water vapor and reheater gas pickup by the flue gas. The SO₂ removals have also been corrected for DuPont SO₂ analyzer calibration errors associated with unstable composition of SO₂ calibration gas (from September 15 to October 13, 1972) and the deterioration of the DuPont analyzer optical filters (from June 23 to December 1, 1972).*

After mid-November, 1972, when a 60 wt. % limestone slurry addition system** was installed for the three scrubber systems, some problems developed with the calibrations of the limestone additive magnetic flowmeters at the reduced slurry flow rates. All of the stoichiometric

*These correction factors were furnished by the DuPont Co. The corrections were small for SO₂ removals greater than 70%.

**Previously, a 15 wt. % limestone addition system was in use.

ratios after mid-November were higher than their "nominal" (see Table 2) values and in excess of 1.5 moles CaCO_3 added/mole SO_2 inlet. For these high values of stoichiometric ratio, and at the prevailing high-inlet SO_2 concentrations (2300-3300 ppm), the SO_2 removals were not significantly affected by changes in stoichiometric ratio (see Section 6.1 and 6.2).

Prior to system modifications made during the five week boiler outage, reasonable material balance closures for calcium and sulfur could only be obtained with the TCA system. During this period of operation, the venturi and Hydro-Filter systems still had the clarifiers and process water hold tanks included in the main slurry loops, while the TCA system had been modified so that the main slurry stream circulated between the hold tank and scrubber, with a bleed stream from the main slurry stream routed to the solids separation area (clarifier, vacuum filter or centrifuge)*. The poor material balances for the venturi and Hydro-Filter systems were attributable to solids build-ups (or depletions) within the clarifiers. For the TCA scrubber, the calcium and sulfur leaving the system could be obtained from the measured flow rate and solids analysis of the "bleed stream" to the solids separation area, and the clarifier could be excluded from the material balance enclosure. Typical system configurations for the open-loop limestone tests have been presented in Ref. 2, along with the material balance results for six TCA runs. The closures were all within the limits of the estimated experimental accuracies during those periods of time.

* During the five-week boiler outage, the flow configurations for the venturi and Hydro-Filter were converted to ones similar to that of the TCA system. These modified configurations have been shown in Figures 4, 5 and 6.

Although satisfactory material balance closures were not obtained during the open-loop factorial testing for the venturi and Hydro-Filter systems, confidence in the generated data is based on the following:

- "Wet" chemical analyses for SO_2 in the inlet and exit gas streams repeatedly corroborated DuPont SO_2 analyzer measurements.
- Sulfur removals in longer-term reliability verification runs, with excellent material balance closures for calcium and sulfur (see Section 7), have been in close agreement with open-loop replicate* runs for the venturi, Hydro-Filter and TCA systems.

It is recognized that SO_2 removal is affected by SO_2 inlet gas concentration and scrubber inlet liquor temperature (Ref. 6). Care, therefore, has been exercised in segregating these non-controlled independent variables in the presentation of the data.

5.1.1 Venturi System

In Figure 8, the effect of gas and liquor flow rates on SO_2 removal for the venturi scrubber with 9 inches of pressure drop is shown. Only data taken after December 1, 1972 has been plotted, since there is some evidence that SO_2 removal corrections (for the deterioration of the DuPont optical filters) were not accurate at low SO_2 removals.

* Replicate runs are made with identical values for all controlled independent variables.

FIGURE 8
PRELIMINARY RESULTS FOR SO₂ REMOVAL IN THE
CHEMICO VENTURI WITH A NINE INCH PRESSURE DROP.

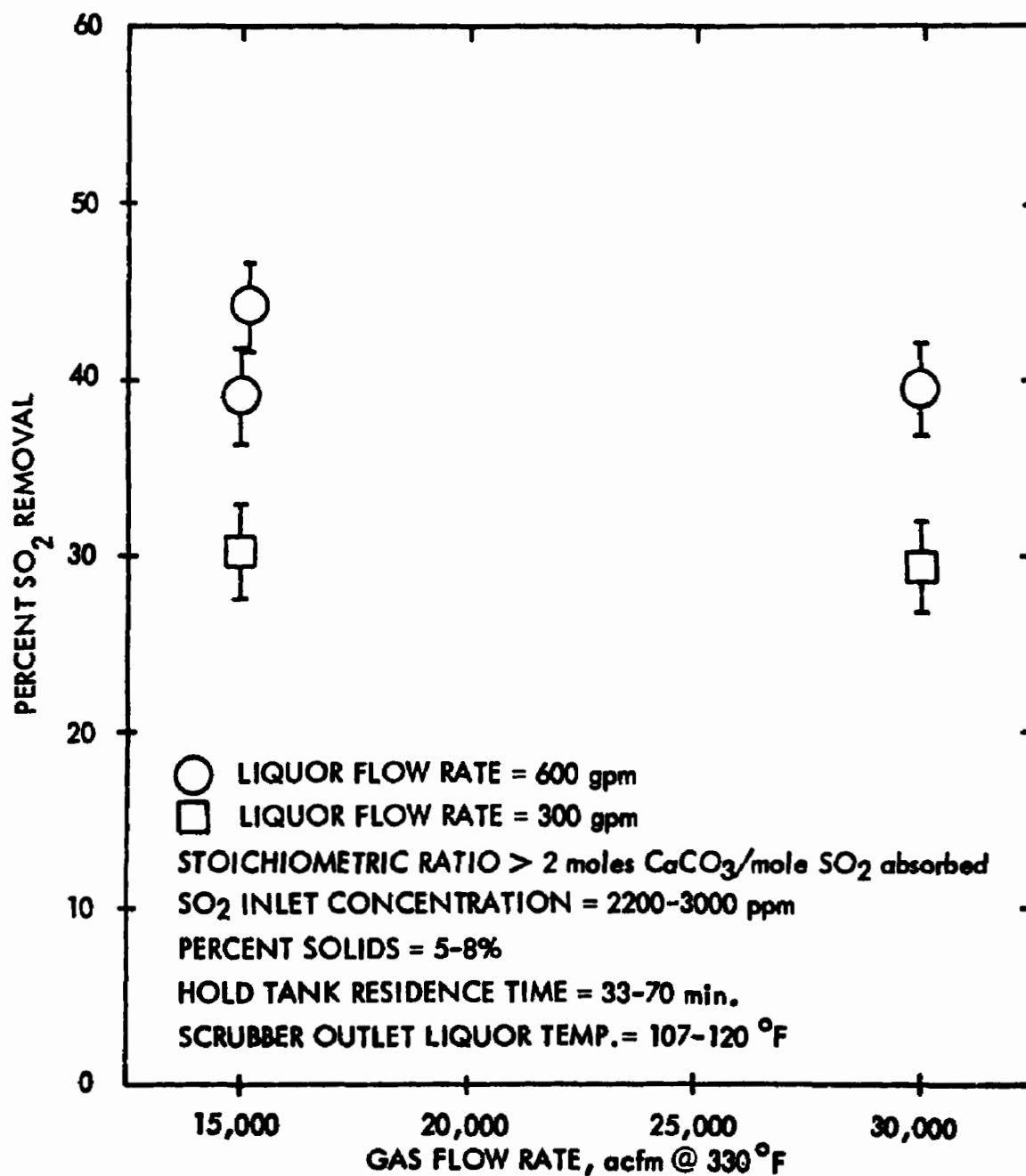


Figure 9 illustrates the effect of gas and liquor flow rates on SO_2 removal in the four-header spray tower. The outlet liquor temperatures (shown in the figure) varied considerably from run to run. The effect of outlet liquor temperature on SO_2 removal was generally consistent, with higher SO_2 removal at lower temperature. A curve representing a median liquor temperature of approximately 100°F has been drawn for each liquor flow rate.

Figure 10 is a cross-plot of Figure 9, showing the effect of liquid-to-gas ratio and gas velocity on SO_2 removal at a scrubber outlet liquor temperature of about 100°F . The SO_2 removals are outside the range of interest for commercially acceptable gas velocities (> 7 ft/sec).^{*} The results from Figure 10 appear to agree reasonably well with the spray tower data taken by the Hydro-Electric Power Commission of Ontario (Ref. 7), after correcting for the effects of inlet gas SO_2 concentration (see Section 5.1.2).

A spray tower limestone depletion^{**} run 463-1A was made to determine the effect of stoichiometric ratio and inlet scrubber liquor pH on SO_2 removal. Results from this run are presented in Table 6 and in Figure 11. SO_2 removals for this run were low because, at that time, the liquid-to-gas ratio could not be maintained greater than

^{*} A modification to increase the maximum liquor rate from 600 to 1200 gpm for the spray tower is scheduled for completion by end of May, 1973. This will allow for a liquid-to-gas ratio of 53 gal/mcf at a gas velocity of 7.5 ft/sec, which should produce an SO_2 removal of about 65%.

^{**} A limestone depletion run is a run in which no limestone make-up is added during the test period.

FIGURE 9
EFFECT OF GAS AND LIQUOR FLOW RATES
ON SO₂ REMOVAL IN THE FOUR-HEADER SPRAY TOWER

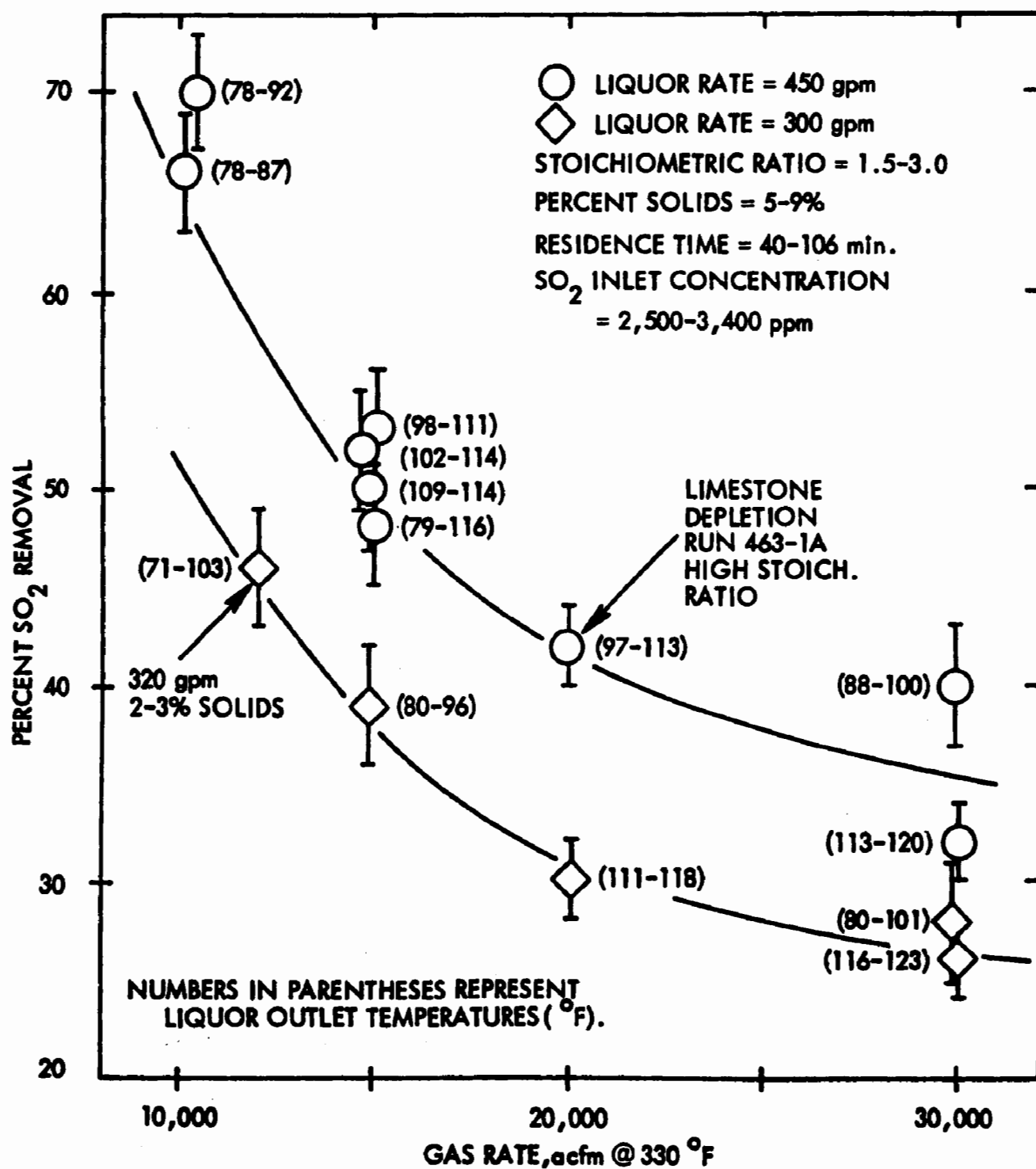


FIGURE 10
EFFECT OF LIQUID-TO-GAS RATIO AND GAS VELOCITY
ON SO_2 REMOVAL IN THE FOUR-HEADER SPRAY TOWER

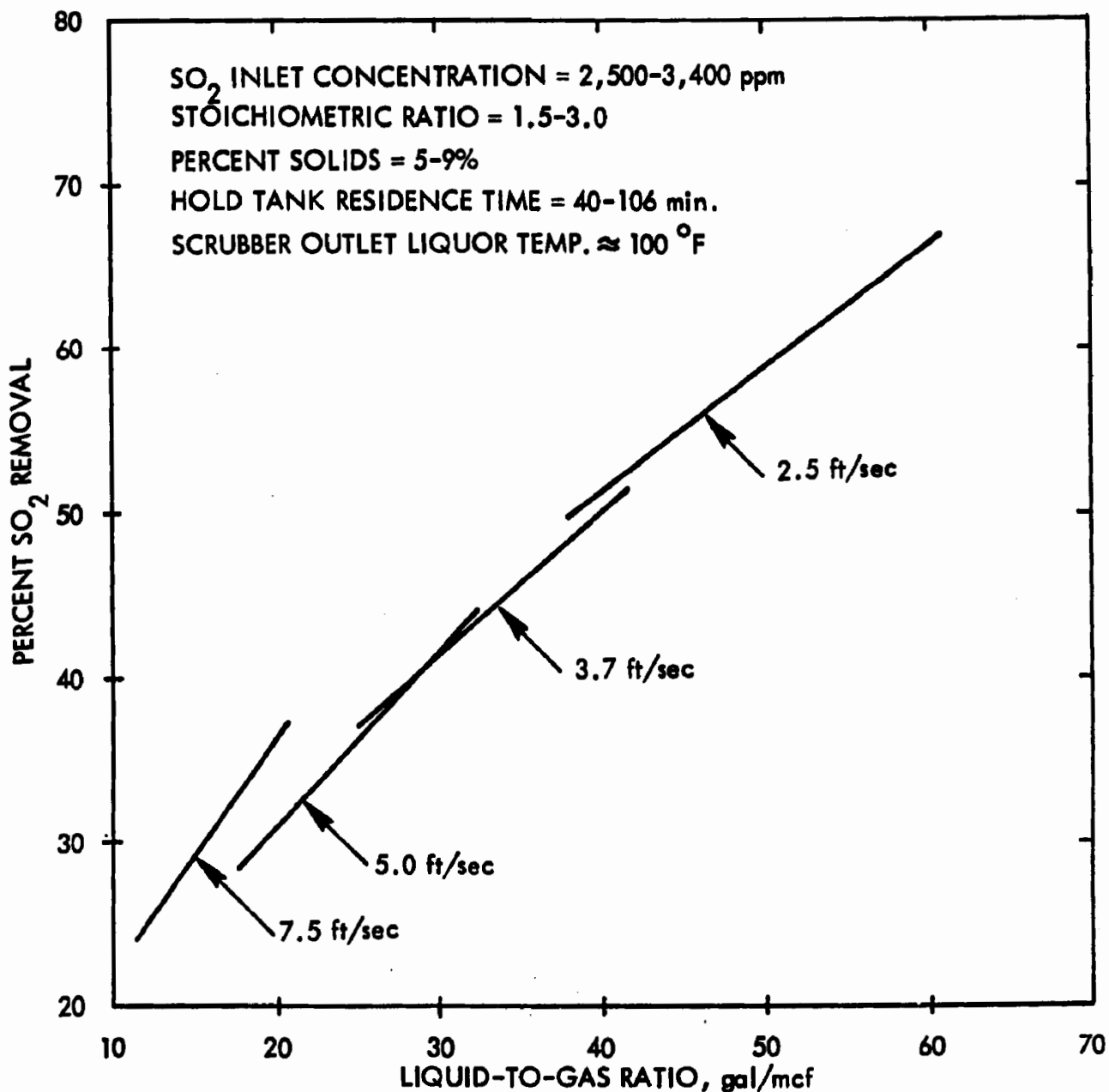
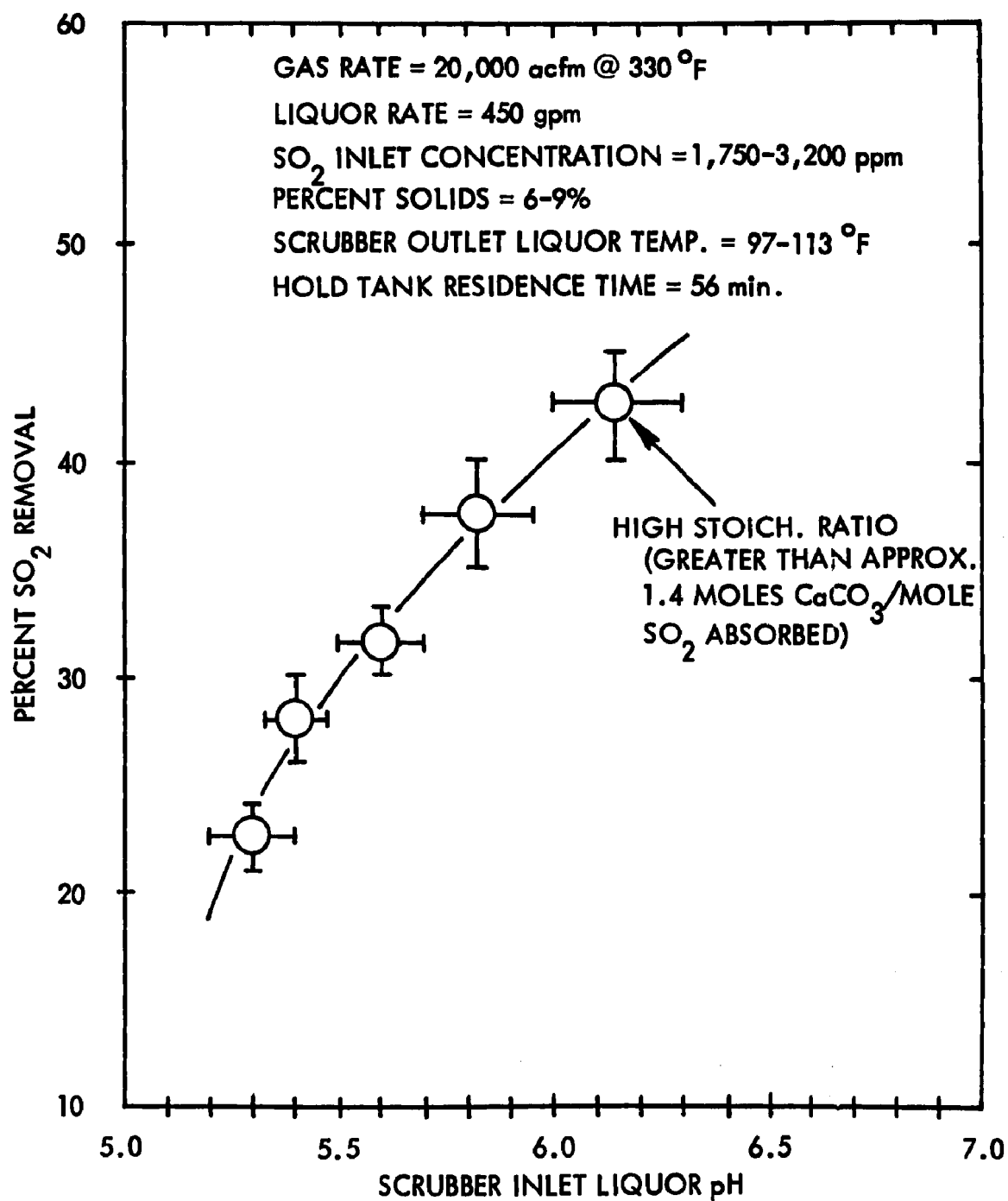


TABLE 6

SPRAY TOWER LIMESTONE DEPLETION
RUN WITH FOUR HEADERS
RUN NO. 464-1A

DATE	TIME HOUR	INLET SLURRY		INLET SO ₂ CONC. ppm	SO ₂ REMOVAL %	STOICHIOMETRIC RATIO, TOTAL MOLES CaCO ₃ MOLE SO ₂ ABSORBED
		SOLIDS CONC., W.T. %	pH			
1/23/73	1100	7.70	7.30	3125	71.0	
	1200			1094	70.0	18
	1300			1094	60.0	19
	1400			1063	58.0	13
	1500	6.33	6.50	3031	53.0	10
	1600		6.50	3031	49.0	8.6
	1700		6.25	3031	48.0	7.4
	1800		6.20	3000	47.0	6.5
	1900	6.40	6.30	2969	47.0	5.8
	2000		6.20	3000	46.0	5.3
	2100		6.20	3125	43.5	4.8
	2200		6.00	3250	44.5	4.5
	2300	6.95	6.30	3187	44.0	4.1
	2400		6.30	3063	44.5	3.9
	0100		6.20	3063	44.5	3.6
	0200		6.30	3063	44.0	3.4
	0300	7.93	6.30	3000	41.5	3.2
	0400		6.30	3063	42.5	3.1
	0500		6.30	3063	41.0	2.9
	0600		6.20	3125	42.0	2.8
	0700	8.92	6.35	3125	42.0	2.7
	0800		6.30	3156	42.5	2.6
	0900		6.25	3156	41.0	2.5
	1000		6.30	3031	42.0	2.4
1/24/73	1100	9.00	6.30	2875	41.0	2.3
	1200		6.30	2813	41.5	2.2
	1300		6.30	2813	42.5	2.1
	1400					
	1500					
	1600					
	1700					
	1800					
	1900					
	2000					
	2100					
	2200					
	2300					
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	0500					
	0600					
	0700					
	0800					
	0900					
	1000					
	1100					
	1200					

FIGURE 11
EFFECT OF INLET LIQUOR pH
ON SO₂ REMOVAL IN THE FOUR-HEADER SPRAY TOWER
(LIMESTONE DEPLETION RUN NO. 463-1A)



approximately 30 gal/mcf.

In Table 6, the stoichiometric ratio^{*} has been calculated from the estimation of the original lb-moles of CaCO_3 in the system and of the SO_2 absorbed. A comparison between the stoichiometric ratios calculated in this manner with those obtained from the solids analysis could not be made, unfortunately, because of uncertain solids analytical results during this period.

As can be seen from Table 6, the SO_2 removal and inlet liquor pH remained at steady values of 40–44% and 6.0–6.3, respectively, for a long period of time (about 35 hours) before the removal and pH began to drop. The stoichiometric ratios for this period of time were greater than 1.4 moles CaCO_3 added/mole SO_2 absorbed. The SO_2 removal for this high stoichiometry region has been included as a data point in Figure 9.

Figure 11 shows the effect of inlet liquor pH on SO_2 removal for Run 463-1A as the limestone in the system was depleted. Similar effects of pH upon SO_2 removal have been reported in Refs. 8 and 9.

* The stoichiometric ratio (moles CaCO_3 /moles SO_2 absorbed) of the scrubber inlet liquor changes with time as the SO_2 is absorbed (i. e., one mole of CaSO_x is formed and one mole of CO_2 is evolved for every mole of SO_2 absorbed).

5.1.2 TCA System

The results of the EPA* TCA limestone runs are summarized in Figures 12 through 15.

Figure 12 shows the effect of height of spheres (5 and 10 inches/stage) and gas rate on SO_2 removal in the TCA with six grids and three stages. The effect of spheres vs. no spheres in the six-grid TCA on SO_2 removal is illustrated in Figure 13.

The liquor and gas rate effects on SO_2 removal in the four-grid three-stage TCA are presented in Figure 14. Figure 15 is a cross-plot of Figure 14, showing the effect of liquid-to-gas ratio and gas velocity on SO_2 removal.

The variation in SO_2 removal for 5 inches of spheres per stage in the six-grid, three-stage TCA (shown as open circles in Figures 12 and 13) is attributed, mainly, to differing average values of SO_2 inlet concentrations. In Table 7, the SO_2 removals and operating conditions for these runs have been compared,

R.H. Borgwardt (Ref. 9) of EPA has reported that, for his pilot scale TCA (see Section 4.4), the percent SO_2 removal is inversely proportional to the one-tenth power of inlet SO_2 concentration. The

* From November 4, 1972 to January 15, 1973, TVA has conducted a special series of tests with the TCA scrubber to provide process and equipment scale-up and design information for the 550 Mw coal-fired TVA Widows Creek Unit 8 retrofit limestone scrubbing system. The results shown on Figures 12 through 15 do not include the TVA tests.

FIGURE 12
EFFECT OF HEIGHT OF SPHERES AND GAS RATE
ON SO₂ REMOVAL IN THE SIX-GRID THREE-STAGE TCA

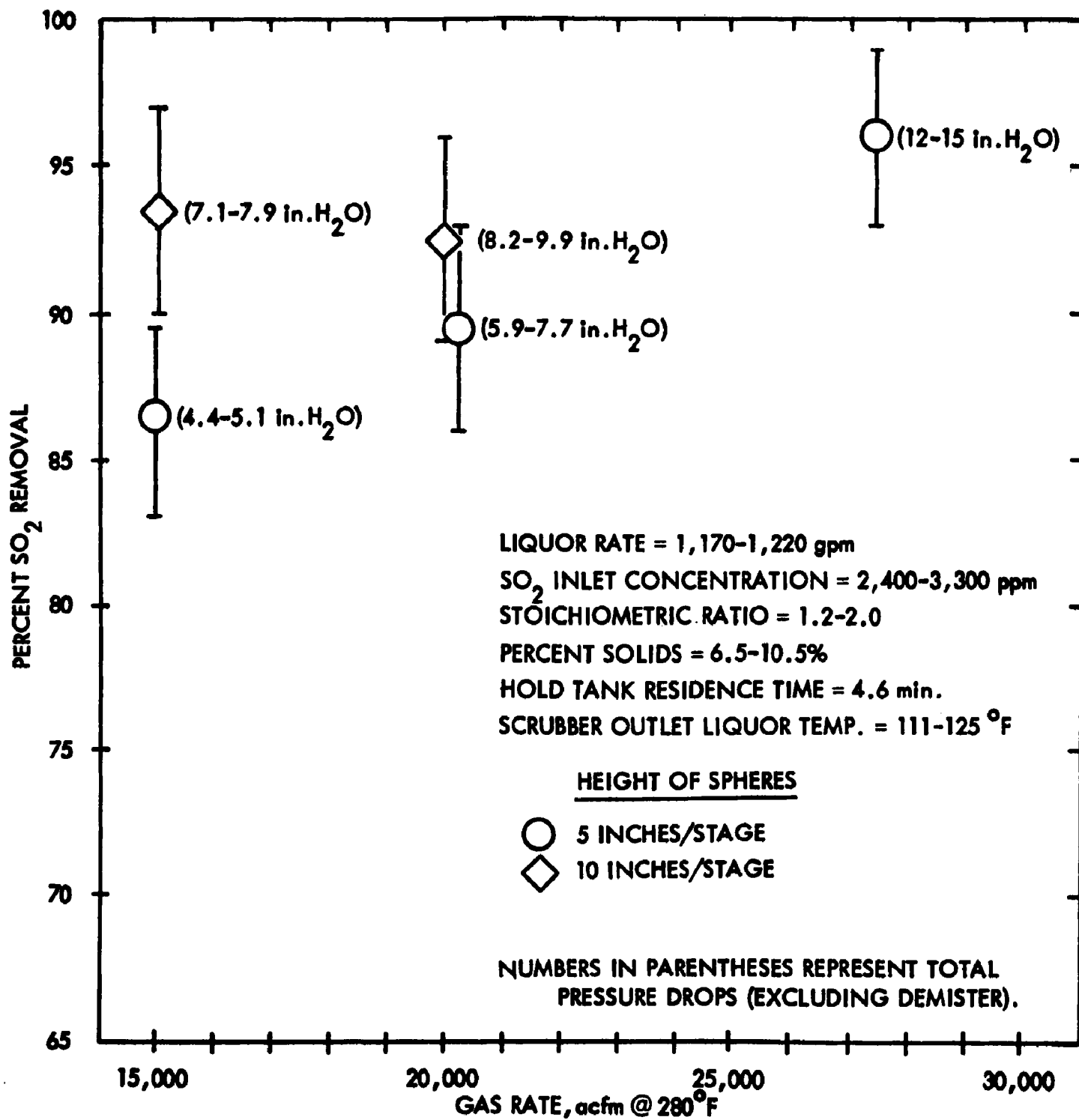


FIGURE 13
EFFECT OF SPHERES VS NO SPHERES AND
GAS RATE ON SO₂ REMOVAL IN THE SIX-GRID TCA

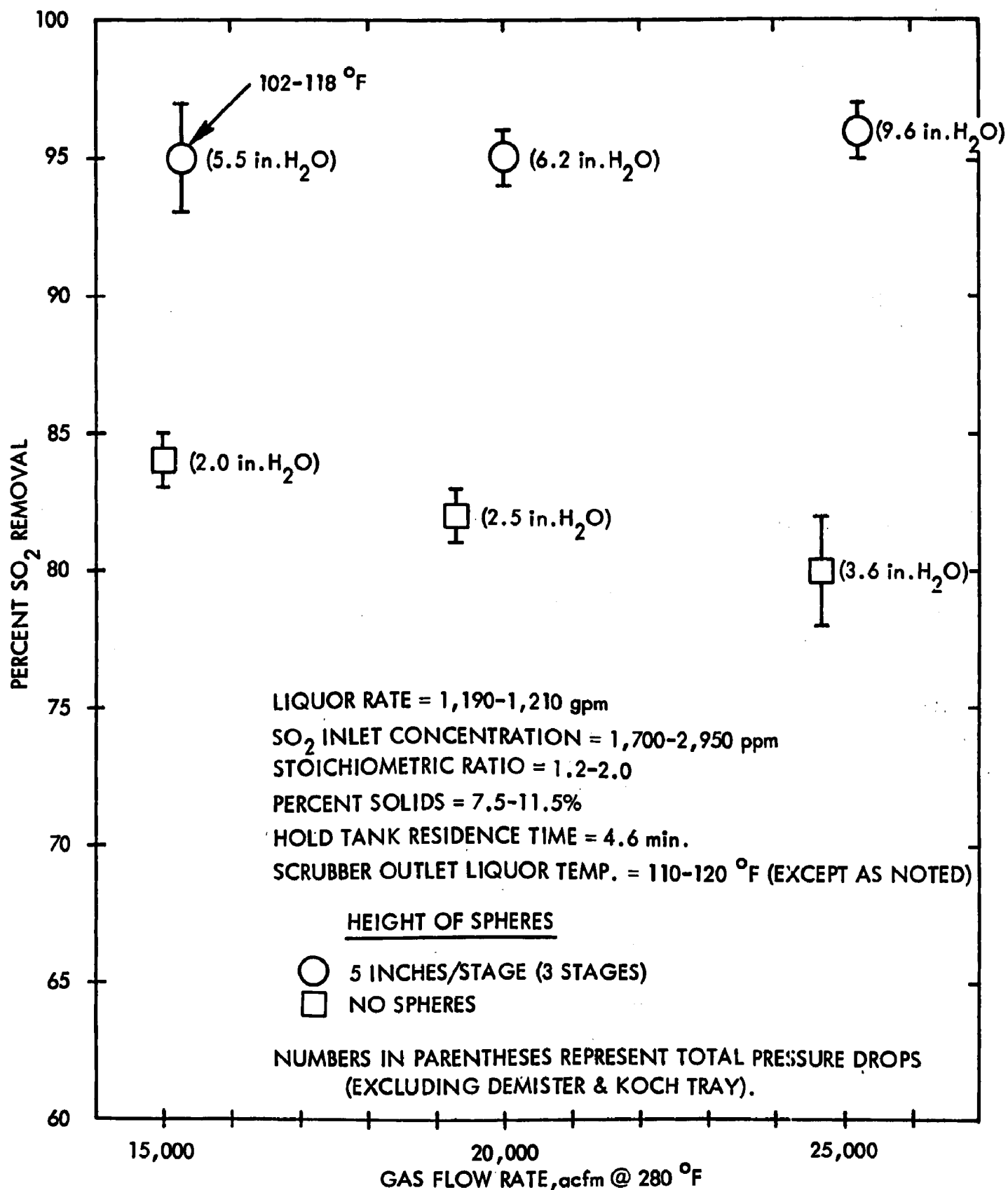


FIGURE 14
EFFECT OF LIQUOR AND GAS RATE
ON SO₂ REMOVAL IN THE FOUR-GRID THREE-STAGE TCA

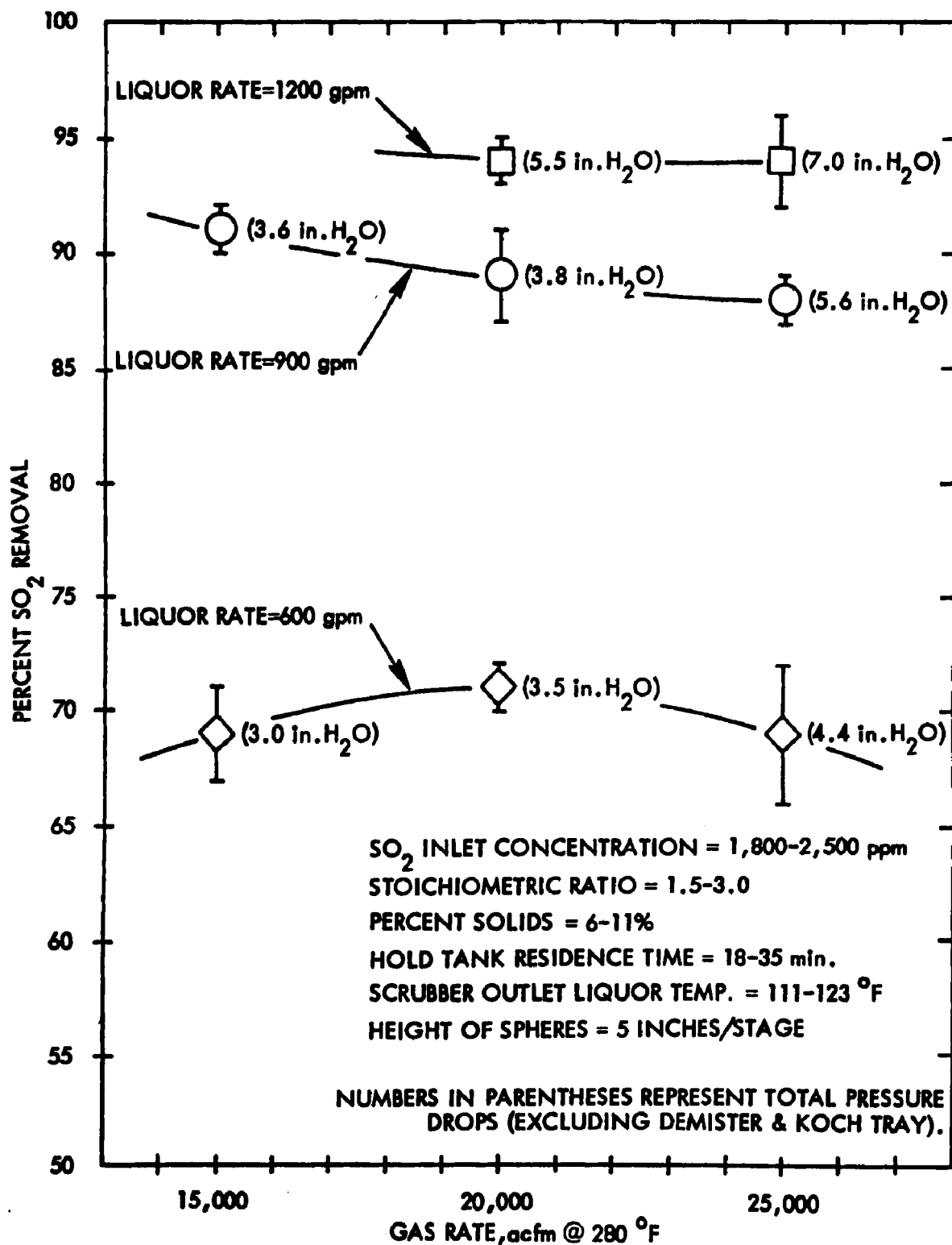


FIGURE 15
EFFECT OF LIQUID-TO-GAS RATIO AND GAS VELOCITY
ON SO_2 REMOVAL IN THE FOUR-GRID THREE-STAGE TCA

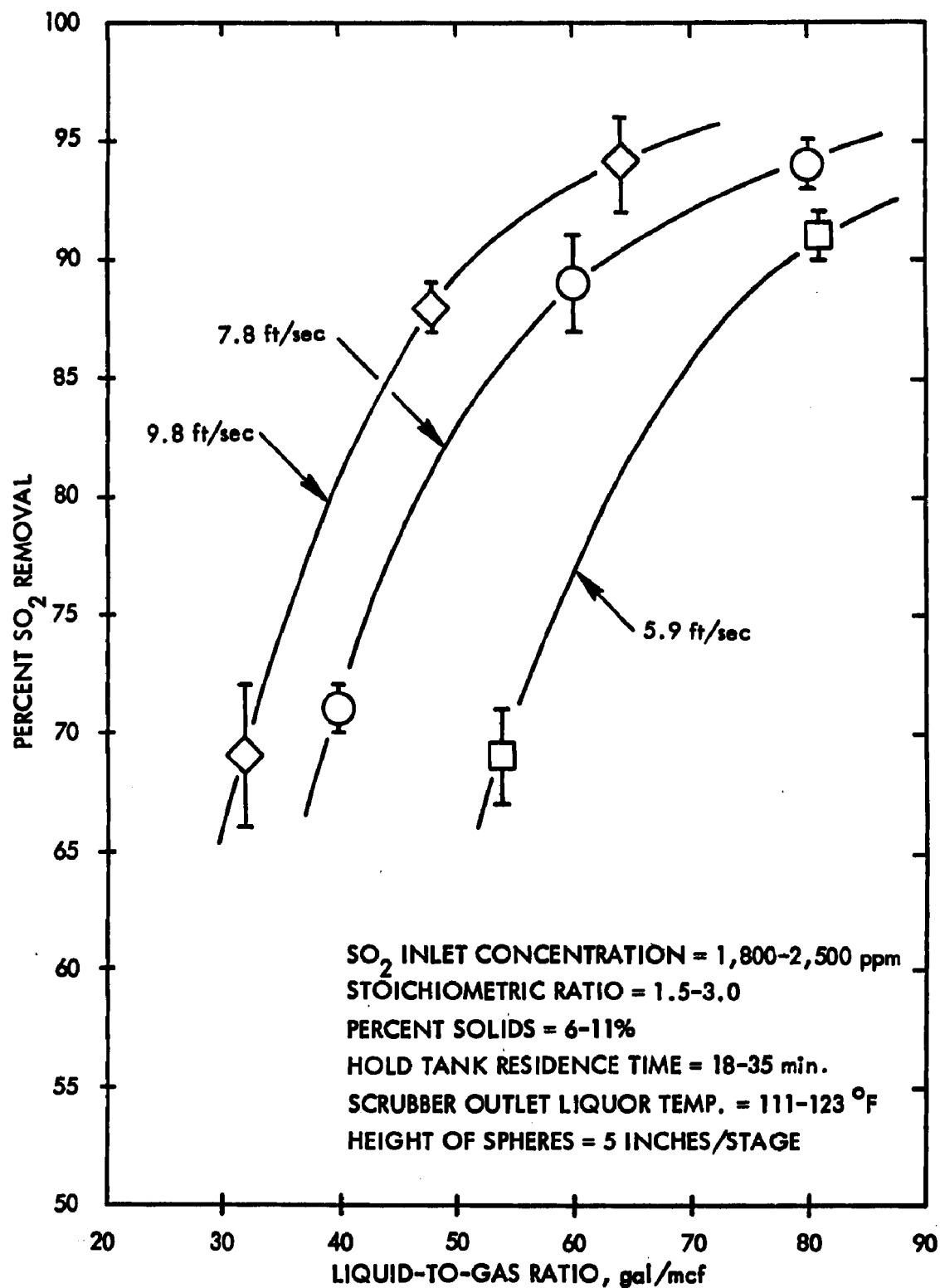


Table 7

**EFFECT OF INLET SO₂ CONCENTRATION ON SO₂
REMOVAL IN A SIX-GRID THREE-STAGE TCA**

Run No.	409-2A & 414-2A	416-2A	410-2A & 411-2A	415-2A
SO ₂ Removal, %	90 \pm 3	95 \pm 1	87 \pm 3	95 \pm 2*
Inlet SO ₂ Conc., ppm	2800-3250	1750-2200	2500-3150	2250-2750
Gas Rate, acfm @ 280°F	20,100	20,000	15,100	15,250
Liquor Rate, gpm	1,190	1,195	1,180	1,200
Stoichiometric Ratio	1.4-1.6	>1.5	1.2-2.0	>1.5
Scrubber Outlet Liquor Temperature, °F	112-122	111-118	111-120	102-118*
Percent Solids Recirc.	7-11	8-9	7-8.5	7-11
Hold Tank Res. Time, min.	4.6	4.6	4.6	4.6
Ht. of Spheres/Stage, in.	5	5	5	5
Pressure Drop, in. H ₂ O	5.9-7.7	5.8-6.6	4.4-5.1	5.0-6.0

*High removal may also be due to lower outlet liquor temperature.

difference of 5% in SO_2 removal between runs 409-2A and 416-2A, for average SO_2 concentration differences of 3000 and 2000 ppm, respectively, is in agreement with EPA's pilot results. The 8% difference in the SO_2 removal between runs 410-2A and 415-2A is attributable both to the differences in inlet SO_2 concentrations and the differences in the scrubber outlet liquor temperatures.

5.1.3 Hydro-Filter System

Figure 16 summarizes the effect of gas and liquor flow rates on SO_2 removal in the Hydro-Filter with five inches of marble bed height. Figure 17 is a cross-plot of Figure 16, showing the effect of liquid-to-gas ratio and gas velocity.

The extended dash-lines showing the ranges of SO_2 removal in Figures 16 and 17 indicate where the ranges of SO_2 removal would have been if corrections had not been made (for the deterioration of the DuPont analyzer optical filters) for these runs. As mentioned previously, there is some doubt about the accuracy of these corrections at low SO_2 removals.

5.2 ANALYTICAL RESULTS

A comparison between measured and predicted liquid and solids analytical data for the venturi and TCA systems during open-loop testing is presented in Section 6.2. Analytical data for the closed-loop testing is presented in Section 7.1.

FIGURE 16
EFFECT OF GAS AND LIQUOR FLOW RATES ON
SO₂ REMOVAL IN THE HYDRO-FILTER WITH FIVE INCHES OF MARBLES

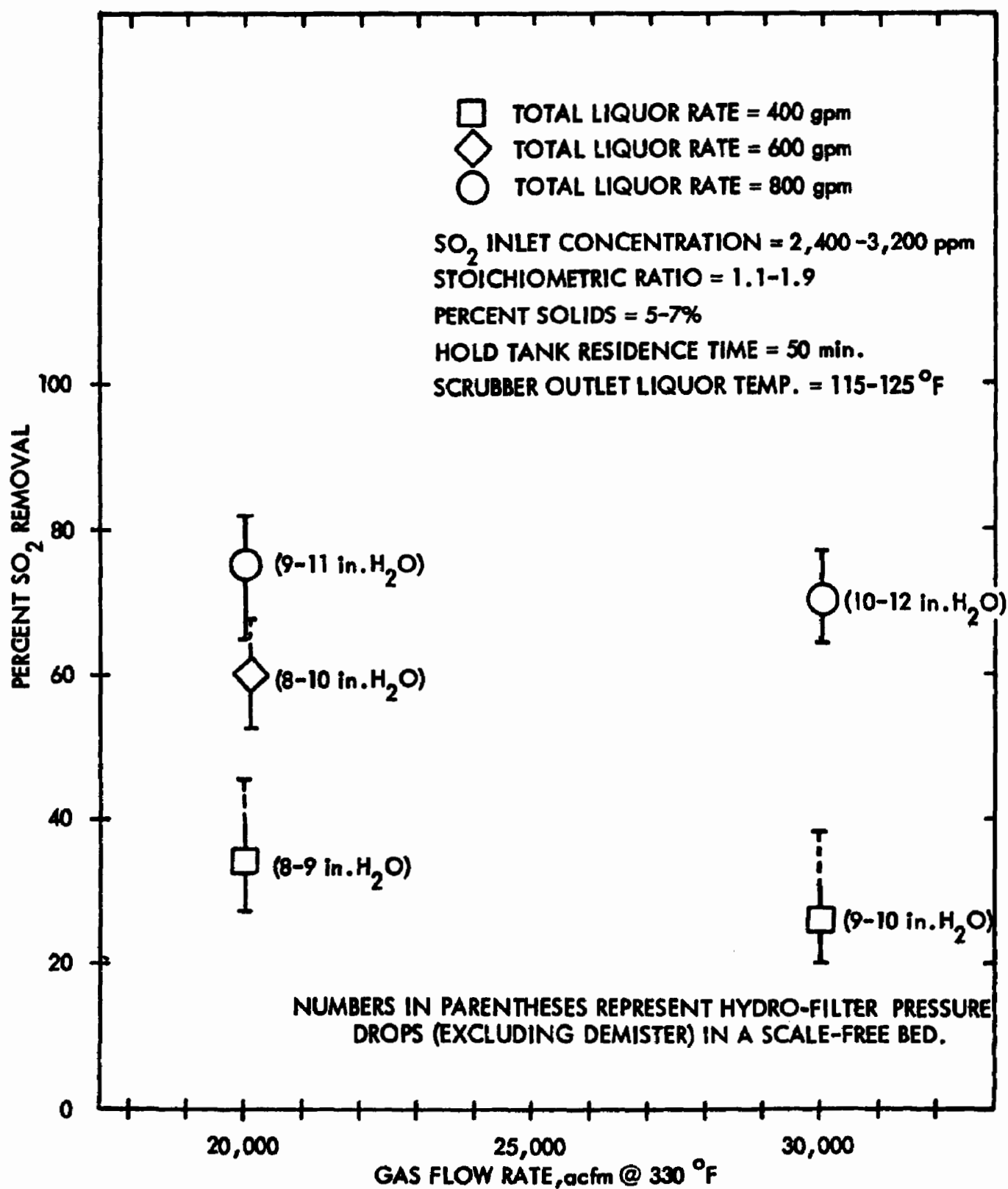
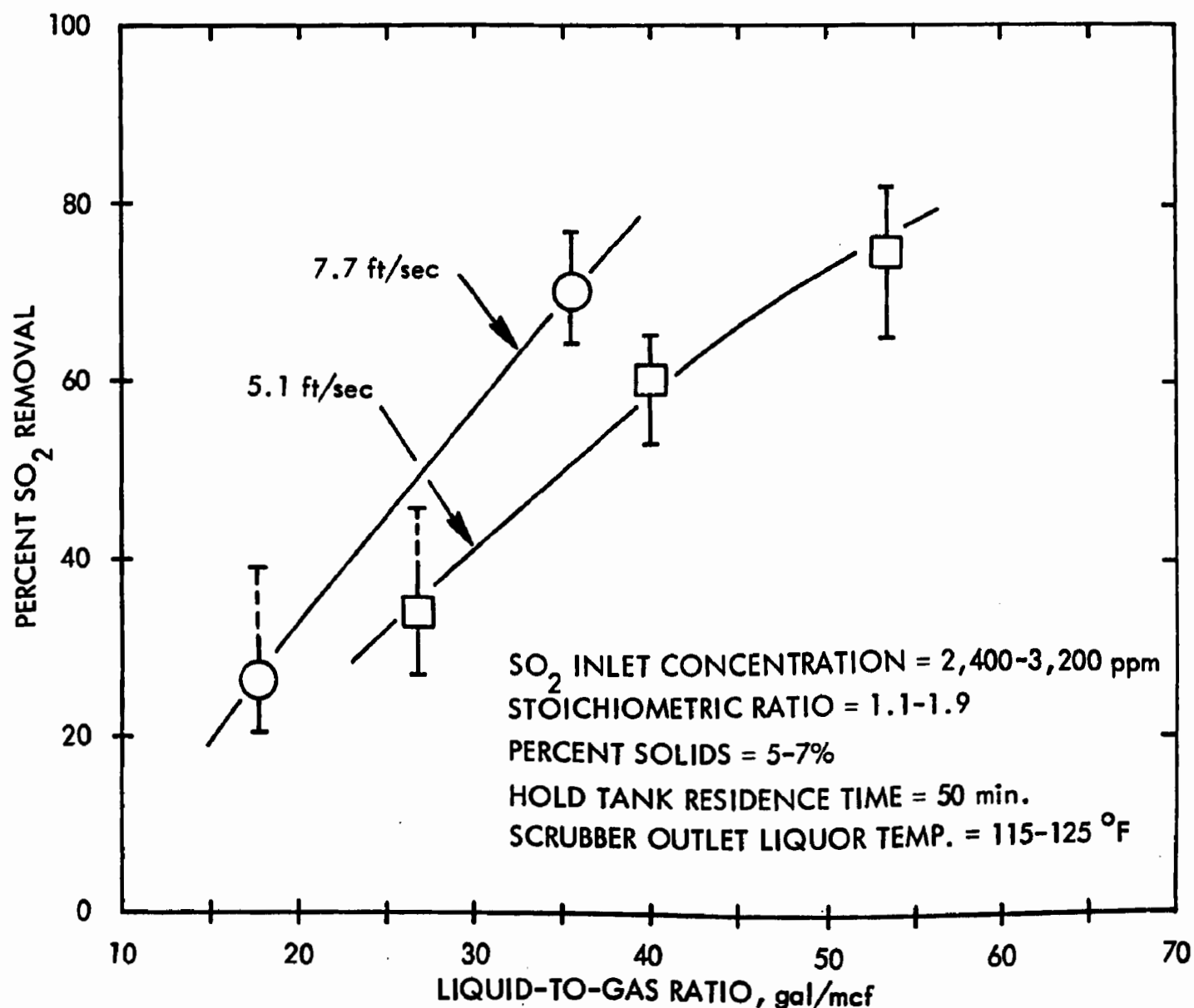


FIGURE 17
EFFECT OF LIQUID-TO-GAS RATIO AND GAS VELOCITY ON
SO₂ REMOVAL IN THE HYDRO-FILTER WITH FIVE INCHES OF MARBLES



5.2.1 Liquid Data

Table 8 shows the average scrubber inlet liquor compositions^{*} for the open-loop factorial runs. During the period of open-loop testing, there did not appear to be a continual build-up of magnesium, sodium or chloride ions within the liquor. The large concentrations of chloride ions are attributable to chlorides present in the coal which were converted to HCl and absorbed from the flue gas in the scrubber. A. Saleem of Ontario Hydro (Ref. 11) has reported similar chloride concentrations during limestone wet scrubbing tests with flue gas from a coal-fired boiler.

Table 8 shows that the venturi and Hydro-Filter systems had lower overall dissolved solids than the TCA system. This was expected, since the quantity of input raw water for these systems was greater than for the TCA system (the TCA system was more "closed-loop"). Actually, the concentration of sulfate within the TCA liquor is close to the predicted "saturation" level for sulfates.

* The liquid analytical data are tested for consistency by inputting the measured compositions and pH's into a modified Radian Equilibrium Computer Program (Ref. 10), which then predicts the ionic imbalance. For the data shown in Table 8, the ionic imbalances were all less than 10%.

Table 8

AVERAGE LIQUOR COMPOSITIONS AT THE SHAWNEE TEST
FACILITY DURING OCTOBER, 1972

Scrubber System	Species Concentration, mg/l (ppm)							
	SO ₃ ⁼	CO ₃ ⁼	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	Cl ⁻	Total
Venturi	200	140	600	1000	60	50	1400	3500
TCA	300	60	1700	1300	100	50	1300	4800
Hydro- Filter	250	100	1200	800	40	30	800	3200

5.2.2 Solids Data

Analyses of the Fredonia Valley limestone used at the Shawnee facility showed an average composition of 90% CaCO_3 , 5% MgCO_3 and 5% inerts. Dry sieve analyses showed approximately 90% of the ground limestone passing through 325 mesh. A MikroPul* particle size analysis showed approximately 7% of the ground limestone less than 3 microns, 30% less than 6 microns and 85% less than 20 microns.

The coal burned in boiler No. 10 during these limestone tests is Old Ben 24 and contains approximately 18% ash, 10% total moisture, 3.2% sulfur and 0.3% chloride. The analyses of ash from boiler No. 10 showed about 50% SiO_2 , 18% Al_2O_3 , 16% Fe_2O_3 , 7% CaO , 1.3% MgO , 1.3% SO_3 , 2.3% K_2O , 1% Na_2O and 3.2% ignition loss.

The composition of solids in the slurry is determined by the moles CaCO_3 added per mole SO_2 absorbed, the overall percent oxidation of sulfite to sulfate within the system and the percent of fly ash. The mole percent oxidations averaged approximately 30% during the open-loop factorial testing and the fly ash comprised from 30 to 50 wt. % of the solids for the three scrubber systems.

5.3 PARTICULATE REMOVAL RESULTS

Particulate removal results for the three scrubbers are presented in Tables 9, 10, and 11. Only those data which were taken at close-to-isokinetic sampling conditions have been included in the tables. All

* A division of United States Filter Corporation

Table 9

PARTICULATE REMOVAL IN VENTURI AND SPRAY TOWER SCRUBBER
DURING OPEN-LOOP TESTS

Run No.	Date	Gas Rate, acfm @ 330°F	Liquor Rate, gpm		Pressure Drop, in. H ₂ O		Grain Loading, g/scf		Percent Removal
			Venturi	Spray Tower	Venturi	Spray Tower	Inlet	Outlet	
415-1A	11-09-72	30,000	305	0	9.0	1.1	4.38	0.012	99.7
414-1D	11-12-72	30,000	305	0	9.0	1.0	2.1	0.010	99.5
414-1D	11-14-72	29,900	305	0	9.0	1.0	3.32	0.013	99.6
414-1C	11-15-72	29,900	305	0	6.4	1.0	3.40	0.02	99.4
417-1A	12-22-72	30,000	605	0	9.5	1.0	3.38	0.012	99.6
414-1E	12-25-72	30,000	300	0	12.0	1.0	4.17	0.009	99.8
418-1C	12-27-72	14,900	600	0	12.5	0.2	6.39	0.114	98.2
453-1B*	12-31-72	14,900	12	460	2.5	0.25	2.6	0.004**	99.8
454-1B*	1-04-73	14,900	12	450	0.75	0.25	4.62	0.07	98.5
456-1A*	1-05-73	14,900	12	450	0.70	0.25	3.38	0.056	98.3

* Spray tower only.

**Data point questionable.

Table 10

PARTICULATE REMOVAL IN TCA SCRUBBER WITH NO SPHERES
DURING OPEN-LOOP TESTS

Run No.	Date	Gas Rate, acfm @ 330°F	Liquor Rate, gpm	Pressure Drop, in. H ₂ O	Grain Loading, g/scf		Percent Removal
					Inlet	Outlet	
WC-5	12-21-72	19,200	730	1.5	1.70	0.004	99.8
WC-5A	1-06-73	19,300	730	1.5	4.16	0.029	99.3
WC-5A	1-09-73	19,300	730	1.5*	1.32	0.019	98.6
WC-11	1-12-73	19,400	745	1.5*	3.29	0.017	99.5
WC-12	1-14-73	19,300	375	1.0*	3.65	0.022	99.4

* These listed values are the assumed pressure drops across the scrubber. Increases in total pressure drop for these runs were most likely due to pluggage of the inlet gas duct during testing.

Table 11

PARTICULATE REMOVAL IN HYDRO-FILTER SCRUBBER DURING OPEN-LOOP TESTS

Run No.	Date	Gas Rate, acfm @ 330°F	Liquor Rate, gpm	Pressure Drop, in. H ₂ O	Grain Loading, g/scf		Percent Removal
					Inlet	Outlet	
427-3A	11-13-72	20,000	810	12.0	2.6	0.030	98.8
427-3A	11-16-72	20,000	810	12.0	3.32	0.035	98.9
426-3B	11-28-72	20,000	810	10.0	4.43	0.032	99.3
427-3C	12-02-72	20,000	800	12.5	4.24	0.033	99.2
427-3B	12-24-72	20,000	805	11.0	2.19	0.027	98.8
428-3A	12-28-72	20,000	810	11.5	3.78	0.025	99.3
428-3A	12-29-72	20,000	810	11.5	4.12	0.016	99.6
428-3A	12-30-72	20,000	810	11.5	3.63	0.035	99.0
438-3A	1-07-73	19,900	400	7.0	4.20	0.020	99.5
440-3A	1-11-73	12,500	600	6.8	3.82	0.042	98.9
440-3A	1-13-73	12,500	600	6.8	3.59	0.066	98.2

of the outlet particulate data have been corrected for soot-contamination from the gas reheaters. The soot amounted to less than 30% of the total mass of the outlet particulates.

During the open-loop factorial testing there were solids accumulations (depositions) in the demisters for much of the test period.* These solids accumulations may explain some of the very low measured outlet grain loadings in Tables 9, 10, and 11, especially for the TCA (multi-grid tower) at 1.5 in. H_2O of pressure drop.

* During open-loop testing, the demisters were all washed from above with raw water (see Figures 1, 2, and 3 in Ref. 2). During the boiler outage, provisions were made for washing the demisters from below, with a mixture of clarified liquor and raw water, and for the installation of a Koch tray in the TCA scrubber (see Figure 2).

Section 6

MODELING OF OPEN-LOOP LIMESTONE DATA

Results of the open-loop factorial limestone test program are presented in Section 6.1 as equations relating sulfur removal to measured parameters for the three scrubber systems. These "linear" equations, which were produced by a statistical analysis of the data, are the simplest available that can adequately depict the data within the range of variables measured.

In Section 6.2, a theoretical approach is employed, for the spray tower, TCA and Hydro-Filter, to again relate SO_2 removal to the measured parameters. A general closed-form equation is developed, which is not incompatible with boundary constraints, and which should permit reasonable extrapolations. Those variables which were found to be significant in Section 6.1 were introduced into the general closed-form equations.

In Section 6.3, complex mathematical models are discussed for computing SO_2 removal and slurry compositions for the scrubber systems. These models are, generally, systems of partial differential equations, which are solved with numerical computer methods.

Other models for predicting pressure drops, particulate removal and gas and liquid-side mass transfer coefficients, will be presented in the first interim report (Table 1).

6.1 STATISTICAL MODELS FOR SO₂ REMOVAL

Presented in this section are the results of a statistical analysis of the data from the open-loop limestone factorial runs. The objective of the linear equations presented in this section is to identify the important independent variables affecting SO₂ removal.

Variables may not appear in the linear equations for a number of reasons. Some of these are:

- The variable did not significantly affect SO₂ removal over the range tested, i.e. the variable was not statistically significant in improving the fit of the equations over the range tested.
- The effect of the variable was masked by a simultaneous variation of more significant variables.
- The variable was substantially constant for the data set being analyzed.
- The variable was "non-controlled" (e.g., inlet gas SO₂ concentration, liquor temperature) and may not have varied in a manner conducive to determination of its effect on SO₂ removal.

6.1.1 Venturi Scrubber

A stepwise regression analysis of the 10 venturi runs (with no slurry in after-scrubber) made in December, 1972, resulted in the following equation:

$$\% \text{ Removal} = 9.4 + 0.04 L + 0.9 \Delta p \quad (1)^*$$

The range of variables covered by these runs, and therefore the region of application, is:

Gas Flow Rate: 15,000–30,000 acfm
 Liquor Flow Rate (L): 300–600 gpm
 Pressure Drop (Δp): 6–12 in. H₂O
 Inlet SO₂ Concentration: 2,400–2,800 ppm
 Stoichiometric Ratio: 1.0–3.0** moles CaCO₃/mole SO₂ inlet
 Percent Solids Recirculated: 6–7%
 Hold Tank Residence Time: 33–70 min.
 Scrubber Outlet Liquor Temperature: 112–117°F

Equation 1 accounts for 89% of the total variation of the data. Gas rate, stoichiometric ratio, hold tank residence time, percent solids, inlet SO₂ concentration and liquor temperature were not statistically significant (over the above ranges) in improving the fit of the equation.

6.1.2 Spray Tower

The following equation was fit to data from the 15 open-loop test runs made with the four-header spray tower with no liquid to the venturi (see Figures 9 and 10):

* The effect of pressure drop on SO₂ removal was only observed below 9 in. H₂O. Changes in pressure drop above this value (e.g., 9–12 in. H₂O) had little effect on SO₂ removal.

** High stoichiometries (>1.75 moles CaCO₃/mole SO₂ inlet), after mid-November 1972, were the result of calibration problems with the limestone additive flowmeters (see Section 5.1).

$$\% \text{ Removal} = 16 + 0.9 \text{ L/G} \quad (2)$$

The range of variables covered by these runs, and therefore the region of application, is:

Gas Flow Rate: 10,000–30,000 acfm
 Gas Velocity: 2.5–7.5 ft/sec
 Liquid-to-gas Ratio (L/G): 13–61 gal/mcf
 Inlet SO₂ Concentration: 2,700–3,300 ppm
 Stoichiometric Ratio: 1.0–3.0 moles CaCO₃/moles SO₂ inlet
 Percent Solids Recirculated: 2–8%
 Hold Tank Residence Time: 40–106 min.
 Scrubber Outlet Liquor Temperature: 98–128°F

Equation 2 accounts for 95% of the total variation of the data. Inlet SO₂ concentration, stoichiometric ratio, percent solids recirculated, hold tank residence time and liquor temperature were not statistically significant (over the above ranges) in improving the fit of the equation. At constant L/G, a gas velocity of 7.5 ft/sec gave slightly more removal (~3%) than 5 ft/sec. This velocity effect was not observed below about 5 ft/sec. Percent solids were actually between 6–8% for most runs, with only one run at 2%.

6.1.3 TCA Scrubber

The following equation was fit to the 31 EPA TCA runs (see Figures 12 through 15):

$$\% \text{ Removal} = 47 + 0.034 \text{ L} + 1.4 \text{ PSR} + 0.5 \text{ Hp} - 0.006 \text{ ppm} \quad (3)$$

The equation accounts for 85% of the total variation of the data. The range of variables covered by these runs, and therefore the region of application, is:

Gas Flow Rate: 15,000–27,500 acfm
Gas Velocity (V): 6–11 ft/sec
Liquor Flow Rate (L): 600–1,200 gpm
Percent Solids Recirculated (PSR): 6–14%
Inlet SO₂ Concentration (ppm): 1,800–3,200 ppm
Stoichiometric Ratio: 1.0–3.0 moles CaCO₃/mole SO₂ inlet
Hold Tank Residence Time: 3.8–35 min.
Scrubber Outlet Liquor Temperature: 105–122°F
Number of Grids: 4, 6
Total Height of Packing (Hp): 0–30 in.

Percent removal decreases with increasing inlet SO₂ concentration (~6% per 1000 ppm). Gas velocity, stoichiometric ratio, hold tank residence time, scrubber outlet liquor temperature, and the number of grids were not statistically significant (over the above ranges) in improving the fit of the equation. Although not an independent variable, the pressure drop in the scrubber was also examined and was found to not have a significant effect on removal. For example, runs giving 92% removal have been made at pressure drops of 4, 6 and 9 in. H₂O.

The 17 EPA six-grid TCA runs were analyzed as a group. The following equation was fit to these runs (see Figures 12 and 13):

$$\% \text{ Removal} = 67 + 0.02 L + 1.0 V + 0.44 H_p - 0.006 \text{ ppm} \quad (4)$$

The equation accounts for 78% of the total variation of the data. The analysis is restricted to the previously mentioned range of variables,

with the exception of percent solids recirculated, which only varied from 7–10%. Note the gas velocity term for this group, which was not statistically significant for the entire set of runs (see Eq. 3). Again, stoichiometric ratio, hold tank residence time, and scrubber outlet liquor temperature did not significantly affect SO_2 removal over the above ranges.

The 14 EPA four-grid three-stage TCA runs were also analyzed as a group. The following equation was fit to these runs (see Figures 14 and 15):

$$\% \text{ Removal} = 53 + 0.04 L + 1.4 \text{ PSR} - 0.007 \text{ ppm} \quad (5)$$

The equation accounts for 96% of the total variation of the data. These test runs were made with 5 inches of spheres per stage, for a total of 15 inches. The range of variables is otherwise the same as that for the 31 test run group. Gas velocity, stoichiometric ratio, hold tank residence time, and scrubber outlet liquor temperature did not significantly affect SO_2 removal over the above ranges.

The following equation was fit to the 16 runs made without spheres in the five-grid TCA tower (TVA tests):

$$\% \text{ Removal} = 90 + 0.034 L - 0.46 T_L \quad (6)$$

The range of variables covered by these runs, and therefore the region of application, is:

Gas Flow Rate: 19,000–30,000 acfm
 Gas Velocity: 7.5–12 ft/sec
 Liquor Flow Rate (L): 375–1,070 gpm
 Inlet SO₂ Concentration: 2,200–3,200 ppm
 Stoichiometric Ratio: 1.0–3.0 moles CaCO₃/moles SO₂ inlet
 Percent Solids Recirculated: 14%
 Hold Tank Residence Time: 5–15 min.
 Scrubber Inlet Liquor Temperature (T_L): 63–110°F
 Scrubber Outlet Liquor Temperature: 89–115°F
 Pressure Drop: 1–7 in. H₂O

Equation 6 accounts for 65% of the total variation of the data. Stoichiometric ratio, inlet SO₂ concentration and hold tank residence time were not statistically significant (over the above ranges) in improving the fit of the equation.

6.1.4 Hydro-Filter Scrubber

A stepwise regression analysis of 27 Hydro-Filter runs* resulted in the following equation (see Figures 16 and 17):

$$\% \text{ Removal} = 17.9 + 0.1 L - 2.0 V \quad (7)$$

The range of variables covered by these runs, and therefore the region of application, is:

* Eleven runs made during October, 1972, were excluded from the analysis due to doubtful low values of SO₂ removal obtained during this period. Recent closed-loop data has validated this exclusion.

Gas Flow Rate: 12,000-30,000 acfm
 Gas Velocity (V): 3-8 ft./sec.
 Liquor Flow Rate (L): 200-800 gpm
 Inlet SO₂ Concentration: 2,000-3,500 ppm
 Stoichiometric Ratio: 1.5-3.0 moles CaCO₃/mole SO₂ inlet
 Percent Solids Recirculated: 6-12%
 Hold Tank Residence Time: 50 min.
 Scrubber Outlet Liquor Temperature: 85-125°F
 Height of Marbles: 3-5 in.

Equation 7 accounts for 94% of the total variation of the data. Inlet SO₂ concentration, stoichiometric ratio, percent solids, liquor temperature, and height of marbles were not statistically significant (over the above ranges) in improving the fit of the equation.

6.2 CLOSED-FORM CORRELATIONS FOR PREDICTING SO₂ REMOVAL

Analysis of the closed-loop limestone data, using the Radian Equilibrium Computer Program (Ref. 10), has shown that the equilibrium mole fraction of SO₂ over the bulk liquid, y^* , is negligible with respect to the SO₂ mole fraction within the gas, for the spray tower, TCA and Hydro-Filter Scrubbers*. For this condition, the following relationship represents SO₂ absorption:

$$\text{Fraction SO}_2 \text{ Removed} = 1 - \exp \left[\frac{-k_{ga} Z / G}{1 + m \frac{k_{ga}}{k_{la}}} \right] \quad (8)$$

* Due to low liquor residence times, the amount of limestone dissolved within the venturi scrubber is relatively small. Hence, y^* can be significant. Also, y^* can be significant for the spray tower, TCA and Hydro-Filter scrubbers operating at low stoichiometries (<1.5 moles CaCO₃/mole SO₂ absorbed) and, consequently, low inlet liquor pH's (<6.0).

where

- k_G = gas-side mass transfer coefficient
 a = gas-liquid interfacial area per scrubber volume
 Z = axial distance
 G = gas rate per cross-sectional area
 m = Henry's law constant
 k_L = liquid-side mass transfer coefficient

Also, scrubber computer models utilizing previously fitted gas-side mass transfer coefficients (see Ref. 2) have shown that liquid-side resistance controls (i. e., $k_L/m \ll k_G$) for the spray tower, TCA and Hydro-Filter scrubbers, for a majority of the limestone data. For this condition, Eq. 8 can be written as:

$$\text{Fraction } SO_2 \text{ Removed} = 1 - \exp \left[-k_L a Z / m G \right] \quad (9)$$

The liquid-side mass transfer coefficient can be expressed as (see Ref. 12, Eqs. 25 through 28):

$$k_L a = k_L^o a (1 + X_B / \nu X_A) \exp [0.013 (T - 77)] \quad (10)$$

where

- k_L^o = liquid-side mass transfer coefficient in absence of chemical reaction.
 X_B = function of concentration of dissolved reagent B (Ca) in bulk liquor.
 X_A = concentration of dissolved reactant A (SO_2) at gas-liquid interface.
 ν = stoichiometric coefficient relating the number of moles of B reacting with one mole of A.

T = liquor temperature, $^{\circ}\text{F}$.

The liquid-side coefficient is expected, therefore, to be a function of gas and liquor flow rates, scrubber configuration, amount of dissolved reactant, interfacial concentration of dissolved SO_2 (H_2SO_3)^{*} and temperature.

The form of Eq. 9 has been fitted (by multiple regression) to the open-loop limestone data for the spray tower, TCA and Hydro-Filter scrubbers. The significance of the independent variables in the fitted equations was demonstrated by the statistical analysis (see previous section).

The open-loop limestone data was all obtained at relatively high stoichiometries (greater than 1.5 moles CaCO_3 /moles SO_2 absorbed) and consequently, high scrubber inlet liquor pH's (from 6.0 to 6.3). Within this regime of operation, stoichiometric ratio showed no apparent effect upon SO_2 removal (see previous section). The effect of stoichiometric ratio for the scrubber systems will, hopefully, be obtained during the closed-loop testing now in progress. Other variables which showed negligible effects upon SO_2 removal during the open-loop testing, such as percent solids recirculated, may also have more significant effects at reduced stoichiometries during closed-loop testing.

* As the concentration of SO_2 in the gas increases, X_A increases and k_L decreases. This is an explanation for the empirical fact that as the SO_2 inlet gas concentration increases, for limestone wet-scrubbing systems, the SO_2 removal decreases.

The effect of inlet gas SO₂ concentration (a non-controlled independent variable) upon SO₂ removal has only been included in the fitted equation for the four-grid three-stage TCA, although it is presumed that a similar effect exists for the other scrubbers. Also, the effect of inlet scrubber liquor temperature (a non-controlled independent variable), which was determined to be significant from the TVA TCA runs (see Eq. 6), has not presently been included in the closed-form equations. The effects of inlet gas concentration and temperature will be included in the final forms of all the correlations, once the analyses of other pilot data and the Shawnee closed-loop data has been completed.

6.2.1 Spray Tower

The following equation was fit to 15 open-loop limestone test runs made with the 4-header spray-tower (see Figures 9 and 10 and Eq. 2):

$$\text{Fraction } \text{SO}_2 \text{ Removed} = 1 - \exp \left[-0.032 (L/G)^{0.85} \right] \quad (11)$$

where:

L/G = liquid to gas ratio in scrubber, gal/mcf

Equation 11 accounts for 94% of the variation in the data (correlation coefficient of 0.97) with a standard error of estimate of 3.7% SO₂ removal.

6.2.2 TCA

The following equation was fit to 11 open-loop limestone test runs made with the four-grid, three-stage TCA scrubber (see Figures 14 and 15 and Eq. 5):*

$$\text{Fraction } \text{SO}_2 \text{ Removed} = 1 - \exp \left[-0.0017 L^{1.28} (1/y_{\text{SO}_2})^{0.46} \right] \quad (12)$$

where

L = liquor flow rate per cross-sectional area, gpm/ft²

y_{SO_2} = SO₂ concentration in inlet gas, mole fraction

Equation 12 accounts for 99% of the variation in the data with a standard error of estimate of 1.3% SO₂ removal. As previously mentioned, it is assumed that the measured effect of y_{SO_2} for the TCA scrubber will be similar for the other systems.

6.2.3 Hydro-Filter

The following equation was fit to 27 open-loop limestone test runs made with the Hydro-Filter scrubber (see Figures 16 and 17 and Eq.

7):**

$$\text{Fraction } \text{SO}_2 \text{ Removed} = 1 - \exp \left[-0.0098 L (L/G)^{0.55} \right] \quad (13)$$

* Two runs at relatively high weight percent solids and one "limestone depletion" run were eliminated from this analysis.

** Eleven runs made during October, 1972, were excluded from the analysis due to anomalously low values of SO₂ removal obtained during this period. Recent closed-loop data has affirmed this exclusion.

Equation 13 accounts for 95% of the variation in the data with a standard error of estimate of 4.1% SO_2 removal.

6.3 COMPUTER MODELS FOR PREDICTING SO_2 REMOVAL AND SLURRY COMPOSITIONS

6.3.1 Scrubber Models

In Ref. 12, mathematical models were presented for predicting SO_2 removal in the venturi, TCA and Hydro-Filter scrubbers. The models are, generally, sets of partial differential equations which describe SO_2 absorption into the process liquor (in accordance with the two-film theory), reaction between the absorbed SO_2 (H_2SO_3) and the species in the liquor and the dissolution of solids (e.g., CaCO_3) within the process liquor. The assumption has been made, for these systems, that the liquor is at all times in equilibrium with an interfacial vapor pressure of 0.1 atm of CO_2 , i.e., the rate of absorption of CO_2 from the flue gas is large. The thermodynamic equilibria for the models are obtained from the Radian Computer Program (Ref. 10).

Computer models have been written for the three scrubber systems, which numerically solve the systems of differential equations. It has been planned to fit the gas and liquid-side mass transfer coefficients to the high and low-concentration soda-ash data (see Section 4.1.2) and then fit the solids dissolution rate constants to the limestone data. The fitting of the gas-side coefficients for all three scrubbers has been presented in Ref. 2. To date, only the liquid-side coefficient

for the venturi scrubber has been fit to the low concentration soda-ash data. The results of this fit will be presented in the first interim report (Table 1), along with the correlations for the gas-side coefficients.

As discussed in the previous section, the equilibrium mole fraction of SO_2 over the bulk liquid is essentially zero^{*} for the spray tower, TCA and Hydro-Filter scrubbers, for the open-loop (high-stoichiometry) data. For this regime, therefore, the models describing SO_2 absorption for the three scrubbers can be greatly simplified (see Eq. 8). For the venturi scrubber, however, the residence time of the liquor is low (<0.1 sec.), the dissolution of limestone within the scrubber is small and, consequently, the equilibrium mole fraction of SO_2 over the bulk liquid not zero everywhere, for the ranges of variables tested. Results from the venturi computer model, using the previously fitted gas and liquid-side mass transfer coefficients, have shown that an assumption of zero dissolution of solids will give a reasonable fit to the open-loop limestone data. These results will be presented in detail in the first interim report (Table 1).

6.3.2 Simulation Model

The simulation model is a computer model which determines the slurry compositions of the waste streams and the scrubber inlet and outlet streams for the three scrubber systems. The major assumption in the model is equilibrium between the liquid and solids in the slurry

* This implies that the kinetic rate of dissolution of limestone within the scrubbers is high.

leaving the effluent hold tank, at a specified equilibrium partial pressure of CO_2 .^{*} The equilibrium relationships between the liquid and solid species are obtained from the Radian Equilibrium Program.

The simulation model takes as input all of the independent variables (e.g., stoichiometric ratio), the percent sulfite oxidation, the percent ash in the solids and the concentration of chloride and magnesium in the process liquor.^{**} If a scrubber model (either simplified closed-form or computer model) is used, the simulation model will (iteratively) predict SO_2 removal, as well as the slurry compositions. If no scrubber model is used, then SO_2 removal must be input into the simulation program, along with the independent variables.

Two results from the simulation model will be presented here. The first simulation, for venturi runs 419-1A and 421-1A, is shown pictorially in Figure 18 and incorporates the venturi scrubber computer model (which assumes zero dissolution of solids). The predicted SO_2 removal of 45% is close to the average measured values of $42 \pm 5\%$ (see Figure 8 and Eq. 1). The second simulation, for TCA run 412-2A, is shown pictorially in Figure 19, and does not incorporate a scrubber model (the measured removal of 96% was input to the

^{*} The specified CO_2 partial pressure was chosen to match the measured E.H. T. outlet liquor pH's and compositions. Predictions with the Radian program indicate relatively constant CO_2 equilibrium partial pressures from 0.05 to 0.1 atm.

^{**} Ultimately, models will be developed for predicting sulfite oxidation, ash in the solids and the concentrations of chloride and magnesium in the liquor.

FIGURE 18
BECHTEL LIMESTONE / LIME WET-SCRUBBING SIMULATION PROGRAM

SO₂ REMOVAL = 45 %

Comments:

SIMULATION OF VENTURI SCRUBBER SYSTEM RUNS

419-1A/421-1A ON DECEMBER 23-25, 1972.

REAL SCRUBBER MODEL USED IN SIMULATION.

Scrubber Inlet Liquor Rate = 600 gpm (16,900 lb-mole/hr)
Gas Rate = 15,000 acfm (1,600 lb-mole/hr) @ 320°F
Inlet SO₂ Concentration = 2,900 ppm
Stoichiometric Ratio = 1.5
L/G = 54 gal/mcf
Percent Solids Recirculated = 6 %
Percent Solids Discharged = 14 %
Percent Flyash in Solids = 40 %
Percent Sulfite Oxidation = 20 %
Concentration of Chlorides = 14 gm-mole/1000 liters
Scrubber Temperature = 117°F

MAJOR ASSUMPTIONS:

- Effluent Hold Tank Slurry in equilibrium with 0.05 atm CO₂.
- CaSO₃ & CaSO₄ concentrations in liquor streams leaving E.H.T. are 1 & 1 times the equilibrium saturation levels, respectively.
- Scrubber Slurry (in contact with flue-gas) in equilibrium with 0.1 atm CO₂, i.e. rate of transfer of CO₂ is large.
- Zero dissolution of solids in scrubber (all dissolution of solids in E.H.T.).

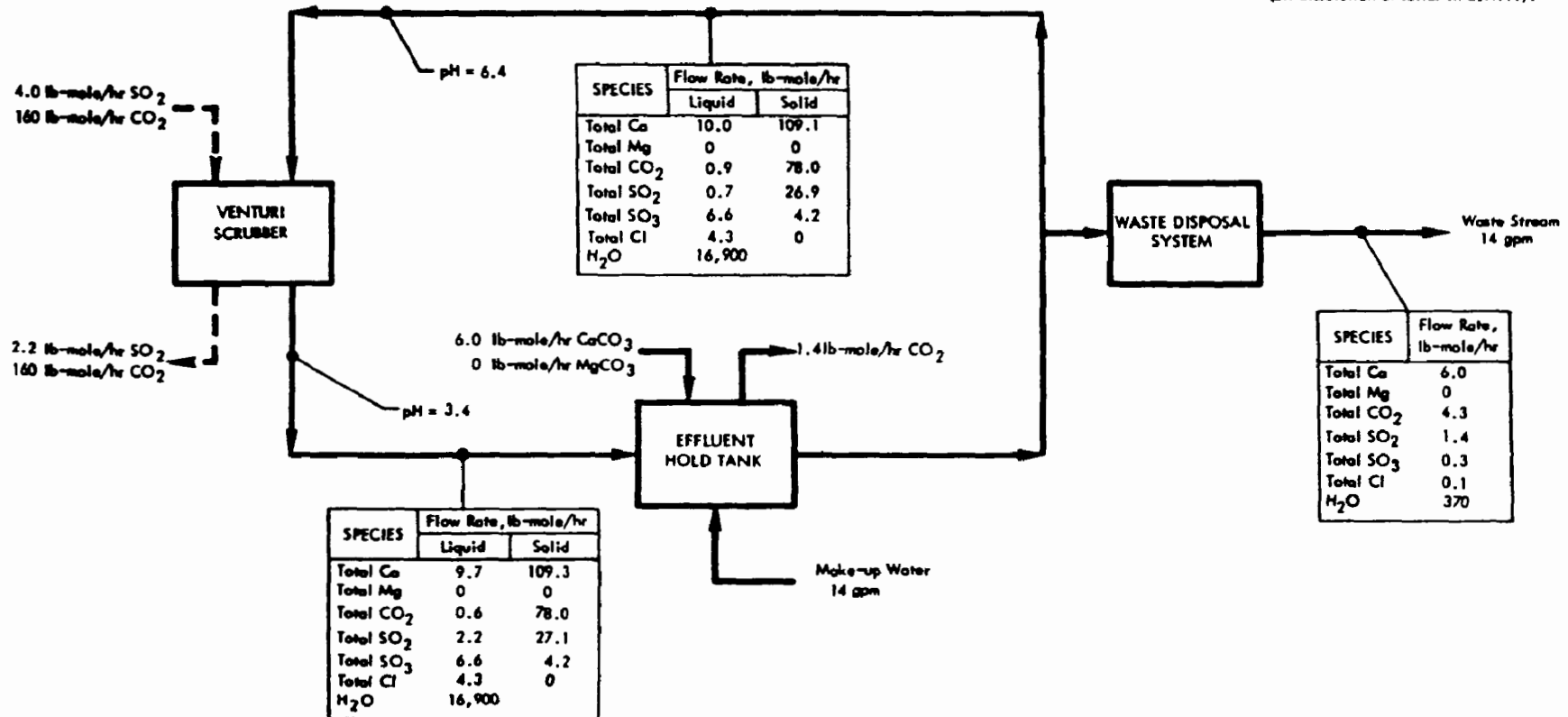


FIGURE 19
BECHTEL LIMESTONE / LIME WET-SCRUBBING SIMULATION PROGRAM

SO₂ REMOVAL = 96 %

Comments:

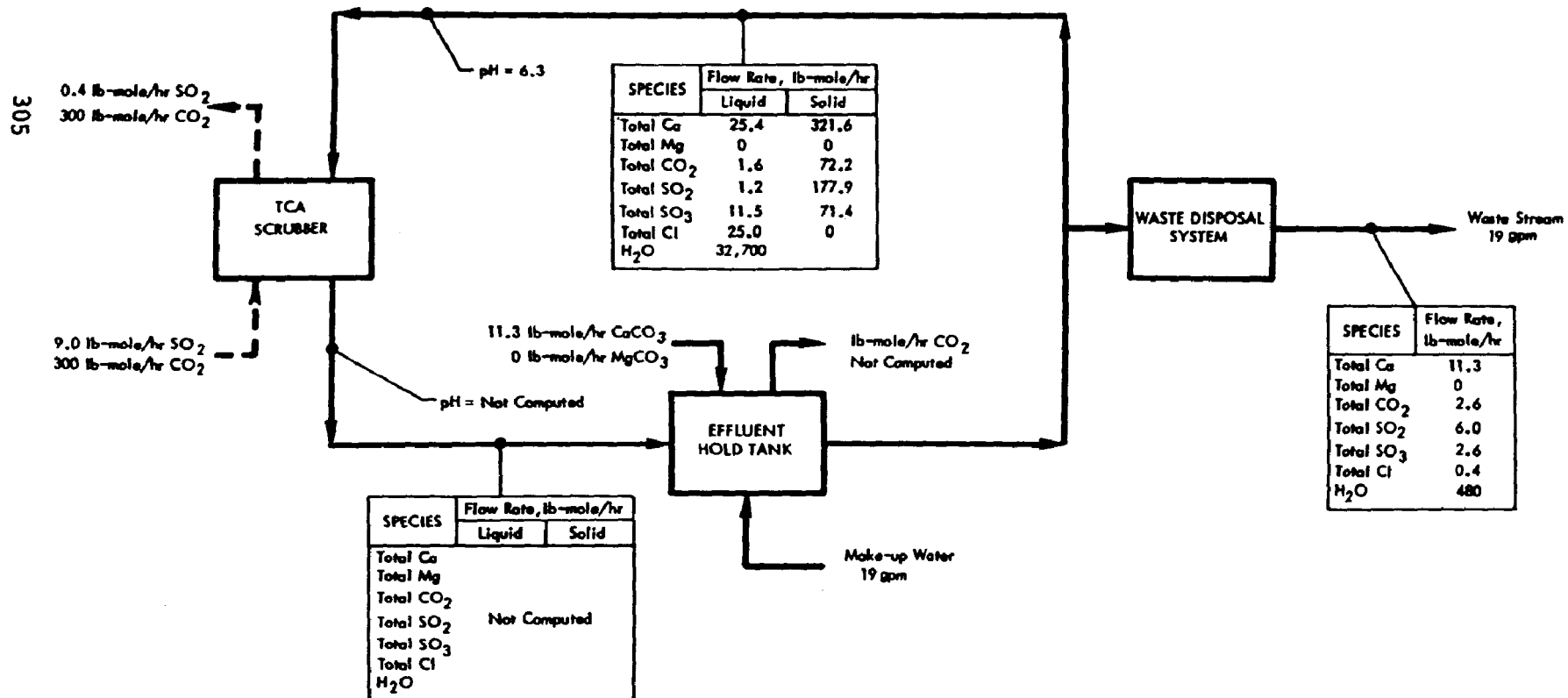
SIMULATION OF TCA SCRUBBER SYSTEM RUN
412-2A ON OCTOBER 29-31, 1972.

REAL SCRUBBER MODEL NOT USED IN SIMULATION
(SO₂ REMOVAL INPUT TO PROGRAM.)

Scrubber Inlet Liquor Rate = 1,180 gpm (32,700 lb-mole/hr)
Gas Rate = 27,500 acfm (3,000 lb-mole/hr) @ 290 °F
Inlet SO₂ Concentration = 3,000 ppm
Stoichiometric Ratio = 1.25
L/G = 55 gal/mcf
Percent Solids Recirculated = 8.5 %
Percent Solids Discharged = 18 %
Percent Flyash in Solids = 30 %
Percent Sulfite Oxidation = 30 %
Concentration of Chlorides = 42.5 gm-mole/1000 liters
Scrubber Temperature = 120 °F

MAJOR ASSUMPTIONS:

- Effluent Hold Tank Slurry in equilibrium with 0.05 atm CO₂.
- CaSO₃ & CaSO₄ concentrations in liquor streams leaving E.H.T. are 1 & 1 times the equilibrium saturation levels, respectively.
- Scrubber Slurry (in contact with flue-gas) in equilibrium with 0.1 atm CO₂, i.e. rate of transfer of CO₂ is large.



program). The agreement between the predicted and measured scrubber inlet slurry compositions for this TCA simulation is shown in Table 12.

Table 12

COMPARISON OF MEASURED AND PREDICTED SLURRY
COMPOSITIONS AT SCRUBBER INLET FOR TCA RUN 412-2A

Gas Rate = 27,500 acfm

Liquor Rate = 1,170 gpm

L/G = 57 gal/mcf

Pressure Drop = 14 in. H₂O

Three stages, 5 inches/stage

Species	Species Concentrations, gm mole/1000 liters			
	Liquid		Solid	
	Measured	Predicted	Measured	Predicted
pH	5.9	6.3	—	—
SO ₃ ⁼	1.8	2.1	210	300
CO ₃ ⁼	1.2	2.7	220	120
SO ₄ ⁼	24	19	86	120
Ca ⁺⁺	35	43	510	550
Mg ⁺⁺	5.5	0*	21	0
Cl ⁻	43	43*	—	—

* Input to computer model.

Section 7

RELIABILITY VERIFICATION TEST RESULTS

As mentioned previously, the objects of the reliability verification tests are to (1) identify areas or regions for reliable operation consistent with reasonable SO_2 removal, (2) choose attractive operating configurations from within these regions, (3) obtain more reliable material balances, and (4) quantify any variations in SO_2 and particulate removal and system slurry compositions with time.

As discussed in Section 4.2.2, the initial tests are to be run at reduced scrubber inlet liquor pH's (5.7–5.9), to increase system reliability and limestone utilization. A modest reduction in SO_2 removal (from high pH performance) is the price of the increased reliability and limestone utilization.

Presently, initial runs are in progress on all three scrubbers (see run Nos. 1 on Tables 3, 4 and 5). The Hydro-Filter (Run 501-3A) was started-up on March 14, the TCA (Run 501-2A) on March 22 and the venturi-spray tower (Run 501-1A) on April 9, 1973.

The performance data for these three reliability verification runs will be presented in Section 7.1 and the results of material balances for sulfur and calcium (which were satisfactory) in Section 7.2.

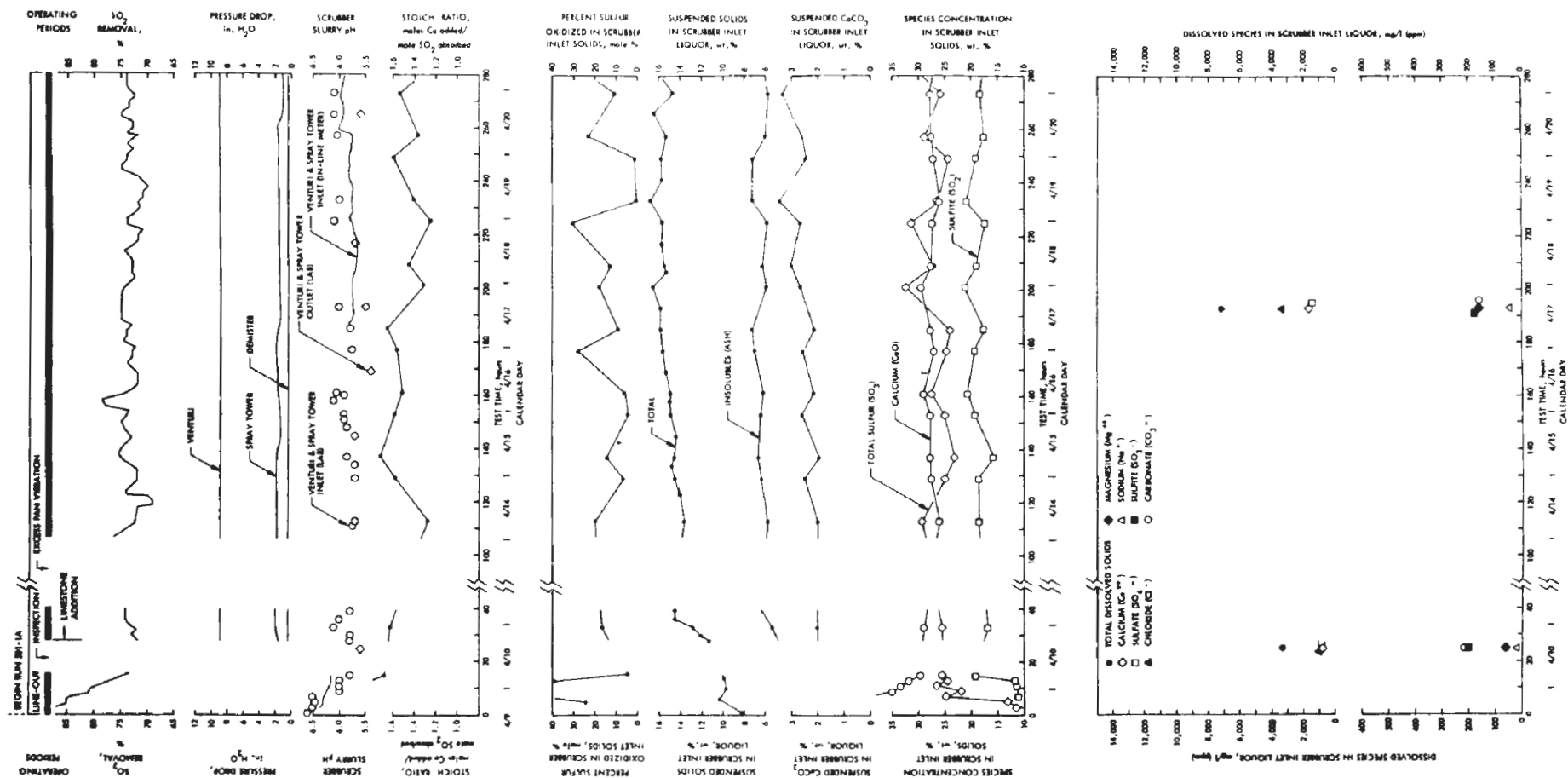
7.1 PERFORMANCE DATA

Data for the first 400 – 500 hours of operation on the initial runs is summarized in Figures 20, 21 and 22. The upper section of each figure shows the operating periods (blank space indicates shut-down), and such critical variables as SO_2 removal, liquor pH and stoichiometric ratio. The middle plot gives some analyses of solids in the scrubber inlet liquor. The lower plot gives concentrations of some dissolved species in the scrubber inlet liquor.

Also shown on Figures 20, 21 and 22, are the depletion (line-out) periods for the tests. Fresh limestone slurries (no CaSO_4 "seeding") were introduced into the effluent hold tanks and SO_2 absorption was used to reduce the slurry pH until the desired level of SO_2 removal was attained. This level was approximately 10% below that attainable in high-pH open-loop operation (see Section 4.2.2).

Before beginning limestone addition, the systems were inspected to be sure that they were free of scaling or erosion that might have occurred in the high-pH period of the line-out. Periodic (approximately weekly) inspection shut-downs are scheduled in order to monitor scaling and erosion in sensitive areas of the systems.

Operability and reliability of the three scrubber systems during the initial runs is discussed in another paper presented at this symposium (Ref. 1).



Gas Rate = 20,000 acfm @ 330 °F
 Liquor Rate to Venturi = 600 gpm
 Liquor Rate to Spray Tower = 600 gpm
 Spray Tower L/G = 40 gal/mcf
 Spray Tower Gas Velocity = 5.0 ft/sec
 E.H.T. Residence Time = 20 min
 No. of Spray Headers = 2

Gas Inlet SO₂ Conc. = 2,600-3,300 ppm
 Scrubber Inlet Liquor Temp. = 120-125 °F
 Liquid Conductivity = 7,000-15,000 μ mhos/cm
 Discharge (Clarifier) Solids Conc. = 23-27 wt %

Figure 20. Operating data for venturi run 501-1A.

Gas Inlet SO₂ Conc. = 2,400-3,200 ppm
Scrubber Inlet Liquor Temp. = 120-125 °F
Liquid Conductivity = 8,800-16,500 μ mhos/cm
Discharge (Clarifier) Solids Conc. = 20-27 wt %

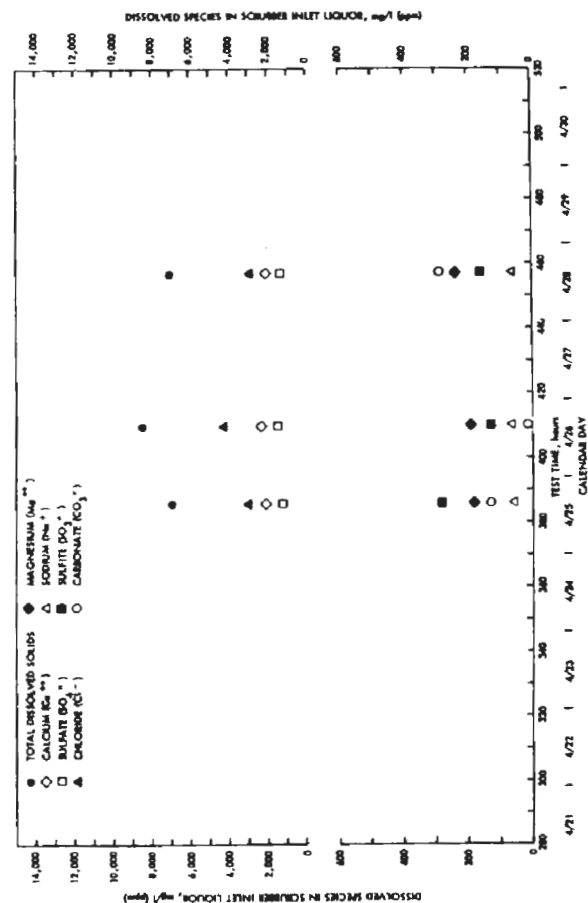


Figure 20 (continued). Operating data for venturi run 501-1A.

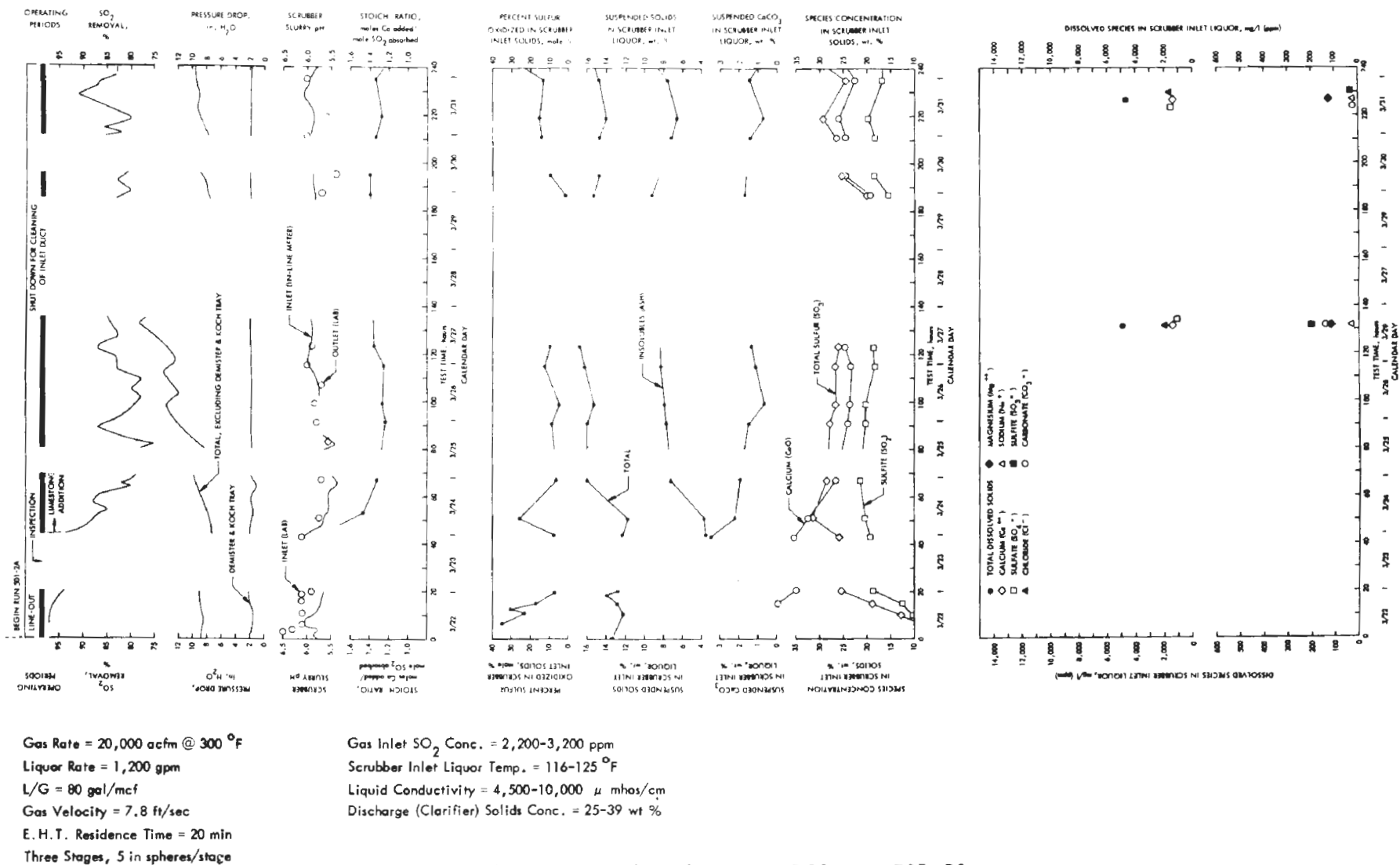


Figure 21. Operating data for TCA run 501-2A.

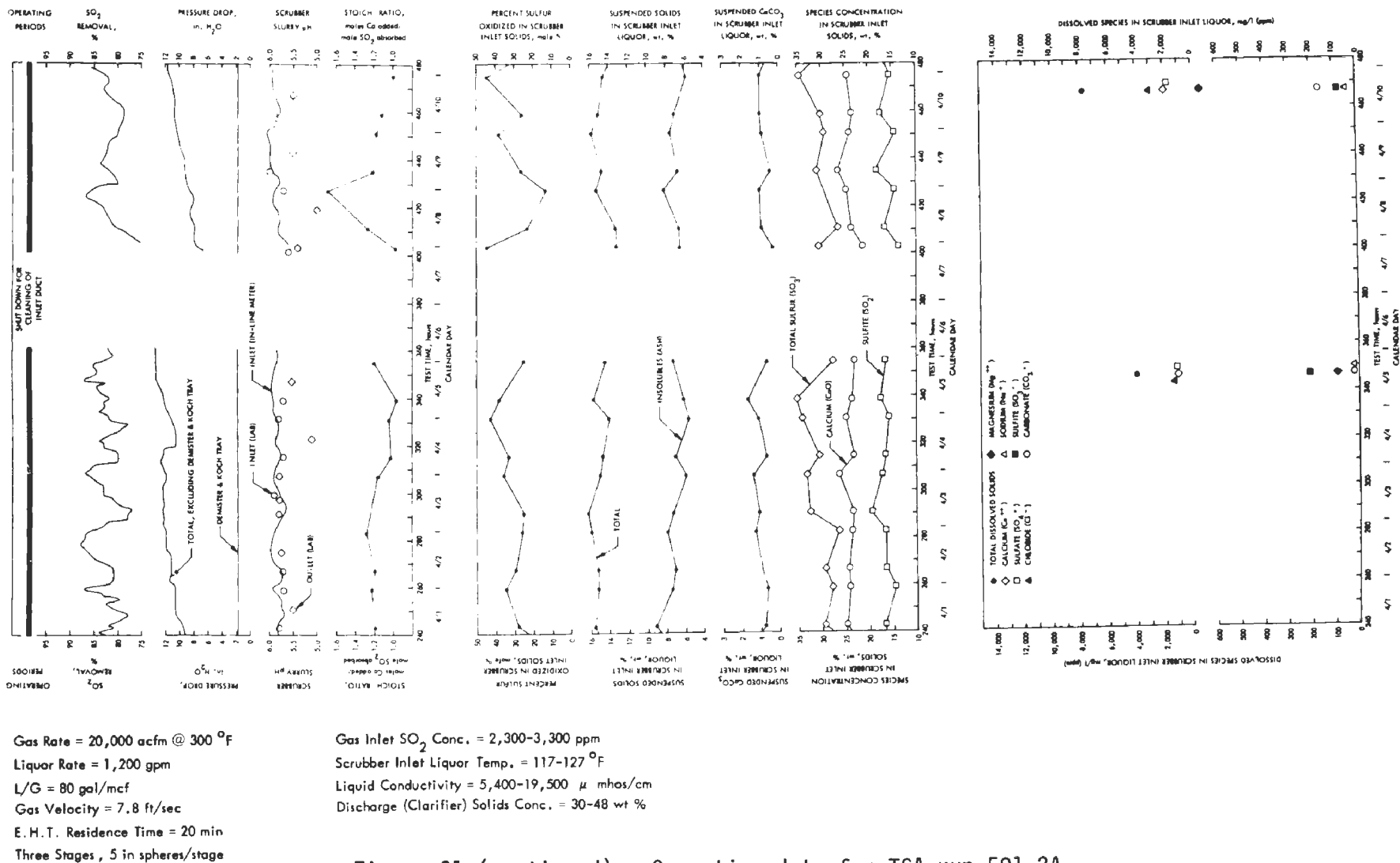


Figure 21 (continued). Operating data for TCA run 501-2A.

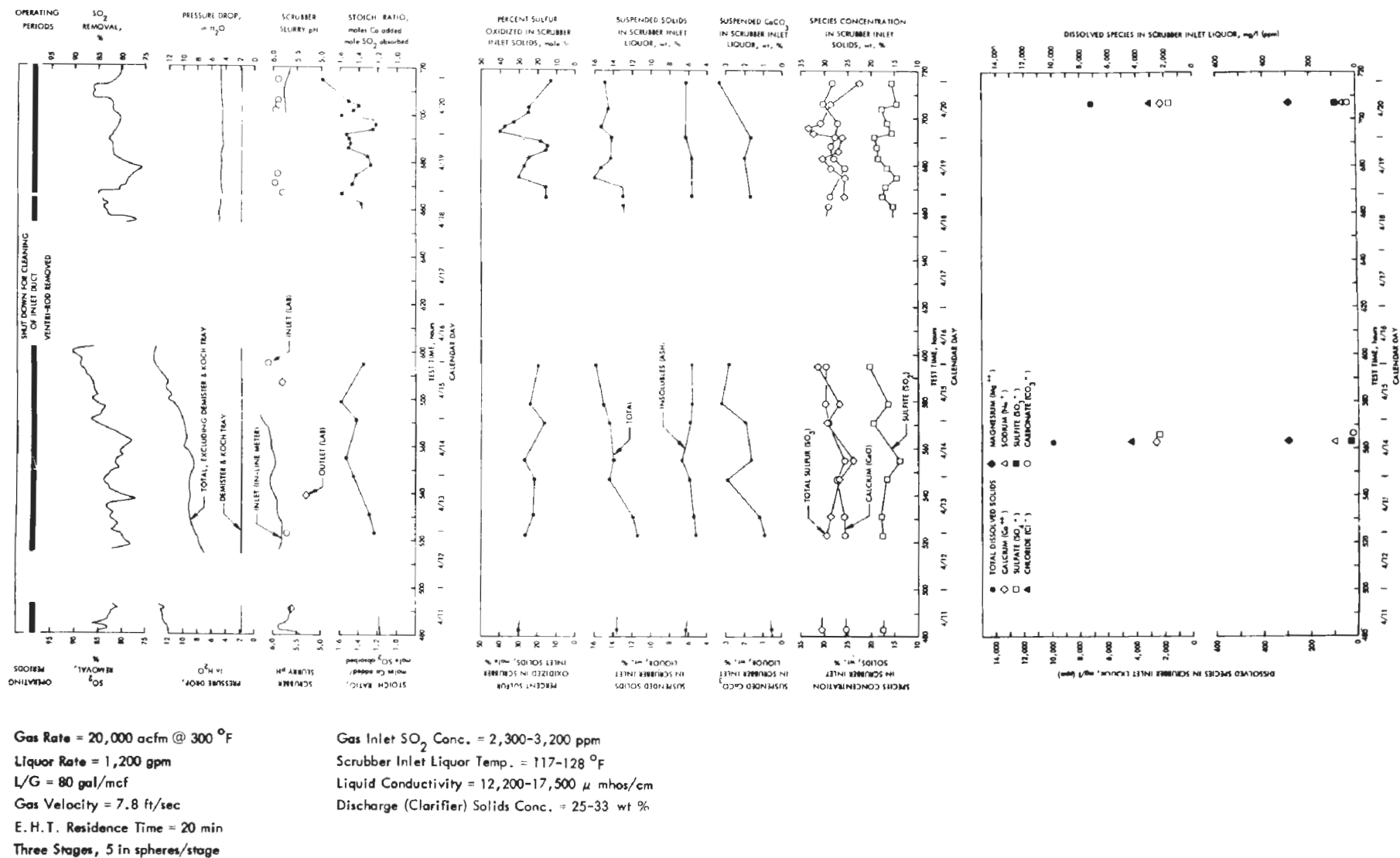


Figure 21 (continued). Operating data for TCA run 501-2A.

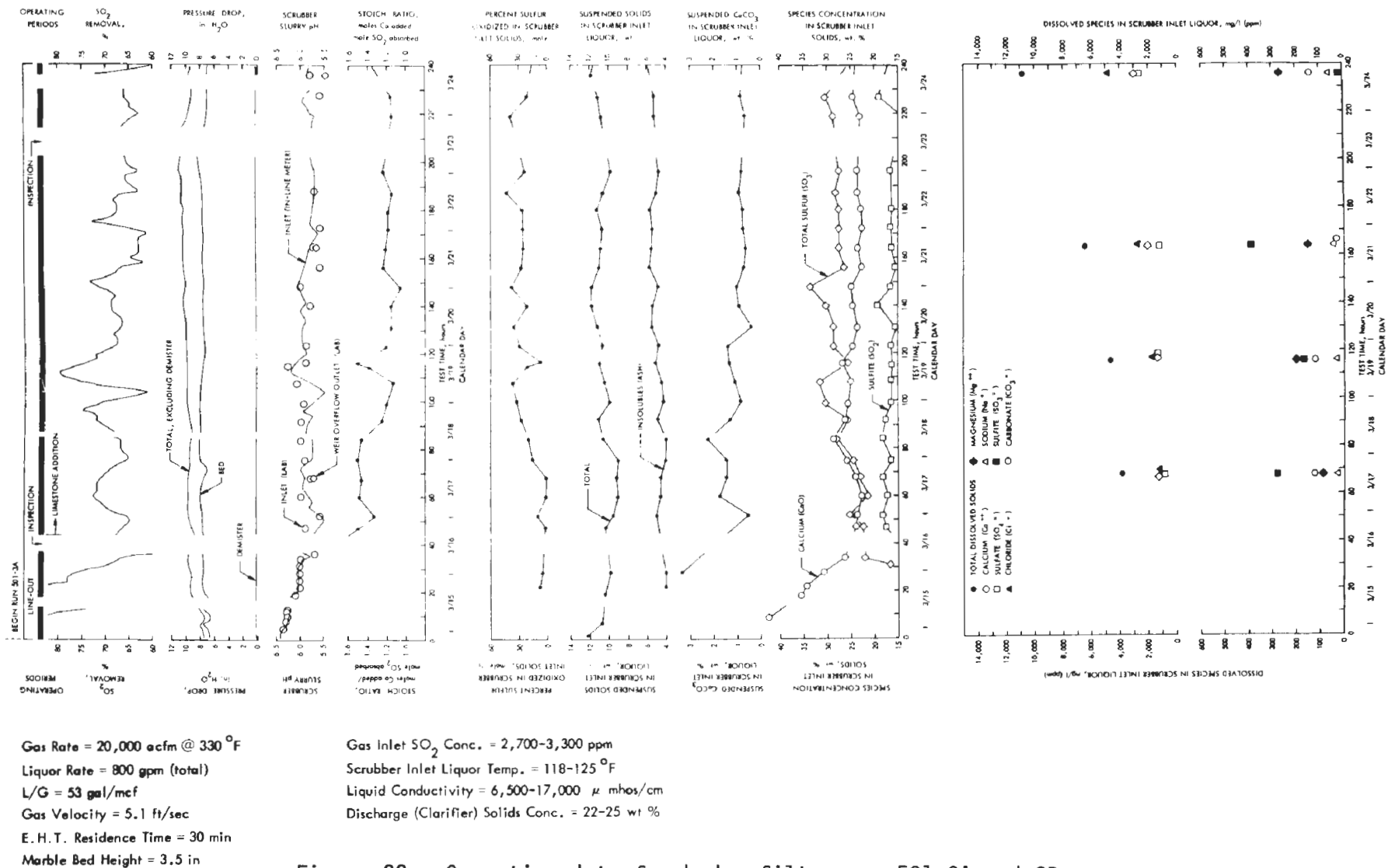


Figure 22. Operating data for hydro-filter run 501-3A and 3B.

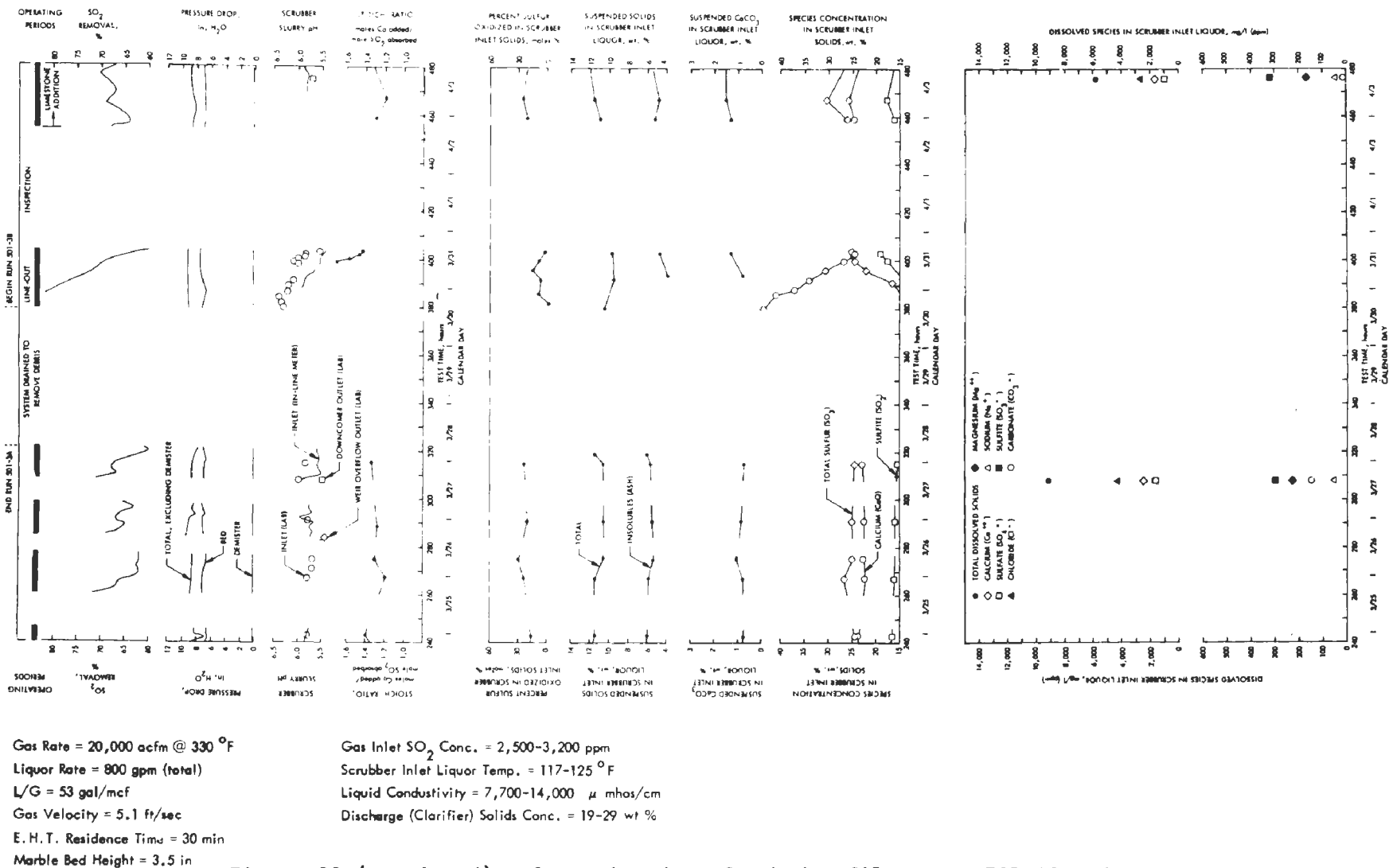
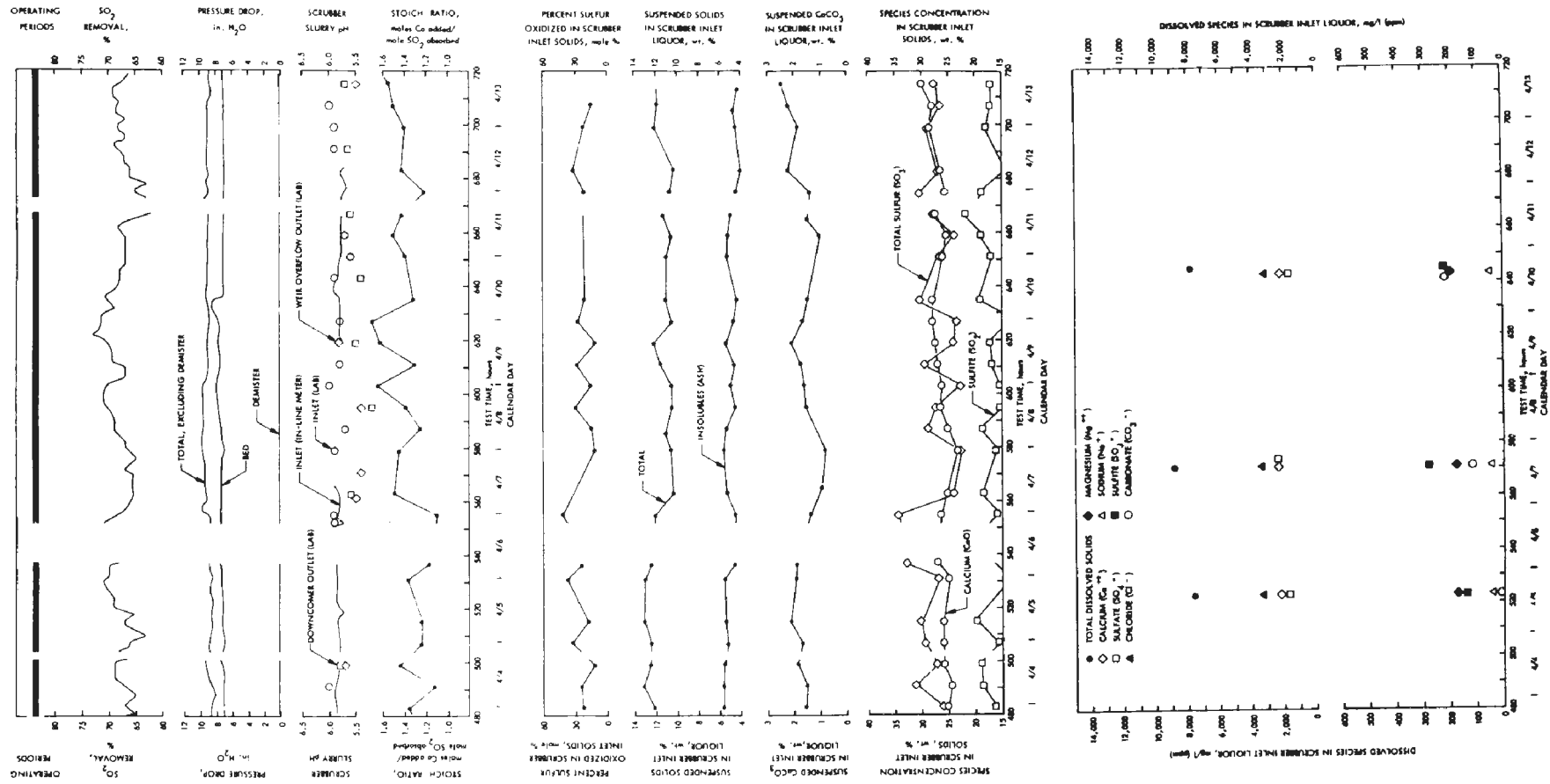


Figure 22 (continued). Operating data for hydro-filter run 501-3A and 3B.



Gas Rate = 20,000 acfm @ 330 °F
 Liquor Rate = 800 gpm (total)
 L/G = 53 gal/mcf
 Gas Velocity = 5.1 ft/sec
 E.H.T. Residence Time = 30 min
 Marble Bed Height = 3.5 in

Gas Inlet SO_2 Conc. = 2,500-3,300 ppm
 Scrubber Inlet Liquor Temp. = 117-126 °F
 Liquid Conductivity = 6,300-13,700 μ mhos/cm
 Discharge (Clarifier) Solids Conc. = 20-29 wt %

Figure 22 (continued). Operating data for hydro-filter run 501-3A and 3B.

An overall summary of the initial run data appears in Table 13, which presents average values for some significant parameters (from Figures 20, 21 and 22). The listed pH values may be in error.*

A summary of the liquid analytical data is presented in Table 14. Most dissolved species appear to have approached steady state concentrations during the period of operation. However, magnesium ion (Mg^{++}) concentration exhibited a steady increase in the venturi and TCA systems (see Figures 20 and 21).

It is of interest to compare the liquid analytical data for the closed-loop and open-loop runs (see Tables 8 and 14). For the TCA system, sulfate concentrations for both periods of operation were close to the "saturation" levels. The chloride concentrations, however, differed significantly. For the venturi and Hydro-Filter systems, the sulfate concentrations during the initial closed-loop runs was well above that measured in the open-loop tests. As expected, in all three systems, the level of total dissolved solids during the closed-loop runs was far greater than that obtained during open-loop testing.

Lack of confidence in the pH meters led to a decision to control SO_2 removal in the initial tests rather than to directly control pH at the desired 5.7 to 5.9 region. Results of open-loop limestone depletion runs were used to estimate SO_2 removals consistent with the desired pH.** In general, these SO_2 removal levels were selected at about

* There have been some problems with pH meters at the facility.

** See Figure 11 and Table 6.

Table 13

AVERAGE CONDITIONS FOR INITIAL
RELIABILITY VERIFICATION RUNS

Parameters	Hydro-Filter Run 501-3A	TCA Run 501-2A	Venturi Run 501-1A
Operating Time, hrs	520	550	410
Gas Velocity, ft/sec	5	7.8	5
L/G, gal/mcf	53	80	40 [*]
Pressure Drop, in. H ₂ O	9	6	10.5 ^{**}
Percent Solids Recirc.	11	15	15
Percent SO ₂ Removal	65-70	80-85	70-75
Stoichiometric Ratio	1.25	1.20	1.5
Limestone Utilization	80%	83%	67%
Inlet Liquor pH	5.8	5.8	5.8-5.9
Percent Oxidation	30	20-30	15
Dissolved Solids, ppm	8000	7500	7000

* L/G's of 40 for spray tower and 40 for venturi.

** 9 inches across venturi and 1.5 inches across spray tower.

Table 14

AVERAGE LIQUOR COMPOSITIONS FOR INITIAL
RELIABILITY VERIFICATION RUNS

Scrubber System	Liquor Species Concentrations, mg/l (ppm)							
	SO ₃ ⁼	CO ₃ ⁼	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	Cl ⁻	Total
Venturi	200	200	1500	2000	250 [*]	50	3000	7200
TCA	150	150	1800	2000	300 [*]	50	3000	7400
Hydro-Filter	300	150	1800	2000	200	50	3500	8000

* This species increased gradually throughout the time period. The values shown on this table are the maximum values, at the end of the plotted periods.

10% below that attainable in open-loop operations at a pH above 6.0 (high pH). Control of SO_2 removal was established by varying the rate of limestone addition.

7.1.1 Venturi Run 501-1A (see Figure 20)

Open-loop testing at high-pH indicated approximate SO_2 removals to be 42% in the venturi and 57% in the spray tower, * which is equivalent to an overall removal, for the combined system, of 75%. Thus, in order to achieve the desired low-pH operation, a target of 65% removal is indicated.

From April 14 to April 21, removal was controlled at about 74%** with an average stoichiometric ration of 1.5 (moles CaCO_3 per mole SO_2 absorbed) and an average oxidation of 15%. This implied higher pH than desired, although the scrubber inlet liquor pH (which is subject to question) was apparently 5.8 – 6.0 during this period.

From April 22 to April 27, SO_2 removal was controlled at about 70%. In this period the stoichiometric ratio rose from 1.3 to 1.8. This increase in stoichiometry, while maintaining the same SO_2 removal,

* This removal was estimated from Eq. 11 and "corrected" for the change in inlet SO_2 concentrations (see Eq. 12 and Section 5.1.2).

** The high-pH removal at the selected venturi run conditions was originally estimated at 85% for the closed-loop operation. The early part of Run 501-1A is thus at a pH and SO_2 removal somewhat higher than desired.

may indicate "degradation" in the system (e.g., drop in limestone reactivity, erosion of spray nozzles). Oxidation and apparent inlet liquor pH remained at 15% and 5.7 – 6.0 respectively.

Toward the end of the operating period depicted on Figure 20, the SO₂ removal dropped below 70% and was restored to a value slightly above 70%. On April 28 (low removal) the stoichiometric ratio was about 1.5 and then rose to above 2.0 by April 30. The apparent scrubber inlet liquor pH remained at 5.9 – 6.0 in this period.

7.1.2 TCA Run 501-2A (see Figure 21)

The estimated high-pH value of SO₂ removal for the TCA system, operating at the test conditions of Run 501-2A, is about 95%* (see Eqs. 5 and 12). Therefore, the controlled SO₂ removal for Run 501-2A was chosen at 85%. After an initial operating period (from March 24 to March 31) in which there were relatively large fluctuations in SO₂ removal, a relatively steady period of about 5 days ensued (from April 1 to April 6), where the SO₂ removal varied from 80 to 85% and the scrubber inlet liquor pH from about 5.7 to 5.9. The stoichiometric ratio during this period was about 1.15 (which corresponds to a limestone utilization of about 87%) and the percent oxidation was about 30%.

* A removal of about 96% was obtained in the line-out (depletion) period for Run 501-2A. This confirms the estimate from the open-loop data.

Towards the latter part of the plotted operating periods (from April 12 to April 15 and from April 18 to April 20), while the SO_2 removal was still controlled between 80 and 85%, there appeared to be an increase in the stoichiometry to an average value of 1.4 (limestone utilization of 71%), which again could indicate "degradation" in the system (e.g., drop in limestone reactivity, pluggage of spray nozzles). The percent oxidation during these periods dropped slightly to about an average of 20% and the inlet pH ranged between 5.7 and 6.0.

The system was shut down a number of times due to solids pluggage of the inlet duct in the vicinity of the humidification section, and resulting increase in total system pressure drop (see Ref. 1).

7.1.3 Hydro-Filter Run 501-3A & 3B (see Figure 22)

The predicted high-pH value of SO_2 removal for the Hydro-Filter system, operating under the test conditions of Run 501-3A, is about 80%* (see Eqs. 7 and 13). Therefore, the controlled SO_2 removal target for Run 501-3A was 70%. During most of the operating period for Run 501-3A, the SO_2 removal was controlled between 65 and 70%, the average stoichiometric ratio was about 1.3 and the average percent oxidation and inlet liquor pH were about 30% and 5.8, respectively. As mentioned previously, the measured pH's, during this operational period, were in doubt.

* During a brief period of high stoichiometric ratio (about 1.5) and inlet liquor pH (about 6.1) at about 110 hrs. in Figure 22, the SO_2 removal rose to about 80%. This substantiates the predicted high pH removal.

After the system was drained to remove debris (marbles) on March 28 and March 29, another depletion (or line-out) period was conducted for Run 501-3B. From April 3 to April 13, the SO_2 removal was held between 65 and 70%, and the average stoichiometric ratio was about 1.4. The stoichiometry, during this period of the run, appeared to gradually increase, from an initial average value of about 1.3 (from April 3 to April 6) to a final average of about 1.5. The percent oxidation remained relatively steady during this period (at about 30%) as well as the inlet liquor pH (at about 5.8). The increase in stoichiometry, for the same SO_2 removal, could again indicate some "degradation" within the system.

7.2 MATERIAL BALANCES

As mentioned previously (see Section 5.1), during open-loop testing, good material balances for calcium and sulfur could only be obtained with the TCA. The poor material balances for the venturi and Hydro-Filter systems were attributable to solids build-ups (or depletions) in the clarifiers, which could not be excluded from the material balance enclosures. * During the five-week boiler outage, the venturi and Hydro-Filter flow configurations were modified to ones similar to that of the TCA system (see Figures 4, 5 and 6). It was expected, therefore, that good material balances for calcium and sulfur would be obtained on all three scrubber systems, based on the measured

* For the TCA, the main slurry stream circulated between the hold tank and scrubber, with a "bleed stream" from the main slurry stream routed to the solids separation area.

flow rate and solids compositions of the bleed streams to the solids separation area and the measured limestone addition rates and SO_2 removals.

7.2.1 Venturi Run No. 501-1A

Table 15 gives the results of a material balance for calcium and sulfur for venturi Run 501-1A, during a continuous 142 hour operating period from April 14 to April 19, 1973 (see Figure 20).

The results of the balance showed that the measured sulfur discharged (4.38 lb-moles/hr) is 3.1% less than the measured SO_2 absorbed (4.52 lb-moles/hr) and that the measured calcium added (6.10 lb-moles/hr) is 6.0% less than the measured calcium discharged (6.49 lb-moles/hr). Both closures are satisfactory, in spite of some difficulties experienced in measuring the limestone feed rate during the initial reliability tests.*

The ionic balances for the solids analyses, from which the calcium and sulfur discharge rates were calculated, averaged less than +3% (more cations than anions) for the bleed stream shown in Table 15.

Note that for both sulfur and calcium the measured inlet and outlet rates do not necessarily balance during each individual computational period in Table 15. This is due to the unsteady conditions which prevail (e.g. changing percent solids) and the resultant accumulation

* This measurement problem will be alleviated after May 4, when replacement flowmeter elements (for smaller flow ranges) are installed in all three limestone feed system magnetic flowmeters.

TABLE 15
MATERIAL BALANCES FOR VENTURI RUN NO. 501-1A

Date	Time	Length of Period, hours	Gas Flow Rate, acfm @ 330 °F	Inlet SO ₂ Conc., ppm	SO ₂ Removal, %	Bleed Stream				Limestone Feed		Sulfur Balance		Calcium Balance	
						Flow Rate, gpm	Solids In Bleed, wt. %	SO _x in Solids as SO ₃ , wt. %	Ca in Solids as CaO, wt. %	Flow Rate, gpm	Solids Content, wt. %	SO ₂ Absorbed, lb-moles	SO _x in Solids Disch., lb-moles	Ca in L-S Feed, lb-moles	Ca in Solids Disch., lb-moles
4/14	0200-0800	6	19,750	3,000	73	12.5	13.7	29.3	26.0	1.22	58.7	27	21	31	26
4/14	0800-2400	16	19,850	2,950	72	14.8	14.0	24.9	27.6	1.47	59.3	70	56	101	89
4/15	0000-2400	24	19,750	3,050	74	16.6	14.6	24.0	27.7	1.53	57.4	111	96	150	158
4/15	0000-0800	8	19,900	3,150	76	16.6	14.9	27.4	29.0	1.25	58.0	40	37	41	56
4/15-17	0800-0800	24	20,000	3,050	73	15.8	15.5	24.4	27.3	1.45	59.1	111	99	149	158
4/17	0800-2400	16	19,900	2,850	75	15.5	16.0	32.4	29.6	1.41	59.8	71	59	98	116
4/18	0000-2400	24	20,000	2,900	73	15.5	15.7	29.3	27.5	1.40	58.1	106	118	140	159
4/19	0000-2400	24	20,000	2,950	72	15.8	16.0	25.3	26.6	1.59	57.5	106	106	156	160
Totals		142										642	622	866	922

Average rates, lb-moles/hr:

SO₂ absorbed = 642/142 = 4.52
 SO_x discharged = 622/142 = 4.38
 Ca added = 866/142 = 6.10
 Ca discharged = 922/142 = 6.49

Average stoichiometric ratio, moles Ca added/mole SO₂ absorbed:

Based on limestone added and SO₂ absorbed = 866/642 = 1.35
 Based on solids analysis = 922/622 = 1.48

(or depletion) of the species in the system. However, over a long period of time (e. g. ~ 150 hours) the accumulation term becomes negligible as compared to the total input or output for the entire computational period.

The average stoichiometric ratio in Table 15 of 1.48 moles Ca/mole SO_2 absorbed based on solids analysis is probably more accurate than the value of 1.35 based on the measured limestone addition rate and SO_2 absorption, because of uncertainties in the limestone slurry feed rate.

7.2.2 TCA Run No. 501-2A

Table 16 gives the results of material balance calculations for TCA Run 501-2A, covering a period of 150 hrs. uninterrupted operation from March 30 to April 6, 1973 (see Figure 21).

The results of the balance showed that the sulfur discharged (4.34 lb-moles/hr) is 7% less than the SO_2 absorbed (4.67 lb-moles/hr), while the calcium added (4.45 lb-moles/hr) is 11% less than that discharged (4.99 lb-moles/hr). The closures are considered to be quite acceptable.

In Table 16, the sulfur input in each individual computational period is generally greater than the output, and the reverse is true for calcium. The ionic imbalances for the solids analyses during these periods were mostly positive (more cations than anions) and averaged about +5%. In other words, the reported sulfur content in the bleed solids might have been too low, or the calcium content too high, or

TABLE 16
MATERIAL BALANCES FOR TCA RUN NO. 501-2A

Date	Time	Length of Period, hours	Gas Flow Rate, acfm @ 300 °F	Inlet SO ₂ Conc., ppm	SO ₂ Removal, %	Bleed Stream				Limestone Feed		Sulfur Balance		Calcium Balance	
						Flow Rate, gpm	Solids in Bleed, wt. %	SO _x in Solids as SO ₃ , wt. %	Ca in Solids as CaO, wt. %	Flow Rate, gpm	Solids Content, wt. %	SO ₂ Absorbed, lb-moles	SO _x in Solids Disch., lb-moles	Ca in L-S Feed, lb-moles	Ca in Solids Disch., lb-moles
3/30-31	2300-0800	9	20,200	2610	84	14.1	14.3	27.8	25.2	1.03	58.4	43	35	39	45
3/31	0800-2400	16	20,000	2460	87	14.5	14.1	24.3	22.6	1.10	59.2	74	54	75	72
4/1	0000-2400	24	20,000	2520	82	13.7	15.3	28.8	24.4	1.17	53.5	107	100	103	121
4/2	0000-2400	24	20,000	2540	85	13.9	15.0	27.8	24.0	1.25	56.3	112	96	119	118
4/3	0000-2400	24	20,000	2700	82	14.9	15.5	33.2	26.6	1.07	60.0	115	127	112	146
4/4	0000-2400	24	20,000	2680	82	14.0	14.2	34.6	24.2	0.96	59.6	114	113	100	113
4/5-6	0000-0500	29	20,000	2580	84	13.7	14.6	31.5	23.5	0.93	60.3	136	126	119	134
Totals		150										701	651	667	749

Average rates, lb-moles/hr:

SO₂ absorbed = 701/150 = 4.67
 SO_x discharged = 651/150 = 4.34
 Ca added = 667/150 = 4.45
 Ca discharged = 749/150 = 4.99

Average stoichiometric ratio, moles Ca added/mole SO₂ absorbed:

Based on limestone added and SO₂ absorbed = 667/701 = 0.95
 Based on solids analysis = 749/651 = 1.15

both. If this factor is taken into account, either or both of the sulfur and calcium balances would be better than those reported.

Again, due to uncertainties in limestone addition measurement, the average stoichiometric ratio of 1.15 moles Ca/mole SO₂ absorbed based on the solids analysis is a more reliable number than the value of 0.95 based on the measured limestone addition rate and SO₂ absorption.

7.2.3 Hydro-Filter Run No. 501-3A

Table 17 gives the results of material balance calculations for Hydro-Filter Run No. 501-3A, covering a period of 150 operating hours from March 16 to March 22, 1973 (see Figure 22).

For sulfur, the average discharge rate (4.11 lb-moles/hr) is only 3% less than the SO₂ absorption (input) rate (4.24 lb-moles/hr). For calcium, the rate of addition (4.49 lb-moles/hr) is 13% less than the discharge rate (5.16 lb-moles/hr). The balance is satisfactory, considering the uncertainties in the limestone slurry addition rate during the period.

The ionic imbalances for the solids analyses, from which the calcium and sulfur discharge rates were calculated, averaged less than +2% (more cations than anions) for the bleed stream shown in Table 17.

Again, the average stoichiometric ratio in Table 17 of 1.26 moles Ca/mole SO₂ absorbed based on solids analysis is probably more accurate than the value of 1.06 based on the measured limestone addition rate and SO₂ absorption.

TABLE 17

MATERIAL BALANCES FOR HYDRO-FILTER RUN NO. 501-3A

Date	Time	Length of Period, hours	Gas Flow Rate, acfm @ 330 °F	Inlet SO ₂ Conc., ppm	SO ₂ Removal, %	Bleed Stream				Limestone Feed		Sulfur Balance		Calcium Balance	
						Flow Rate, gpm	Solids in Bleed, wt. %	SO _x in Solids as SO ₃ , wt. %	Ca in Solids as CaO, wt. %	Flow Rate, gpm	Solids Content, wt. %	SO ₂ Absorbed, lb-moles	SO _x in Solids Disch., lb-moles	Ca in L-S Feed, lb-moles	Ca in Solids Disch., lb-moles
3/16	1600-2400	8	20,400	2950	66	24.7	9.9	25.4	23.7	0.98	35.0	33.1	33.1	16.0	44.1
3/17	0000-0800	8	20,000	3050	70	22.5	9.2	21.6	22.8	1.12	57.6	35.6	23.7	36.8	35.7
3/17	0800-1600	8	20,300	3100	72	26.3	9.0	23.0	23.7	1.42	59.8	37.7	28.8	49.4	42.4
3/17	1600-2400	8	20,500	3150	68	25.4	9.0	24.4	25.8	1.60	50.6	36.6	29.5	43.2	44.6
3/18	0000-0900	9	20,300	3320	66	22.3	9.8	27.9	28.7	1.75	49.9	41.7	36.5	52.1	53.6
3/18	1100-1600	5*	20,300	3050	70	22.6	10.8	30.0	26.2	1.68*	51.3	22.6	24.5	40.5	30.6
3/18	1600-2400	8	20,200	2800	73	23.7	10.4	30.4	25.6	1.47	53.1	34.4	40.0	42.5	48.1
3/19	0000-0800	8	20,700	2900	68	21.6	10.2	31.6	24.9	1.93	33.5	34.0	37.1	30.0	41.8
3/19	0800-1600	8	20,350	2800	77	21.6	10.7	26.0	25.6	1.87	55.6	36.5	32.1	58.2	45.2
3/19	1600-2400	8	20,300	2750	71	25.0	10.7	28.7	24.3	1.35	45.4	33.0	41.1	31.4	49.7
3/20	0000-0800	8	20,350	2800	67	22.1	10.9	28.7	23.3	1.52	41.7	31.8	37.1	31.3	43.0
3/20	0800-1600	8	20,600	3020	68	19.9	11.5	30.3	24.5	1.45	43.9	35.2	37.3	32.1	43.1
3/20	1600-2400	8	20,200	2950	69	19.0	11.7	33.5	24.9	1.19	57.0	34.2	40.2	38.4	42.6
3/21	0000-0800	8	20,250	2850	70	19.2	11.3	26.4	22.7	0.80	62.8	33.6	30.8	30.1	37.8
3/21	0800-1600	8	20,150	2850	64	17.3	10.9	27.5	23.3	0.84	60.7	30.6	27.8	30.0	33.7
3/21	1600-2400	8	20,150	2730	63	16.5	10.7	27.1	22.5	0.97	61.3	28.9	25.6	35.2	30.4
3/22	0000-0800	8	20,350	2750	69	18.2	10.9	27.5	22.8	0.98	59.9	32.2	29.3	34.1	34.6
3/22	0800-1600	8	20,450	2900	67	19.6	10.8	28.3	22.5	0.96	60.7	33.1	32.1	34.3	36.4
3/22	1600-2400	8	20,300	2870	65	19.6	10.2	27.3	23.7	1.00	62.1	31.5	29.1	37.0	36.1
Totals		150										636	616	673	774

Average rates, lb-moles/hr:

SO₂ absorbed = 636/150 = 4.24
 SO_x discharged = 616/150 = 4.11
 Ca added = 673/150 = 4.49
 Ca discharged = 774/150 = 5.16

Average stoichiometric ratio, moles Ca added/mole SO₂ absorbed:

Based on limestone added and SO₂ absorbed = 673/636 = 1.06
 Based on solids analysis = 774/616 = 1.26

* The scrubber was shut down on 3/18, 0900-1100 hours (no flue gas addition). However, the limestone addition was continued during this 2-hour period, and the length of limestone addition was 7 hours instead of 5 hours.

Section 8

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OPERABILITY AND RELIABILITY
OF EPA LIME/LIMESTONE SCRUBBING
TEST FACILITY

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ABSTRACT

Results of research and development programs to study lime/limestone wet scrubbing have shown that effective sulfur dioxide removal is feasible. One of the major questions remaining is the long-term reliability of the process when applied under actual conditions on a power generating unit. The objective of the EPA-Bechtel-TVA test program at Shawnee is to define a system which operates both effectively and reliably. The test facility design considerations to permit investigations of operability are covered in this presentation along with the experience during about 1 year of operation. Preliminary conclusions which might affect selection of components for full-scale systems are presented.

Introduction

As part of an extensive research and development program by the Environmental Protection Agency (EPA), an experimental test facility was designed and constructed to study and evaluate the feasibility and economics of closed-loop lime/limestone wet-scrubbing processes and develop mathematical models to allow effective and economic scale-up of practical operating configurations to full-size scrubber facilities. Interest in alkali scrubbing has grown because of its basic simplicity and comparatively low capital cost. The drawbacks of alkali scrubbing are the need to dispose of large quantities of solid wastes and the tendency of accumulation of solids to plug the system.

The emphasis on development of technology for sulfur dioxide control during a relatively short period of time resulted in pilot-plant studies of limestone and lime scrubbing by several organizations. These programs led to the conclusion that lime/limestone scrubbing is based on feasible technology. However, the process alternatives are not well defined and the long-term reliability of the configurations tested to date is still questionable. One of the main objectives of the prototype-scale test program is to provide a better understanding of the technology and to study the factors which affect reliability. The program is funded and directed by EPA; Bechtel Corporation prepared the detailed design of the test facility, and developed the test program; and TVA constructed and operates the test facility.

Three parallel scrubbing systems (10-mw each) were installed at TVA's Shawnee station near Paducah, Kentucky. The system was described at the limestone symposium in New Orleans during October 1971. The facility has been operated now for approximately 1 year. The process results are covered in a paper presented by Dr. M. Epstein (Bechtel Corporation) at this meeting. The intent of this paper is to review the operability and reliability of the test equipment during the early phases of the program. The design considerations in providing methods for evaluation of reliability are reviewed followed by a description of operating experience.

Design Considerations

The test facility is not sufficiently large to have a significant effect on stack gas effluent quality at the station where it is installed--its only function is to provide information on lime/limestone scrubbing technology. Therefore, it was designed to be a versatile, relatively sophisticated system with emphasis on data generation and collection.

Unit Size

Most of the test facilities used to study sulfur oxide and particulate matter removal are small ones capable of treating only up to a few thousand cfm of flue gas. Because of the differences in both the performance characteristics of the equipment and scrubbing efficiencies of small-scale test facilities and commercial-size units, and the associated uncertainty and difficulty involved in using small-scale data in full-scale unit design, the three scrubbers at the Shawnee test facility are of prototype size, capable of treating up to 30,000 acfm of flue gas (320°F, 14.3 psia).

The size selected will allow extrapolation by a factor of 10 (an acceptable scale-up) to commercial-size units. The system is designed so that the three scrubbers can be operated simultaneously in order to acquire information on different types in the shortest period. In retrospect, because of the multitude of problems associated even with routine operation, maintenance, and evaluation of process data, it might have been more prudent to concentrate on a single, versatile, system.

Flexibility

The selection of the scrubbers was based on the evaluation of the performance characteristics of the various designs in terms of their overall effectiveness as SO₂ absorbers and particulate collectors under the operating conditions expected for the process in commercial applications. The selected types of scrubbers are:

1. Variable throat venturi scrubber followed by an after-scrubber absorption section (spray tower or Pall-ring packed bed).
2. Turbulent contact absorbers (TCA).
3. Hydro-Filter marble-bed absorber.

It is beyond the scope of this paper to discuss the types of scrubbers considered and their advantages and disadvantages.

The following describes some of the flexibilities that have been designed into the test facility:

- The three scrubbers, including the flue gas inlet and exhaust facilities, slurry handling equipment, and clarifiers are installed in parallel. Only the alkali addition system and the final solids dewatering and disposal facilities are common.
- Scrubber internals can be changed. For example, the packed-bed section of the venturi after-scrubber can be replaced by a four-header spray tower (the four headers can be operated in any combination). The TCA can be operated as a one-, two-, or three-bed unit, with a variety of liquor flow piping arrangement.
- Arrangements are being made to provide parallel limestone and hydrate addition systems.
- The scrubbers can accommodate different types of mist eliminators.
- Each scrubber system has its own oil-fired reheater for independent evaluation of exhaust gas characteristics with up to 125°F (above scrubber exhaust temperature) reheat capability.
- A heat exchanger was provided to evaluate the effect of cooling of the slurry feed on scrubber performance (only one scrubber at a time).
- Various solid disposal configurations can be evaluated. They include: clarifier/pond, clarifier/centrifuge/pond, and clarifier/rotary vacuum filter/pond.
- To evaluate the degree of supersaturation in the circulating slurry system and the associated possible scaling problems, the residence time of the circulating slurry solutions in the scrubber effluent hold tanks can be varied between 4 and 60 minutes (not necessarily in all three scrubber systems).

- To determine uncertain model coefficients for gas side controlling mass transfer and obtain design information for sodium carbonate aqueous scrubbing, a common SO_2 additive system was provided. This system can also be used to compensate for rapid and significant drop in SO_2 concentration in the flue gas feed.
- The ducts, piping, and pumps in each scrubber system are designed to allow the required variation of the turndown ratio and the ratio of liquid to gas flow rates.
- Variable speed pumps have been used for flow control wherever possible in order to avoid potential solids buildup and/or rapid erosion of throttling mechanisms (rubber pinch valves or metal control valves).

Instrumentation

The control of the test facility operation is carried out from a central control room. Important process control variables are continuously recorded or indicated on graphic panelboards by remote conventional (pressure, temperature level, and water, liquor, and air flows) and specialized instrumentation (radiation-type densitometers, magnetic-type flow meters). The SO_2 concentration of both the flue gas feed and scrubbed gas streams to and from the scrubbers can be automatically analyzed by UV spectrophotometer; also CO_2 , H_2O , O_2 , and H_2 can be continuously monitored by gas chromatographs. The analytical results of these instruments are also remotely recorded in the central control room.

The number of local and board-mounted instruments is about 1500. Some of the more important control loops are listed below:

- The flue gas flow to each scrubber is controlled by a flow-indicating control loop which senses the flow via a venturi flow element and sets the position of the damper at the inlet of the induced-draft fan.
- The SO_2 injection system to the flue gas feed is on a control loop set by the Du Pont UV analyzer using a valve in the SO_2 line as the final control element.
- The reheater outlet temperature is controlled by a temperature-indicating control loop which senses the exit temperature and adjusts the fuel oil and combustion air rates to the burners.
- The reheater and the induced fan are interlocked such that the fan has to be operational in order to fire the reheater.

- The internals of the venturi after-scrubber and the TCA and Hydro-Filter scrubbers are lined with neoprene rubber. To protect the rubber lining, a temperature sensor is provided at the bottom of each scrubber which trips the ID fan and reheater systems and admits water to the emergency sprays in the scrubber gas inlet duct. (The temperature trip is set at 190°F.)
- The induced draft fans are protected by automatic shutdown control loops in case of high bearing vibration and temperature.
- Each scrubber is protected by a vacuum relief system which protects the induced draft fan against high vacuum (-34 in. water gage).
- The amount of limestone and water to be added to the limestone slurry tank is controlled by a cascade of a level indicator controller, to a weight of limestone, to volume of water ratio controller. This system maintains the desired limestone slurry concentration at any set level in the mixing tank. The limestone slurry is then pumped by remotely controlled pumps to feed the scrubber systems separately.
- The scrubbing slurry to each system is tied to a flow-indicating control loop. The loop uses a magnetic flow meter as a sensing device and a variable speed pump as the final element to maintain the desired flow.
- The levels in the effluent hold tanks are controlled by the amount of slurry bled to disposal. The levels are sensed by diaphragm-type elements.
- The clarifier underflow is set by a density-indicating control loop. The underflow density is sensed by a gamma radiation type element and the flow rate is set by a signal to the variable speed pump.
- Alarms for high and low values of different variables are also provided where necessary.

An electronic digital data acquisition system is utilized to record automatically and continuously over 150 selected operating data points. In addition, about 125 channels are provided for alarm condition printouts. This system is hard wired for data output in engineering units directly on magnetic tape which is transmitted from the field to Bechtel Corporation in San Francisco for data evaluation along with manually recorded pertinent information.

An X-ray Fluorescence Spectrometer is used to determine the following species in liquid samples:

Ca^{++} , S, K^+ , Cl^-

Solid samples can also be analyzed after dissolution in an appropriate solvent (e.g. HCl). All functions of the X-ray unit (such as sample presentation, goniometer angle, slit, collimator) are controlled by a Nova 1200 minicomputer. Sample identification is fed to the system via an ASR 35 teletype. All the data are reduced by the computer and printed out on a line printer in addition to being recorded on a magnetic tape.

Provision for Inspection and Cleaning

An equipment inspection program for the test facility is scheduled to observe the performance and condition of the equipment after periodic intervals of operation. The results of the inspection are correlated to process conditions (temperature, pH, chemical composition, particle size, distribution of limestone slurry feed) and the time period for which the equipment was exposed to the above conditions. Trends based on quantitative data and observations are being analyzed and evaluated, and corrective actions will be taken to resolve the problems.

Two general categories are covered by the program:

- Evaluation of the corrosive tendencies of the various process fluids using corrosion coupons installed in preselected locations in the process equipment.
- Observation and evaluation of the equipment performance with regard to erosion, solids deposition, scaling, etc.

Corrosion test racks are installed in the flue gas inlet ducts, scrubber exhaust ducts downstream of the reheaters, at different locations in each scrubber, in the effluent hold tanks, recirculating tanks, and clarifiers; twenty coupons are mounted on each test rack.¹ The selection of the coupons and the location of the racks were based on experience and anticipated locations of corrosive conditions.

The equipment performance checks are made periodically at various points in the system for:

- Erosion
- Deposition of solids and slurry sludge
- Corrosion (this is separate from the evaluation of the corrosion coupons)
- Formation of chemical scale
- General conditions

¹ Carbon steel (A-283), Cor-Ten B (A-588), 304L S.S., 316L S.S., 18-18-2 S.S., Alloy 20 Cb-3, 410 S.S., 446 S.S., E-Brite 26-1 S.S., Hastelloy B, Hastelloy C-276, Incoloy 800, Incoloy 825, Inconel 625, Monel 400, 70-30 Cu-Ni, Aluminum 3003, Flakeline 200 (Coated M.S.), fiberglass-reinforced plastic (Bondstrand), Transite. In addition, specimens of fiberglass-reinforced Furan, resin, natural rubber, neoprene and butyl rubber, and five stressed alloy specimens were installed at selected locations.

The location of the inspection points and the frequency of inspection are based on the severity of the process conditions (temperature, pH, etc.), hydraulic characteristics of the system, equipment vendor recommendations, and experience by others. Wherever possible, photographic records of the condition of the equipment are established and used in the evaluation of the system.

The observation windows provided on the venturi, TCA, and Hydro-Filter scrubbers have only limited use in limestone service because the slurry interferes with visibility.

Access doors on major equipment and Victualic couplings on the slurry piping system permit quick cleaning and disassembly.

Materials of Construction

The selection of material for construction was based on anticipated process conditions and design and economic considerations. For example: Rubber lining of the scrubbers was selected for erosion and corrosion protection; the stainless steel construction of the venturi scrubber was necessitated by high throat velocities.

The following list gives an overall picture of the materials of construction:

- The inlet flue gas ducts are of carbon steel and are insulated.
- The scrubber exhaust gas ducts are of 316L stainless steel.
- The induced-draft fan internals are of 316L stainless steel.
- The venturi scrubber internals are of 316L stainless steel. The after scrubber shell is of carbon steel coated with 1/4-inch neoprene lining.
- The TCA and the Hydro-Filter scrubber internals are of carbon steel lined with neoprene.
- The chevron demisters are of stainless steel.
- The direct-fired reheater shells are of carbon steel lined with refractory.
- The tanks are of carbon steel with internals lined with Flake-line (polyester glass) or with neoprene rubber. The tank agitators are rubber coated.

- The limestone slurry tank is of 316L stainless steel.
- The carbon steel clarifiers are lined with Flakeline and the rakes are stainless steel.
- All of the slurry piping above 2-1/2-inch diameter is of carbon steel with internal neoprene rubber lining. The lines are not heat traced or insulated.
- All of the slurry piping smaller than 2-1/2-inch diameter is of stainless steel. The lines are not heat traced or insulated.
- The water lines are of carbon steel and are heat traced and insulated.
- The slurry pumps have rubber-lined casings and impellers.
- The slurry piping is valved with rubber-lined plug valves or rubber pinch valves.
- The entire SO₂ injection system is of 316L stainless steel.
- The instrument probes (temperature for example) in the scrubber and duct internals are of 316L stainless steel.
- The solid bowl centrifuge and the rotary drum vacuum filter are constructed of 316L stainless steel.
- Slurry piping to the pH and conductivity meters is made of PVC.

Operating Experience

Firm conclusions regarding the effect of operating variables on reliability can be made only after relatively long-term tests. Operation to date has been mainly restricted to short duration testing of performance variables. However, observations of trends and short-term effects are pertinent. Also, the experience with instrumentation, solids handling, and materials evaluation should be of interest.

Effect of Operating Variables on Reliability

Although the effects of all variables may not be evident from the experience to date, the factors are listed below together with applicable observations from the test program and from supporting studies.

Open Versus Closed-Loop Operation. One of the objectives of development work on lime and limestone scrubbing is to establish conditions for operation without liquid discharge. The criteria for quality of liquid effluent streams are not well developed; therefore, zero discharge may not be required but certainly is a safe level. One of the main factors which affects reliability of lime/limestone scrubbing technology is the low solubility of the calcium absorbents and reaction products. If the scrubbing slurry were discarded after a single pass through the scrubber, a minimum amount of precipitation would occur. When the slurry is recycled, dissolved solids build up in the liquid phase and more precipitation occurs in the scrubber. The precipitation of calcium sulfite and calcium sulfate leads to scaling in the scrubber if provisions are not made for controlling the precipitation.

The test facility design included pumps with water seals for bearing protection, water quench sprays for gas cooling, water sprays for mist eliminator wash, and dilute slurry feed. The water required for operation exceeded the makeup requirement so that the systems operated for about 6 months with partially open liquor loops during limestone scrubbing tests. This was not considered to be a serious problem because the results of factorial testing of performance variables are not likely to be significantly influenced by the water balance. However, not a great deal was learned about the effect of scaling potential on reliability during this period. Essentially no scaling occurred.

During February and early March of this year, the systems were modified to permit closed liquor loop operation. The absorbent feed system was changed to allow feeding of slurry with up to 60% solids. The water seals on the pumps were converted to mechanical seals supplemented with air purge. The quench spray system was modified to use slurry and the mist eliminator wash system was converted to use clarified water. Required revisions to flow measurement and control devices were made.

Since the modifications were completed in mid-March the systems have been operated with liquid discharge approaching the quantity of moisture that would reside with settled sludge. No serious scaling has been observed during the relatively brief period of operation. One serious encounter with scale during a special test is discussed in the section below related to stoichiometry.

Gas Velocity. The effect of gas velocity on entrainment is a major reliability factor. The need for high solids concentration in the recirculated slurry aggravates mist recovery because the extent of entrainment influences the amount of solids that impacts on eliminator surfaces and must be removed by washing.

Most of the tests in the Hydro-Filter scrubber have been carried out at about 5 ft/sec; a few were made at about 7.5 ft/sec. Because of the few comparative data points the correlation between velocity and pressure drop increase in the mist eliminator is not clear. However, the rate of solids accumulation was higher at the higher velocity. During the tests at the lower velocity, manual cleaning of the mist eliminator was required about once per month. Only limited wash with fresh water was used during this period. An improved wash configuration has been installed to reduce the cleaning requirement.

The TCA scrubber has been operated during most of the test periods at three different velocity levels, 5.9, 7.8, and 9.8 ft/sec; a few tests were run at 11 ft/sec. This system has been operated less than the Hydro-Filter scrubber and no conclusions can be reached regarding effect of gas rate on carryover.

During a special test to simulate the TVA pilot-plant configuration, slurry entrainment was excessive at 12 ft/sec and the gas rate had to be reduced to 8 ft/sec for the run. The higher value had been acceptable in the pilot-plant (1-mw size) work; this indicates that gas-liquor distribution may not have been as good in the larger scrubber.

Most of the testing in the venturi-spray tower system has been with slurry fed only to the venturi; in this mode of operation, the spray tower serves as a large disengaging chamber and carryover to the mist eliminator was not a problem. When slurry was introduced in the spray tower, the gas velocities were generally low, 2.5 to 5.0 ft/sec, although a few tests were run at the maximum velocity of 7.5 ft/sec. Mist eliminator deposits were minor in all tests.

Until the recent modifications were made, the mist eliminators were washed intermittently with limited amounts of fresh water on the top side only. Piping was changed so that wash liquor can be applied to both sides which should improve the flushing action; a mixture of makeup water and clarified recycle liquor (about half and half) is now being used. There has been no indication of significant scaling in the demister since the changes were made. However, use of recycle liquor for wash has caused sulfate scaling in pilot-plant studies and this could be a potential problem during extended tests.

Liquid Rate. The primary effect of liquor rate on operability is to control scaling by providing sufficient volume to accommodate the "make" of reaction products. Of equal importance is the flushing action in the scrubber to avoid silting of suspended solids. The latter requirement is met incidentally because the trend in development of lime/limestone scrubbing technology has been toward higher and higher liquor rates. At the test facility, operation has generally been at maximum liquor rate--800 gal/min (L/G of 27-54) in the Hydro-Filter, 1200 gal/min (L/G of 40-80) for the TCA, and 450 gal/min (L/G of 20-40) for the spray tower. The spray tower system is being modified to increase the liquor rate to 1200 gal/min.

Except for minor deposits in the Hydro-Filter bed, silting has not occurred. Scaling has not been a problem because of the open-loop operation during most of the program to date. The minor amounts of scale formed during the brief period of closed-loop operation is encouraging.

Solids Concentration. The suspended solids concentration in the recirculated slurry is important to the process because sufficient unreacted absorbent to provide the required dissolved calcium is needed and recycled calcium salts provide seed sites for precipitation; the effect of fly ash has not been established. On the other hand, erosion increases as the suspended solid concentration goes up; therefore, an optimum level should be established and, although this has not been done, it remains one of the objectives of the program. The composition of recirculated solids is probably also important, but the degree of control is questionable. If the sulfate content could be increased, the total solids requirement might be reduced. Tests of methods to promote oxidation are planned.

Percent solids recirculated has been varied from 5 to 12; a few tests were made with 15% solids. The most serious effect of suspended solids has been erosion of spray nozzles. The Hydro-Filter nozzles are constructed from stainless steel and have polyurethane internal liners and swirl vanes. The liners failed after about 1800 hours of use and have been replaced with an improved design. Open-type spiral nozzles constructed from stainless steel were chosen for the spray tower and these are also showing signs of wear; the same type except with stellite tips have been ordered for replacements. The large (300 gpm) open-type nozzles used in the TCA scrubber have given good performance.

Because of frequent changes and short periods of operation at each solids level, the effect of solids concentration on erosion rates was not determined. This information will be obtained during the longer term tests.

Stoichiometry. Much of the pilot-plant work on limestone scrubbing has been done with a limestone feed rate equivalent to 1.2-1.5 times the amount required to remove all the sulfur dioxide from the inlet gas. During a special test carried out in the TCA system to simulate the TVA pilot plant, the intended feed stoichiometry was 1.5. Problems with flow control resulted in an actual stoichiometry of about 2.7. The scrubber walls and grids were heavily scaled during the 3-week, closed-loop test. It has since been determined in pilot-plant studies that the excess limestone was the primary cause of scaling.

EPA is conducting a test program in a small pilot plant (500 cfm) to support the Shawnee program. This program, under the direction of R. H. Borgwardt, has been highly productive. In one series of tests the pilot plant was configured to simulate the TVA grid-packed tower and several potential causes of scaling were studied including limestone type, limestone particle size, inlet gas temperature, presence of fly ash, and stoichiometry.

The factors were systematically tested and all except stoichiometry had no effect on scaling in the ranges studied. With the same stone ground to the same particle size, scale formed rapidly (less than 40 hours) at a stoichiometry of 2.5; the scale was similar to that found at Shawnee (primarily CaSO_3). The scale growth rate was estimated to be 60 mg/m². At a stoichiometry of 1.25, no scale formed during 400 hours of operation even when the hot gas (285°F) entered the scrubber without a precooling step. The effect of high stoichiometry was also confirmed in the TVA pilot plant.

From the results of the EPA pilot-plant studies, it appears that calcium sulfite scaling occurs when the precipitation of calcium sulfite in the tower exceeds a critical rate that is influenced by pH (rate of dissolution of limestone). It was estimated that the critical pH for the system tested is 6.2 ± 0.1 . When this value is exceeded, scaling is likely to occur. The effect of pH (stoichiometry) on the dissolved calcium sulfite in the scrubber discharge is shown below.

Average Liquid-Phase Composition of Scrubber Slurry^a

at 1.25 and 2.5 Stoichiometry

(L/G = 37.4, no fly ash)

<u>Scrubber effluent</u>	<u>Stoichiometry</u>	
	<u>1.25x</u>	<u>2.5x</u>
SO ₃ , mg/l	3,340	1,580
SO ₂	774	424
CO ₂	240	292
Ca	774	670
pH	5.8	6.2

^a From "Limestone Scrubbing of SO₂ at EPA Pilot Plant," Progress Report 8, March 1973, p. 11.

The difference in sulfite level represents the increased precipitation (and scaling) at the higher stoichiometry.

The test program planned for Shawnee specified a stoichiometry range of 1.25 to 1.75. Actual values were normally higher than 1.5 as a result of problems with the feed system. Based on the results of the pilot-plant tests, the stoichiometry will be lowered in order to reduce the risk of scale formation. Minimum levels will be established by desired sulfur dioxide removal efficiency. A potential problem of operation at relatively low pH is loss of limestone reactivity, probably because of calcium sulfite precipitation on the particles. This phenomenon has been observed in the TVA pilot-plant program.

Limestone Particle Size. The effect of stoichiometry on pH points out the importance of any factors which will influence dissolution rate of the absorbent. Limestone particle size is one of these factors and although no systematic study has been carried out in the test program, differences in sulfur dioxide removal have been attributed to particle size of the stone. An empirical test to relate particle size, feed stoichiometry, and unreacted stone in recycled slurry to dissolution rate is needed for application of results to different situations.

Reheat. The scrubbed gas is saturated when it leaves the scrubber and entrainment plus any condensation which might result from cooling would be detrimental to downstream equipment. Therefore, some level of reheat is required. Reheat for each system is provided by combustion of oil in direct-fired burners installed in a combustion chamber in the exhaust duct. Operation of these units has been unacceptable. The cooling effect of the cool, oxygen-deficient, saturated scrubber exhaust plus poor atomization of oil as a result of operation of a single nozzle over a wide range of flow rates have caused incomplete combustion. In addition to interference of soot with particulate measurements, the poor combustion resulted in deposits of unburned oil and soot in the ductwork above the reheater. These accumulations of combustibles ignited on two occasions and could have caused injury to personnel or damage to equipment. Fortunately the fires were extinguished without serious effects. After the second incident, the local plant management advised that the test facility should not operate until the hazard was eliminated.

Both parts of the problem were investigated simultaneously during a period while the test facility was not operating because of a scheduled boiler outage. Stainless steel sleeves (40-in diameter by 4-ft high) were installed to isolate the combustion mixture from the scrubber exhaust until combustion of the oil could be essentially completed; the effective combustion volume is about 50 ft³. Mechanical atomizing nozzles were installed instead of the turbulent mixing type provided initially with the combustion system. The types now in use are designed for a narrow range of oil flow rates and will have to be changed when the reheat requirement changes. However, nozzle replacement is a simple job.

The changes have been effective. Essentially no soot is visible in the stack gas and particulate samples have shown no evidence of carbon from the reheaters. Plans for installation of an external combustion system have been deferred.

Instrumentation

SO₂ Analyzers. Experience with the six Du Pont Model 400 UV SO₂ analyzers at the test facility has generally been good. Most problems have been associated with the sample handling system rather than with the instruments. Initially the sample handling system was particularly vulnerable to condensation, dust, oil, corrosion, or combinations of these factors. This led primarily to line leakage, line plugging, plugging of the filters, or coating of the lens. All of these effects resulted in erroneous SO₂ readings. It was also found during early attempts to calibrate using standard reference gas, that the certified values are given for a specified temperature. Use of the reference gas at other than the specified temperatures can also lead to erroneous results.

In order to eliminate the problem areas, the sample handling system was modified in November 1972 as follows:

1. All heat sinks and sharp bends in the sample lines were eliminated. A new 3/8-inch diameter Dekeron sample line was installed to replace the original 1/4-inch stainless steel line. Heat tracing was installed the full length of the sample line.
2. Stainless steel shields furnished by Du Pont were installed around the probe filters. The original ceramic probe filters were also replaced by type 316 stainless steel probe filters recently developed by Du Pont.
3. An automatic zero and air blow-back system was installed on the SO₂ analyzers in the inlet gas duct as had originally been installed on those in the outlet gas ducts.
4. All stainless steel lines and fittings were replaced with Dekeron or teflon wherever possible.
5. Calibration methods were changed to use a stainless steel wire mesh reference filter rather than use of standard reference gas bottles.

One additional problem associated with the instrument rather than the sample handling system was also encountered. The interference filter in the optic section of all six analyzers was found to deteriorate with time. All of these filters, which screen out all except the desired light wave lengths, were replaced. The failure and subsequent deterioration was attributed by Du Pont to have been caused by exposure to freezing conditions prior to installation. The freezing resulted in minute cracks which then deteriorated with time as theorized by Du Pont.

Following the modifications made to the sample handling system and the replacement of the interference filters, operation for the past 5 to 6 months has been essentially trouble-free with only a minimum of preventive maintenance time.

Magnetic Flow Meters. Operating experience with the Foxboro magnetic flow meters at the test facility has generally been good. The main problem has been in obtaining accurate flow measurements at very low flow rates with meters designed to measure flow over too wide a range. This is a problem inherent in the nature of a test facility where testing over a wide range of variables is desired. To assure accuracy, Foxboro recommends a minimum linear velocity of 3 ft/sec through the flow element. Periodic cleaning of the electrodes and calibration checks are also required to compensate for drifting of the meters. Routine cleaning and maintenance checks are now made on a monthly basis.

Control Valves. Operating experience with control valves at the test facility is similar to experience with flow meters. Operation has been generally good when control valves are used in reasonable design flow ranges. However, when excessive throttling is required to obtain very low flow rates, severe erosion in a relatively short period of time results from the increased velocity through the throttled valve. This has been observed with both stainless steel plug valves and rubber pinch valves used as control valves.

pH Meters. Operating experience with pH meters at the test facility has thus far been limited to in-line flow-type meters. No significant scaling of electrodes has been noted to date with limestone. However, frequent calibration checks using a buffer solution are required to maintain the desired accuracy. The current frequency in use at the test facility is twice per week on a routine basis or more frequent if required. Because of the desirability to be able to control pH to within ± 0.1 pH unit, future test program plans include evaluation of another type of pH meter.

Density Meters. Operating experience with density meters at the test facility includes both the Ohmart radiation-type meter and the bubble-type meter. Both systems require further study and modification to achieve adequate reliability in their respective control service.

Data Acquisition System. Operating experience with the EMC data acquisition system at the test facility has been improved during the past 6 months. Early in the test program much difficulty was experienced in recovering the data from the tapes recorded automatically onsite. Extraneous characters were being recorded on the tapes and were interfering with the data recovery. Changes were made to reduce the industrial noise of the system and a special computer program was also written to help recover the data from the tapes. The system is also sensitive to dust, and particularly to coal dust. Since the system is neither enclosed nor located within a pressurized area, periodic cleaning of the recorder on a weekly basis was initiated. Subsequent to these changes, operation of the data acquisition system has been very good.

Based on the operating experience at the test facility, two areas appear to be critical. Some of the field effect transistor (FET) circuits appear to be extremely sensitive and should probably be redesigned if time permits. Compatibility of the tape recorder with the equipment used to recover the data from the tapes also appears to be very sensitive to dust, noise, alignment, etc. However, neither problem area appears to be insurmountable with proper care or design of the equipment.

X-Ray Computer System. Operating experience with the Siemens X-ray computer system at the test facility has been similar to that on the data acquisition system. Some mistakes made earlier in the program on the data acquisition system were avoided on the X-ray computer system. Both the X-ray unit and the computer were enclosed in a pressurized air conditioned room. This has minimized the problems of recovering the data from the tapes. Also when problems do occur in removing the data from the tapes, the special computer program prepared for use with the data acquisition system is available.

Operation of the X-ray unit has been very satisfactory. Most problems have been associated with either the interface between the X-ray and the computer or in the peripheral hardware equipment. Once these problems were corrected and a weekly cleaning schedule was established, operation of all associated equipment has improved significantly.

Waste Solids Handling

One of the most important considerations in use of lime/limestone scrubbing technology is disposal of waste solids. A section of this meeting is scheduled for discussion of the work related to handling and disposal of sludge. The test facility is equipped to study alternate methods for separation of solid and liquid phases in the scrubber discharge stream.

Pond. A three-section settling pond was constructed in an area that had previously been an ash storage pond. The dikes are made from fly ash and are covered with local clay. A small starter pond was used during the early open-loop tests and has been filled and retired. The pond arrangement which will be used for the remainder of the closed-loop program is discharge of sludge into a large settling area and return of the supernate through a smaller "polishing" pond. The slurry to the pond can come directly from the scrubber circuit, from the thickener underflow, or from the filter and centrifuge as reslurried cake. The ponds are being equipped with instrumentation for evaluation of seepage. During the early stage of use before a significant area of the pond is covered with settled solids, seepage has been excessive. Small-scale permeability tests are being made in an effort to determine the ability of settled sludge to seal the clay lining. An impervious membrane may be required to reduce seepage to an acceptable level.

Clarifier. Each scrubbing system is equipped with a separate clarifier; the venturi and Hydro-Filter systems have 20-ft diameter units and the TCA system, because of a higher recirculation rate, has a 30-ft diameter thickener. The performance of the larger unit has been satisfactory but the solids carryover in the overflow has been a problem with the smaller units. The settling characteristics of the reaction products (particularly calcium sulfite) are poor and insufficient time is available during the compression or hindered settling period to produce a clear overflow. Variation in the feed rate may contribute to poor performance. It might be necessary to operate with a turbid overflow. This probably would not be serious if the solids in the overflow concentration could be controlled.

The concentration of solids in the underflow approaches the expected final settled density of sludge (approximately 40%).

The program for improved clarification and thickening includes:

- Maintain the feed flow to the clarifiers as steady as possible.
- Optimize the oxidation of calcium sulfite to calcium sulfate.
- Investigate the effect of the particle-size distribution of the ground limestone on both the SO_2 absorption efficiency and settling characteristics and adjust limestone grinding accordingly.
- Maintain the percent solids in the clarifier underflow under density control and let the sludge level vary in the tank. The set point of the density controller could then be adjusted (i.e., the underflow rate increased) to prevent sludge overflow.
- Operate the clarifier in series with the vacuum filter or centrifuge to attain minimum solids concentration in the recycle liquor and maximum final solids concentration in the solids disposal stream.
- Use of flocculents.

Filter. Initial tests of a rotary vacuum filter to separate the solid and liquid phases in the clarifier underflow were not successful. The cake is thixotropic and, although it appeared dry and firm under vacuum, internal water was released and the cake became fluid when the vacuum was released. The wet, sticky cake would not separate from the filter cloth. Further dewatering was restricted by formation of cracks in the cake which allowed bypassing of air.

The vendor has recommended installation of compression rolls and air blast discharge to reduce the final moisture to approximately 40%. These changes are being made.

Centrifuge. Short-term, exploratory tests of the centrifuge were carried out in late April. Both clarifier underflow and a sidestream from the scrubber recirculation loop were tested. The results of these cursory tests are shown below.

Summary of Centrifuge Tests

<u>Test series</u>	<u>Machine speed, rpm</u>	<u>Centrifuge feed source</u>	<u>Feed rates, gpm</u>	<u>Wt % solids in feed</u>	<u>Wt % moisture in cake</u>	<u>Wt % solids in centrate</u>
I	2000	HF clarifier bottoms	11-22	15-22 ^a	43-47	0.2-0.6
II ^b	2000	HF clarifier bottoms	10-22	16-24 ^a	44-46	0.3-0.5
III	2000	HF clarifier bottoms	10-22	19-29 ^a	39-42	0.1-0.5
IV	2500	HF clarifier bottoms	9-33	19-27 ^a	36-40	0.1-1.1
V	2500	Scrubber bleed (clarifier bypassed)	11-35	10-14	37-41	0.1-0.6

^a Increase the values by about 3 for pump seal water correction.

^b Test Series II was a replicate of Test Series I.

It appears that the centrifuge is effective in reducing the solids content well below the level attained by settling and that the centrate clarity is satisfactory. The centrifuge will be incorporated into the loop of one of the scrubbing systems for long-term tests.

Materials Evaluation

Selection of construction materials for components of scrubbing systems is an important economic consideration. One objective of the test program is to evaluate corrosion/erosion rates for alternate materials. The evaluation involves comparison of several different materials in installed components as well as exposure of test coupons at appropriate locations.

Equipment Inspection. A thorough inspection of all system components was conducted during the extended boiler outage. The systems had been operated during limestone scrubbing tests that totaled about 1800 hours for each train.

The mild steel gas ducts between the boiler and scrubber inlet transitions had localized deposits of loose fly ash. The surfaces had a thin coating of iron oxide scale except at uninsulated flanged connections where moderate pitting had occurred; these flanges are now insulated.

The rubber lining in the scrubbers was in excellent condition; no erosion or deterioration was noted. The rubber linings in pumps, piping, and process water tanks were also in excellent condition. Slight wear was noted on some of the rubber-coated agitator blades.

The only damage noted in the Flakeline lining in effluent hold tanks and clarifier tanks were several hairline cracks which did not appear to penetrate the entire thickness. The cracks were most prevalent at the junctions between the baffles and tank walls.

The most severe corrosion was found on type 316 stainless steel surfaces particularly on mist eliminator blades in the TCA system. The general attack was in the form of pitting and some pits were as large as 1/16-inch diameter and 30 to 35 mils deep.

The only significant erosion of equipment noted was on pump sleeves and at intersections of wires of support grids in the TCA scrubber. Weight loss of mobile bed packing material has also been detected. The polypropylene (and polyethylene) spheres in the TCA scrubber have worn noticeably. Some are so thin that they have lost mechanical strength and the walls have collapsed; a random sample of these showed about 60% weight loss. The bulk of the spheres were still intact but had an average weight loss of 20%. The glass marbles in the Hydro-Filter have lost about 6% of their initial weight.

Test Coupons. Test coupons of several different materials of construction were exposed for 70 days or more in various slurry and gas environments. Stressed and welded metallic materials were also tested.

Corrosion of Hastelloy C-276 was negligible to 5 mils per year; this alloy showed no evidence of localized attack in any test location. Next in resistance were alloys Inconel 625, Incoloy 825, Carpenter 20Cb-3, and Type 316L stainless steel with corrosion rates for each material ranging from negligible to 5, 7, 14, and 15 mils per year, respectively. These alloys had very few minute pits and/or crevice corrosion. One specimen of Type 316 stainless steel was grooved and the weld of another specimen was attacked. Type 316L is the fifth alloy in resistance and the least expensive of this group.

Three nonferrous alloys, Cupro-Nickel 70-30, Monel 400, and Hastelloy B each had minimum rates of < 1 mil and maximum rates of 49, 57, and 100 mils per year, respectively, with 1 or 2 specimens pitted. In three tests of Monel and in one test of Cupro-Nickel 70-30, the welds were inferior to the parent metal.

A group of five alloys, Type 446 stainless steel, E-Brite 26-1, Incoloy 800, USS 18-18-2, and Type 304 stainless steel, had rates that ranged from negligible to a "greater than" (>) value which indicates that the specimen was completely destroyed at one or more test locations. The values for failures ranged from > 140 mils per year for Type 446 to > 200 for both USS 18-18-2 and Type 304L stainless steels. These five alloys were highly susceptible to localized corrosion.

Another group of alloys, Type 410 stainless steel, aluminum 3003, mild steel A-283, and Cor-Ten B, had minimum rates of < 1 mil per year and maximum rate of >250 for Type 410 to > 1400 for mild steel and Cor-Ten B. Pitting and crevice corrosion occurred on the four alloys.

In general the stressed specimens (five alloys only) were not corroded at rates higher than their counterpart disk-type specimens.

Specimens of Bondstrand 4000, Flakeline 200, and Transite were tested at 21 locations. Bondstrand showed good resistance in 12 tests and poor in 9 tests. The evaluations for Flakeline and Transite were: good, 2 and 14; fair, 14 and 2; and poor, 5 and 5, respectively. Only 6 specimens each of Qua-Corr plastic and of butyl, natural, and neoprene rubbers were tested. The results were 5 good and 1 poor for Qua-Corr and 6 good for each of the rubbers.

Recommendations Based on Experience to Date

Some of the preliminary conclusions discussed in this section may change as more information is obtained during long-term tests. However, several large-scale installations are in the design stage and some of the trends which have been noted during operation of the test facility are worth considering.

Process Control

During the open-loop testing, runs at a given set of conditions were normally short (2 days or less). Process control during these tests was accomplished by setting the limestone feed rate at the value required for the desired stoichiometry based on SO_2 concentration in the inlet gas; slurry pH and removal efficiency were, therefore, dependent variables. This approach met the objectives of the test program.

When closed-loop testing was begun in March, the program emphasis was placed on long-term reliability tests. Because of the effect of pH on scale formation in the tests discussed under stoichiometry, it was decided to operate with pH control; the limestone feed rate is manually adjusted to maintain a nearly constant value of pH. System response has been good in the relatively low pH range (5.8-6.0) studied. It appears that if reliable pH meter operation can be established, automatic control of limestone feed rate to maintain pH at values below 6.0 would be feasible.

Gas Cooling

If a heat sensitive lining is used in the scrubber for erosion/corrosion protection, gas cooling ahead of the scrubber is required. Efforts to control solids deposits at the point of liquor or slurry addition have been only marginally effective when sprays are used. The venturi scrubber configuration provides a clean separation between the wet and dry areas and solids have not accumulated at the transition point.

When gas cooling by humidification ahead of the absorber is required, a venturi scrubber may be the most effective device for addition of the liquor.

Mist Eliminator

Most of the testing to date has been with excessive fresh water addition for washing the mist eliminators. This operation is not consistent with the long-term reliability evaluation. The systems recently have been

modified to permit use of recycled water for wash of the mist eliminators. The liquor has varied from a ratio 1 part fresh water to 3 parts clarified liquor to a half and half mixture. In the Hydro-Filter and venturi scrubbers the full underside is washed intermittently at a rate of about 1 gpm/ft² on a cycle that has averaged 1 minute on and 3 minutes off. In the TCA, the wash is added on a valve tray beneath the mist eliminator and entrained liquor from the tray flushes the underside of the eliminator.

No significant scaling has been detected although some solids deposits have occurred. It appears that precipitation on mist eliminator surfaces can be controlled by dilution of clarified liquor with available makeup water.

Reheaters

Use of direct-fired, in-line, oil burners for reheat can lead to incomplete combustion and accumulation of oil-saturated soot. The problem apparently has been solved at the test facility but turndown is complicated by the need for nozzle substitution.

Use of an external combustion system and admixture of completed burned combustion products with the scrubber exhaust gas would be a more satisfactory system for direct-fired reheat.

Clarifiers

The small (20-ft diameter) clarifiers appear to be underdesigned to provide both a dense underflow (40% solids) and a clear overflow. The settling rates and settled density of the sludge are poorer than the design basis and preliminary results indicated the volume of the clarifiers should be increased; the additional volume required has not been established.

The clarifiers appear to be underdesigned to provide both a dense underflow (40% solids) and a clear overflow. The settling rates and settled density of the sludge are poorer than the design basis and preliminary results indicated the volume of the clarifiers should be doubled.

SO₂ Analyzer

The continuous, on-line SO₂ analyzers (Du Pont Model 400 UV) are accurate and reliable provided that high-quality gas samples are delivered to the units. A nonplugging probe is needed and heated, well-insulated sample lines (Dekoron) are required to prevent condensation and plugging. Precise calibration techniques are necessary.

Materials of Construction

Rubber lining of scrubbers, tanks, pumps, and piping has been entirely satisfactory. Use of less expensive polyester-glass lining may be acceptable, but further exposure is required before a firm conclusion can be reached. Erosion of mobile-bed spheres has been excessive; improved materials

are being tested. Type 316L stainless steel has been badly pitted in partially wetted areas, particularly the surfaces of mist eliminators. Nonmetallic materials will be tested in these areas. Test coupons of highly resistant alloys (Hastelloy, Carpenter 20) have shown no signs of attack, but these are relatively expensive.

SCRUBBING EXPERIMENTS
AT THE MOHAVE GENERATING STATION

by

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PREFACE

The pilot testing program was set up to make comparative tests of different scrubber types and reagents to determine SO₂ and particulate removal capabilities. Reliability testing of mechanical equipment and hardware was not a part of the program. The performance results in the succeeding discussions therefore do not imply that reliable operation of these levels can be attained. The follow-on module program described will hopefully give a better measure of the total performance. It should be pointed out though that with the press of time a large step is being taken in proceeding from the pilot to the full size module, viz., good engineering practice would dictate an intermediate prototype first.

This paper presents work performed at the Mohave Generating Station during 1971 and 1972. Eight pilot plant scrubbers and four different reagents - soda ash, limestone, lime and ammonia - were studied. We intend to present some of the highlights of this work as well as the conclusions which allowed us to select two of the scrubber types for construction of two 450,000 scfm scrubbers. The work reported here was performed by a number of contractors and paid for by an even larger number of organizations.

Figure 1 (attached) presents some of the organizations which participated in this work.

Figure 2 presents a further description of the scrubbers.

The scrubbers were all essentially cylindrical in shape and, as may be seen, most of the scrubbers tested were between two and three feet in diameter, with the exceptions being the six foot diameter spray drier and the 19-inch diameter TCA. The scrubber lengths ranged from eight feet to 27 feet. However, although the scrubbers were somewhat comparable in physical size, their maximum gas handling capacity varied considerably ranging from 1100 scfm in the WPS to 3500 scfm in the SCE scrubber. It should be noted that the flow rates listed were not necessarily the optimum flow rate for SO_2 or particulate removal but the maximum (except for the SCE scrubber) under which the scrubber would operate. The capacity of a scrubber, rated in scfm per megawatt varies from station to station, depending on the type of fuel, the excess air used in combustion, the amount of leakage through air preheaters and other factors. At Mohave we have determined that 2800 scfm is approximately equal to one megawatt downstream of the electrostatic precipitators resulting in tested scrubber capacities from 0.4 to $1\frac{1}{2}$ megawatts. Actually, the capacity of the scrubbers is a function of the actual linear velocity through the scrubbers. While the temperature of the gas entering the scrubber varies considerably, the exit gas temperature remains constant, ranging from 120° to 130° F regardless of the outside air temperature. The gas at the exit is saturated with water. By using the exit gas conditions, the cross-sectional area of the scrubber, and the maximum scfm capacity of the scrubber we are able to calculate the "superficial" (i.e. disregarding scrubber packing) linear velocity through the scrubber and thus determine a relative "size factor" for extrapolation to larger scrubbers. In Figure 2 the scrubbers are listed in order of increasing linear velocity.

Finally, the last column in Figure 2 indicates the reagents tested with the scrubbers. Most of the experiments with AIS scrubber were performed with soda ash but a few experiments

Figure 1

MOHAVE SCRUBBER PROGRAM

360

	<u>SCRUBBER</u>	<u>MANUFACTURED BY</u>	<u>TESTING PERFORMED BY</u>	<u>WORK SPONSORED BY</u>
	WPS HYDRO PRECIPITROL	DESEVERSKY ELECTRO-NATOM CORP.	SCE-TRUESDAIL LABS	SCE
	CVS CHEMICO VENTURI	CHEMICAL CONSTRUCTION COMPANY	SCE-BECHTEL CORP.	NAVAJO AND MOHAVE PARTICIPANTS
	LIS PEABODY-LURGI IMPINGEMENT SCRUBBER	PEABODY ENGINEERING CO.	SCE-BECHTEL CORP.	NAVAJO AND MOHAVE PARTICIPANTS
	PPA POLYPROPYLENE ABSORBER	HEIL WITH FLUOR PACKING	SCE-BECHTEL CORP.	NAVAJO AND MOHAVE PARTICIPANTS
	TCA TURBULENT CONTACT ABSORBER	UNIVERSAL OIL PRODUCTS	SCE-BECHTEL	NAVAJO AND MOHAVE PARTICIPANTS
	SCE EDISON SCRUBBER	STEARNS-ROGER, INC.	SCE-TRUESDAIL LABS	SCE
	AIS ATOMICS INTERNATIONAL AQUEOUS CARBONATE SCRUBBER	BOWEN ENGINEERING CO.	SCE-ATOMICS INT'L.	16 UTILITIES WHO ARE MEMBERS OF WEST ASSOCIATES
	RHS ROTATING HORIZONTAL SCRUBBER	HAZEN RESEARCH, INC.	SCE, U.S. LIME, HAZEN RESEARCH AND NLA	NATIONAL LIME ASS'N. AND SCE

Figure 2

MOHAVE PILOT PLANT SCRUBBER TEST CONDITIONS

	<u>SCRUBBER</u>	<u>HEIGHT OR (LENGTH) FT.</u>	<u>DIAMETER (INCHES) I.D.</u>	<u>MAX. GAS FLOW RATE TESTED (SCFM 60°F)</u>	<u>LINEAR VELOCITY AT EXIT</u>	<u>TEST REAGENTS</u>
AIS	CONVENTIONAL SPRAYDRIER FOLLOWED BY CYCLONE SEPARATOR	12	72	1375	0.9	SODA ASH (LIME)
RHS	HORIZONTAL LIME KILN CONTAINING BALLS OR CHAINS	10	36	1300	3.4	LIME
CVS	SINGLE STAGE VENTURI WITH FIXED ANNULAR THROAT FOLLOWED BY CENTRI- FUGAL SEPARATING CHAMBER	8	26 3/4	1037	5.0	SODA ASH LIME LIMESTONE
WPS	VERTICAL ABSORBER FOLLOWED BY WET ELEC- TROSTATIC PRECIPITATOR	15 1/2	27 1/4	1100	5.1	AMMONIA
LIS	VARIABLE THROAT VENTURI FOLLOWED BY THREE-STAGE IMPINGE- MENT TRAY VERTICAL ABSORBER	14	30	1332	5.1	SODA ASH LIME LIMESTONE
PPA	VERTICAL ABSORBER PACKED WITH 7 1/2 FT. OF PLASTIC "EGG-CRATE" PACKING	12 1/2	24	1850	11.0	SODA ASH LIME LIMESTONE
TCA	VERTICAL TURBULENT CONTACT ABSORBER CONTAINING THREE STAGES OF "PING PONG BALLS"	27	19	1230	11.7	SODA ASH LIME LIMESTONE
SCE	FOUR-STAGE HORIZONTAL CROSS- FLOW SCUBBER	15	22	3500	24.9	LIME (LIMESTONE)

were performed with lime. On the other hand, most of the experiments with the SCE scrubber were performed with lime, with only a few experiments being performed with limestone. Ammonia, as gaseous ammonia and as ammonium hydroxide, was used only with the WPS.

Some of the variables studied in addition to the scrubber and reagent type included reagent composition (including pH and percent solids) and, in the case of lime and limestone slurries, the effect of soluble sodium salts such as occur in cooling tower blowdown water. The gas flow rate was an important parameter. As previously mentioned, there appeared to be an optimum gas flow rate for each of the scrubbers tested. Some of the scrubbers were operable over wider ranges than the other due to their construction. For example, with the TCA scrubber at too low a gas velocity the ping pong balls stayed immobile on the lower support screen while at a higher velocity they congregate at the top of the stage, i.e., the bottom of the next higher stage. The liquid flow rate and the L/G ratio (GPM/1000 scfm) were also important variables.

The number of stages was varied with the TCA scrubber and the SCE scrubber and we were quite pleased to find that our theoretical predictions on the effect of staging were confirmed experimentally.

The gas pressure drop was measured under a variety of conditions and this, of course, determined the fan requirements for larger size scrubbers. We operated with both FD and ID fans and perhaps we can summarize our findings in this area by indicating that both of our 450,000 scfm test modules will have FD fans even though the power required because of the higher gas temperature will be greater.

We also studied sludge separation with centrifuges, rotary filters and thickeners, the degree of oxidation from sulfite to sulfate and the properties of the slurry and the sludge itself.

It is not possible in the time allotted to present much more than a cursory overview of the effect of the different variables or to itemize all of the operating problems encountered with the various scrubbers. Primarily, the latter resulted from plugging in scrubbers, demisters, reheaters, centrifuges, and piping.

Effect of Inlet SO₂ Concentration and L/G

The Mohave Generating Station is located some 90 miles south of Las Vegas and burns low sulfur coal transported by a 285-mile slurry pipeline from the Black Mesa Mine. The average sulfur

content of the coal burned over the last two years was about 0.38% sulfur which results in less than 200 ppm of SO_2 in the exhaust gas.

After we initiated our experiments, it became evident that the SO_2 inlet concentration varied with the station operating conditions. In order to have consistent data we had to maintain the inlet SO_2 concentration at a constant value. Accordingly, we arbitrarily spiked the inlet gas to 400 ppm of SO_2 . This corresponds to about 0.83% sulfur coal, the highest sulfur content coal predicted for Mohave. In the two 450,000 scfm scrubbers that are currently under construction we will have to burn about five tons per day of sulfur per each scrubber in order to increase the concentration to 400 ppm for test purposes.

Most of the data presented in the remainder of this paper is based on an inlet gas concentration of 400 ppm of SO_2 .

We did perform some experiments, however, with five scrubbers on the effects of inlet SO_2 concentration. The data from one of these scrubbers is presented in Figure 3.

Prior to performing these experiments, our calculations, based on a rather simplistic theory, indicated that we should obtain straight, parallel lines at lower SO_2 concentrations, the degree to which they can be considered parallel is debatable. The shape of the curve near the origin varies with different scrubbers, being convex in some cases rather than concave as shown here.

Figure 3 does show, however, the effect of L/G on SO_2 exit concentration, i.e. increasing L/G increases the SO_2 removal. However, the CVS scrubber exhibited a minimum in the curve. That is, after a certain L/G was reached an increase in L/G resulted in an increase in SO_2 exit concentrations.

Often considerations of SO_2 removal specify scrubber performance in terms of percent sulfur removal without regard to the inlet SO_2 concentration. When the data in Figure 3 is presented in terms of percent SO_2 removed, as is shown in Figure 4, it is obvious that the inlet SO_2 concentration is an important factor in characterizing scrubber performance. While this data is for one scrubber at one gas flow rate, we have observed similar trends at other flow rates with four other scrubbers. Apparently this is due to the solubility of the reagent, the gas flow rate and the gas-liquid contacting mechanism.

In summary, Figure 4 indicates that for a given L/G ratio and gas flow rate, a decrease in the inlet SO_2 concentration results in an increase in the SO_2 removal efficiency, until some maximum

Figure 3

EFFECT OF L/G ON OUTLET SO_2
CONCENTRATION AT DIFFERENT INLET
CONCENTRATIONS SCE SCRUBBER
- 2500 SCFM

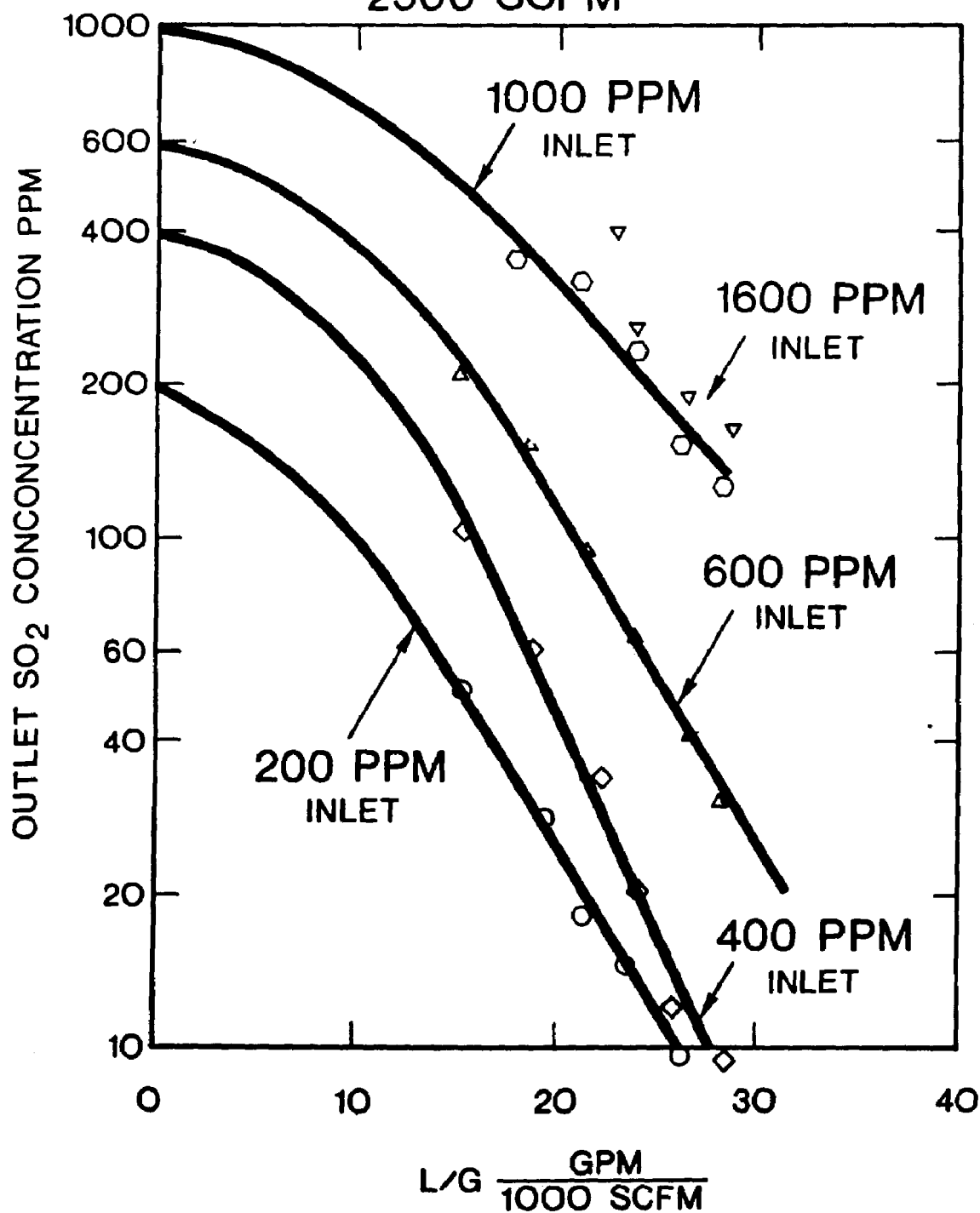
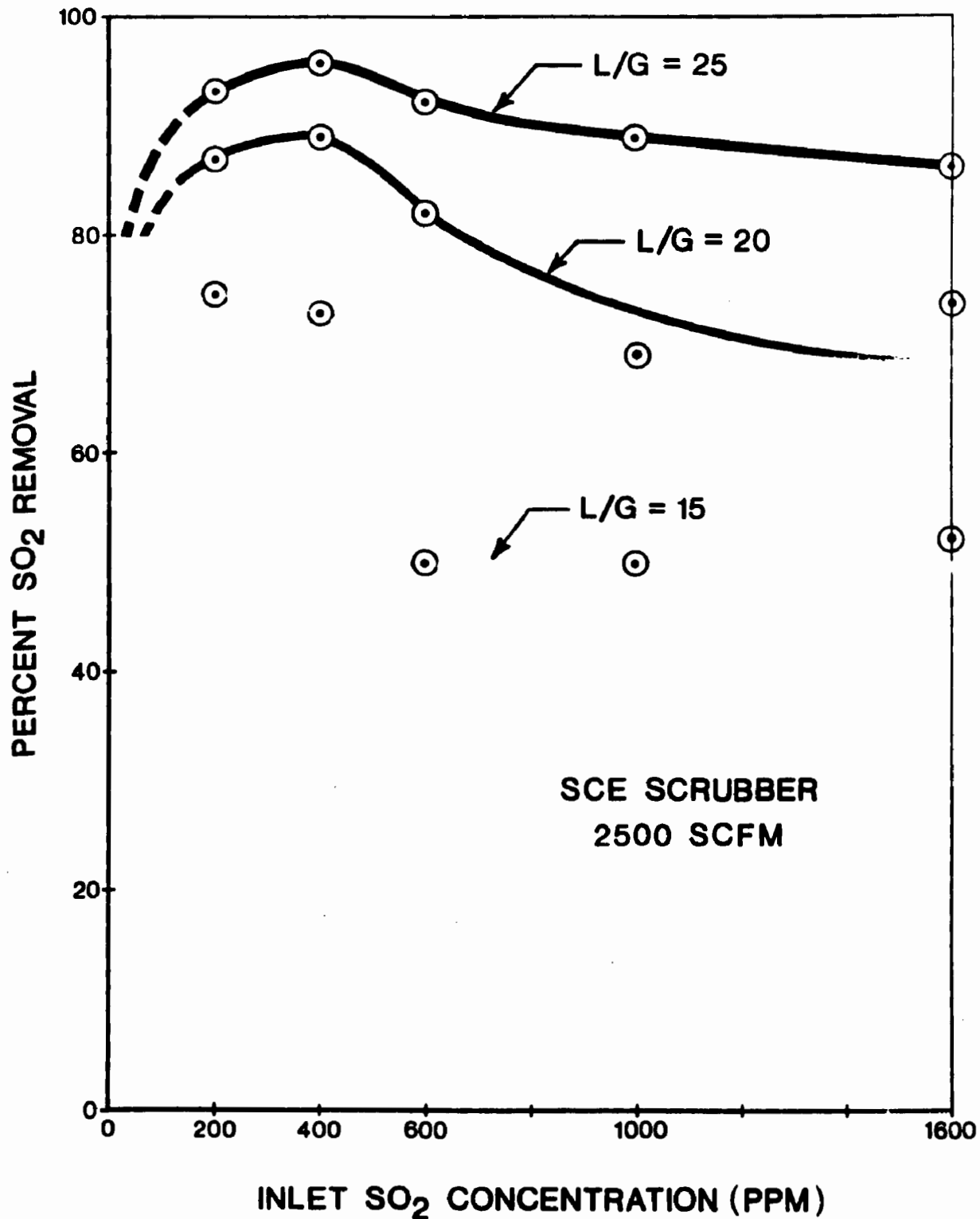


FIGURE 4

**EFFECT OF INLET SO₂ CONCENTRATION
ON PERCENT SO₂ REMOVAL**



removed efficiency (around 400 ppm of SO_2) is reached. At lower values of SO_2 inlet concentration, it becomes increasingly difficult to achieve high percentage SO_2 removal. Thus blanket edicts to remove a certain percentage of the sulfur in the fuel pose a problem for the scrubber designer as well as the utility user.

Reagent Comparison

Figure 5 presents a comparison of three different reagents in the same scrubber, the packed grid tower (PPA). As may be seen, with this scrubber soda ash is a much more efficient scrubbing reagent than limestone while lime is intermediate between the two. Also shown on Figure 5 are a few data points obtained with ammonia. Similar data for soda ash, lime and limestone obtained with the TCA scrubber are presented in Figure 6 along with the same ammonia scrubbing data obtained with the WPS. The data of Figures 5 and 6 indicate that the combination of ammonia used with the WPS scrubber is superior in SO_2 removal to soda ash, lime, or limestone used in either the PPA or TCA scrubbers. However, the experiments with ammonia were discontinued because of plugging difficulties in the scrubbing section of the WPS when operating on boiler flue gas. In addition, significant amounts of unreacted ammonia passed through the scrubber which creates an additional air pollution problem by substituting NH_3 for SO_2 .

The problems associated with NH_3 : its cost, the solubility of the sulfite-sulfate in water, disposal, the lack of a regeneration process, and the possibility of substituting ammonia for SO_2 , contributed to the decision not to perform any further tests with NH_3 , even though it appears to be the most reactive reagent.

While Figure 5 indicated that soda ash was the most effective scrubbing reagent at any given L/G ratio with the PPA, the data of Figure 6, with the TCA scrubber operating at its optimum gas flow rate of 1020 scfm, present a different story. With this scrubber, the data presented indicate that lime is a superior reagent to soda ash over the operable L/G range, and that limestone is superior to both lime and soda ash at L/Gs greater than 58. A similar anomaly also exists with the LIS scrubber as shown in Figure 7. With this scrubber, while soda ash is superior to lime, limestone is superior to soda ash at L/G ratios above 47. The superiority of limestone to lime in this scrubber was explained by the plugging with lime slurry on the underside of the impingement trays. The reason for the superiority of limestone to soda ash is difficult to explain. You will note, however, that the SO_2 levels in the region of interest in Figure 7 are below 6 ppm SO_2 . The same type of instruments (Dynasciences)

Figure 5
REAGANT COMPARISON

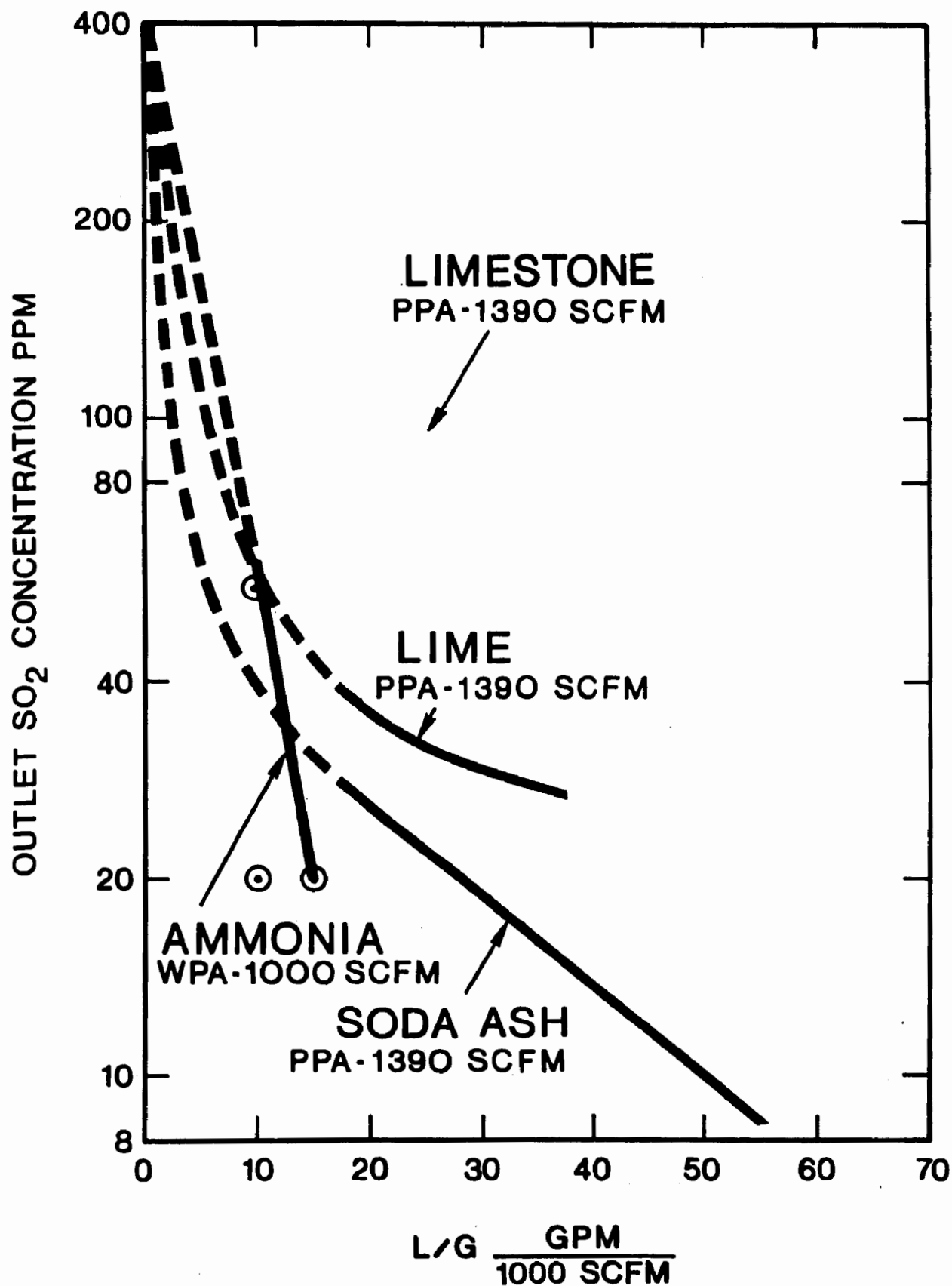


Figure 6
REAGANT COMPARISON

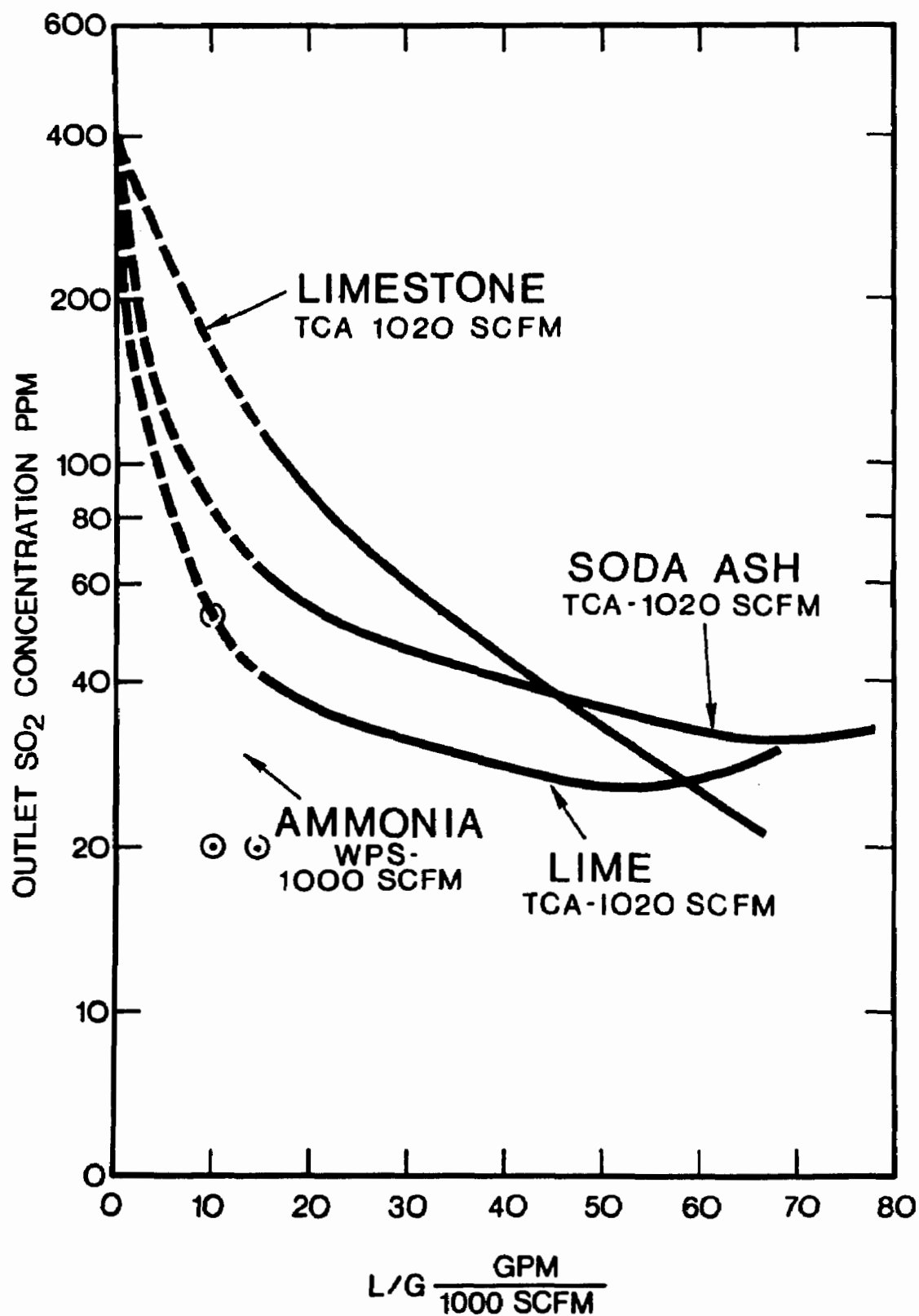
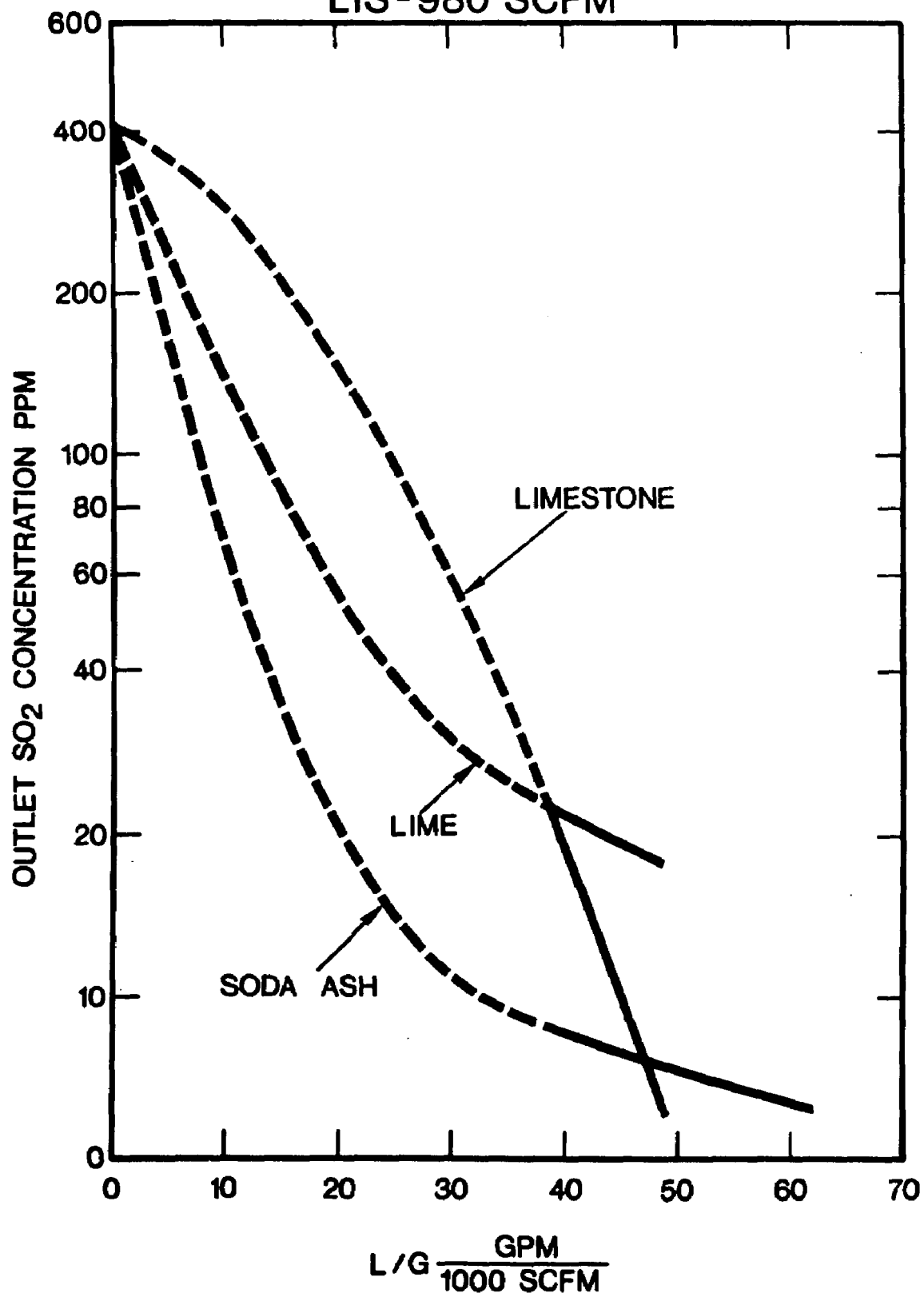


Figure 7
REAGANT COMPARISON
LIS-980 SCFM



were used in testing the PPA, TCA, LIS, CVS, SCE and AIS scrubbers and in all four instruments the presence of NO_x influenced the wet electrochemical cell. Specifically NO_x interference in the instrument resulted in readings of SO_2 8-10 ppm higher than actual. This correction had to be subtracted from the instrument reading.

It is possible that the superiority of limestone to soda ash in these two scrubbers is possibly due to measurement error. However, the superiority of lime over soda ash in the TCA scrubber is more difficult to explain and neither our test contractor nor their consultants was able to explain this anomaly.

With the few experiments with lime performed in the AIS scrubber, soda ash was more reactive, while in the SCE scrubber lime was a more reactive reagent than limestone. Comparative data with the three reagents utilizing the Chemico Venturi scrubber is presented in Figure 8. With this scrubber the exit SO_2 levels are high enough (168 ppm with limestone, 120 ppm with lime, and 55 ppm with soda ash, based on 400 ppm inlet concentration) to eliminate possible instrument measuring errors. This data indicates, as expected, that soda ash is superior to lime which in turn is superior to limestone. In this scrubber, operating at its optimum gas flow rate of 950 scfm, the SO_2 removal efficiency (based on 400 ppm inlet SO_2 concentration) at the optimum L/G ratio of 43, was about 86% with soda ash compared to 58% with limestone.

Because of the solubility of sodium salts, a sodium system offers many advantages due to reduced probability of scrubber plugging. However, the cost, without regeneration, is high. Approximately \$500,000 dollars was spent trying to regenerate the sodium scrubbing solution on a pilot plant scale without success. Laboratory experiments indicated that we could regenerate a sulfite-bisulfite solution with lime, but not with limestone. However, on the pilot plant scale using actual stack gases, we found considerable oxidation of the sulfite to sulfate and we were not able to regenerate the sulfate. In addition, the regeneration pilot plant design was such that the calcium and sodium systems become intermingled and we had plugging of scrubbers and centrifuges with the calcium salts. We hope that the other papers in this symposium on double alkali processes will be able to report more success with their experiments than we are able to report.

Scrubber Comparison

Comparative data on five scrubbers operating with soda ash is presented in Figure 9. This indicates that the AIS scrubber requires a much lower L/G ratio to reach an exit gas concentration of 40 ppm (90% removal) than the TCA, PPA, LIS or CVS scrubber

Figure 8
REAGANT COMPARISON
CVS-950 SCFM

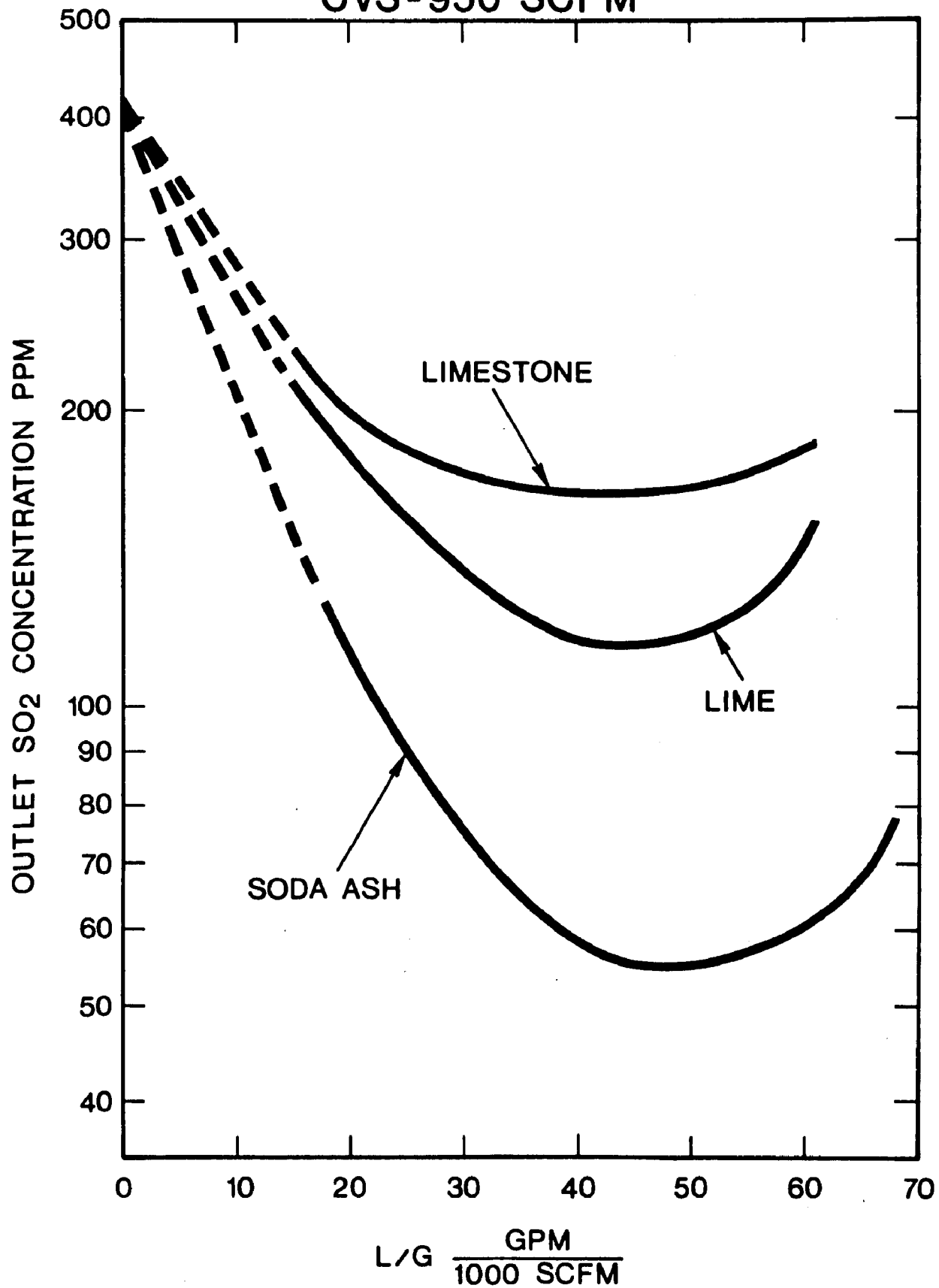
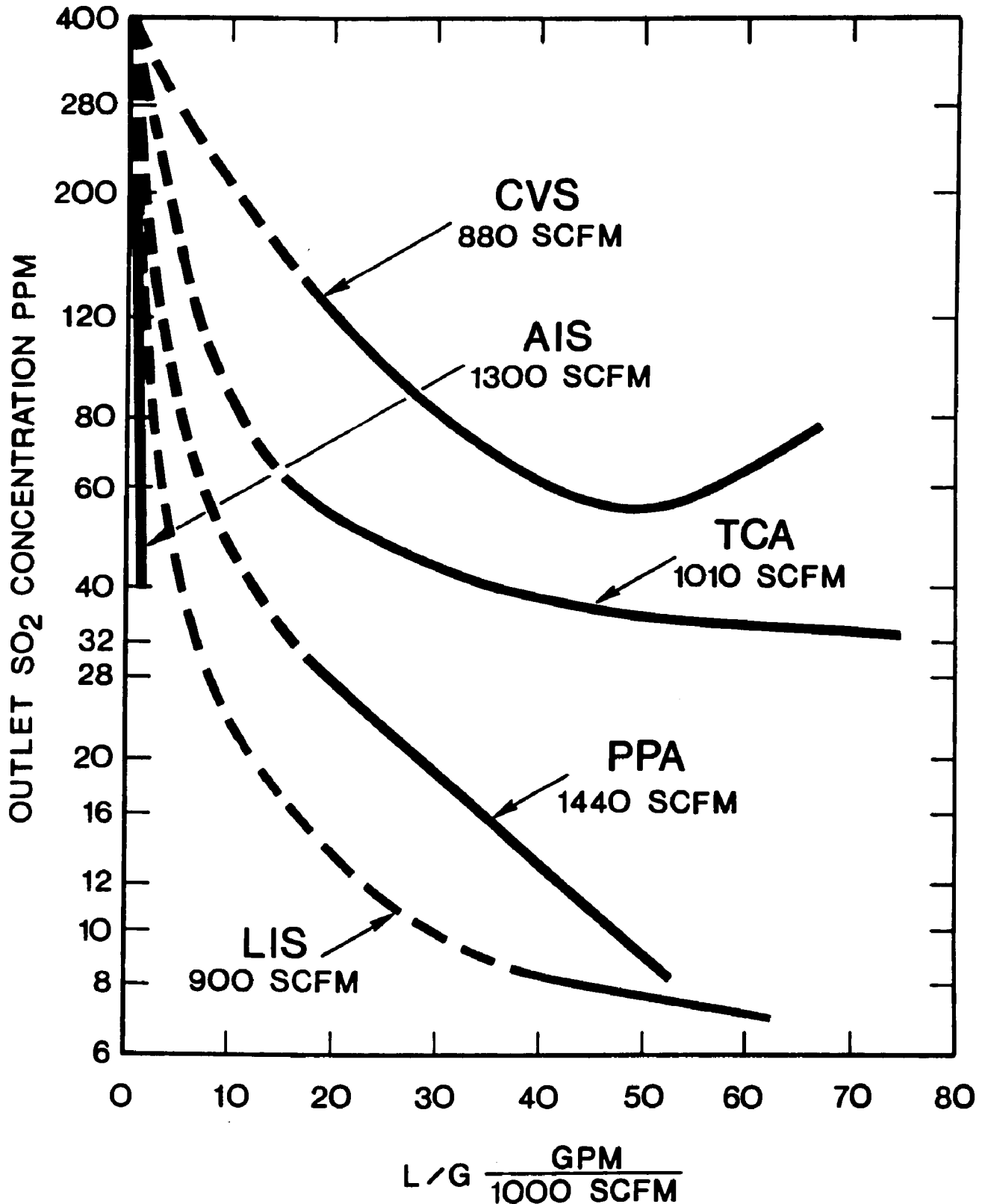


Figure 9

SCRUBBER COMPARISON - SODA ASH



as well as indicating that the CVS scrubber, as tested, was unable to achieve an exit SO_2 level of 40 ppm even with soda ash.

Similar data with limestone is presented in Figure 10. As indicated, the LIS scrubber (a Lurgi Venturi followed by a three-tray tower) was able to achieve the lowest SO_2 exit concentrations (around 7 ppm SO_2) while the CVS scrubber minimum SO_2 concentration (ca. 170 ppm) was considerably above the desired 40 ppm.

Data on six scrubbers with lime is presented in Figure 11. This data indicates that the RHS scrubber requires the lowest L/G ratio to achieve the desired 40 ppm SO_2 outlet concentration. The mechanism of operation of this scrubber makes it difficult to really determine the real ratio of liquid to gas because of the "random" method of contacting. The L/G presented in Figure 11 for the RHS is based on the lime feed rate, the actual amount of liquid contacted per unit of gas flow is undoubtedly higher.

The L/G ratio used for the SCE scrubber was the actual amount of liquid contacted with the gas, but since this scrubber is a four-stage device, this amount of liquid is contacted with the gas four different times. Thus, the L/G as plotted is correct for comparison of mass transfer performance, but the amount of liquid pumped should be multiplied by four to compute the horsepower required for liquid pumping to be on a comparable basis with the other scrubbers tested. The total horsepower required is composed not only of the liquid pumping horsepower (and in the case of the RHS, the power required to rotate the scrubber) but also that of mixers, thickeners, instruments, etc. The major contributor in most of the scrubbers tested, the fan power required, is a function of the pressure drop through the system.

Reagent Utilization

The composition of the scrubbing reagent influences the degree of reagent utilization as well as scrubber performance. At Mohave, cooling tower blowdown water is to be used as makeup water for the scrubbers, therefore experiments with added soluble sodium salts were performed. This was found to increase the scrubber performance with limestone slurries. Calculations indicated that with a 5% NaCl - 5% Na_2SO_4 solution saturated with CaCO_3 , the sorption capacity on a once-through basis was almost five times greater than with a solution saturated with CaCO_3 alone. These calculations also indicated that the contribution of sodium sulfate is more effective than that of sodium chloride. Experiments with sodium salts added to a soluble lime slurry did not seem to improve the performance of the SCE scrubber.

Figure 10

SCRUBBER COMPARISON - LIMESTONE

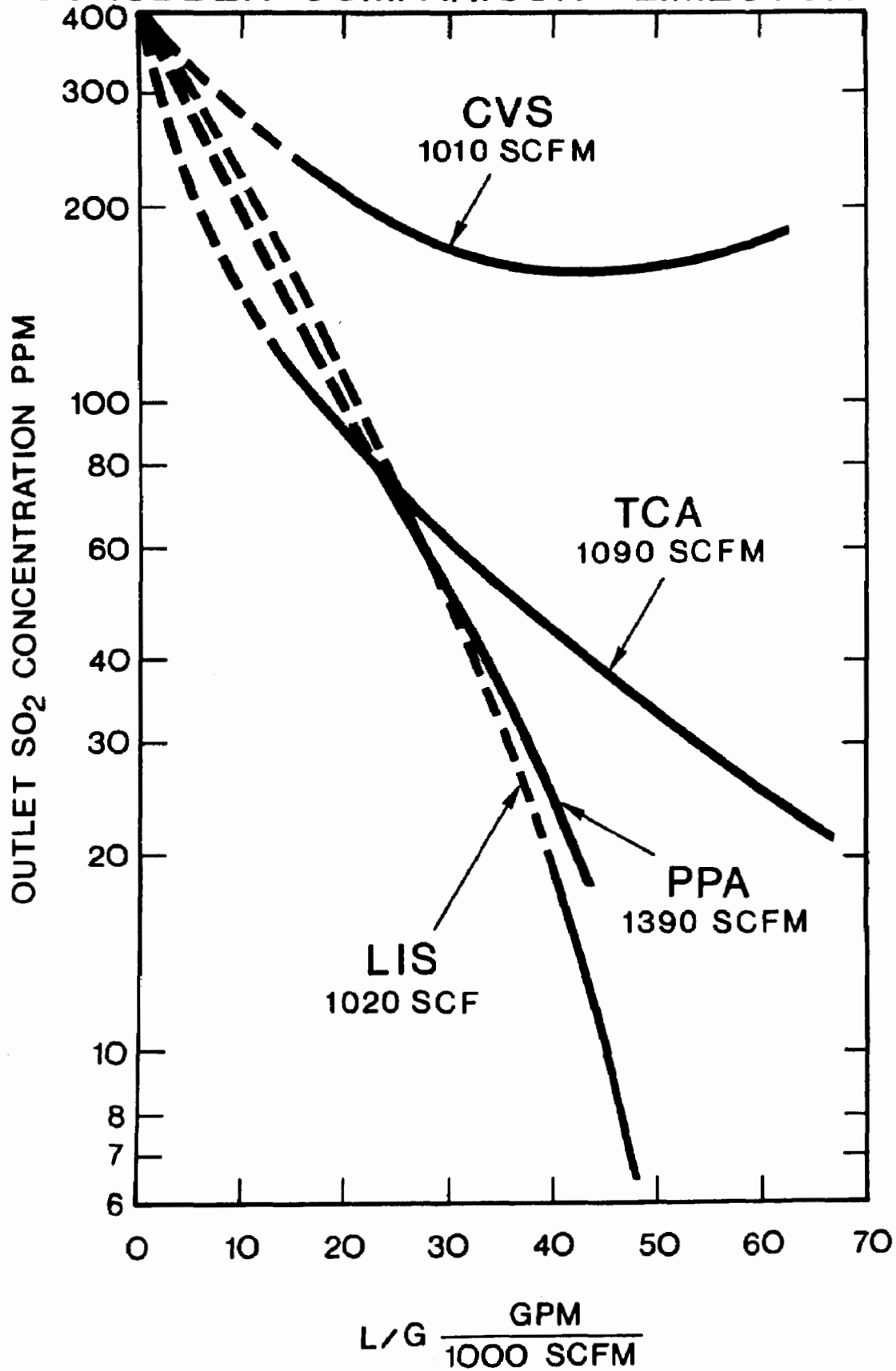
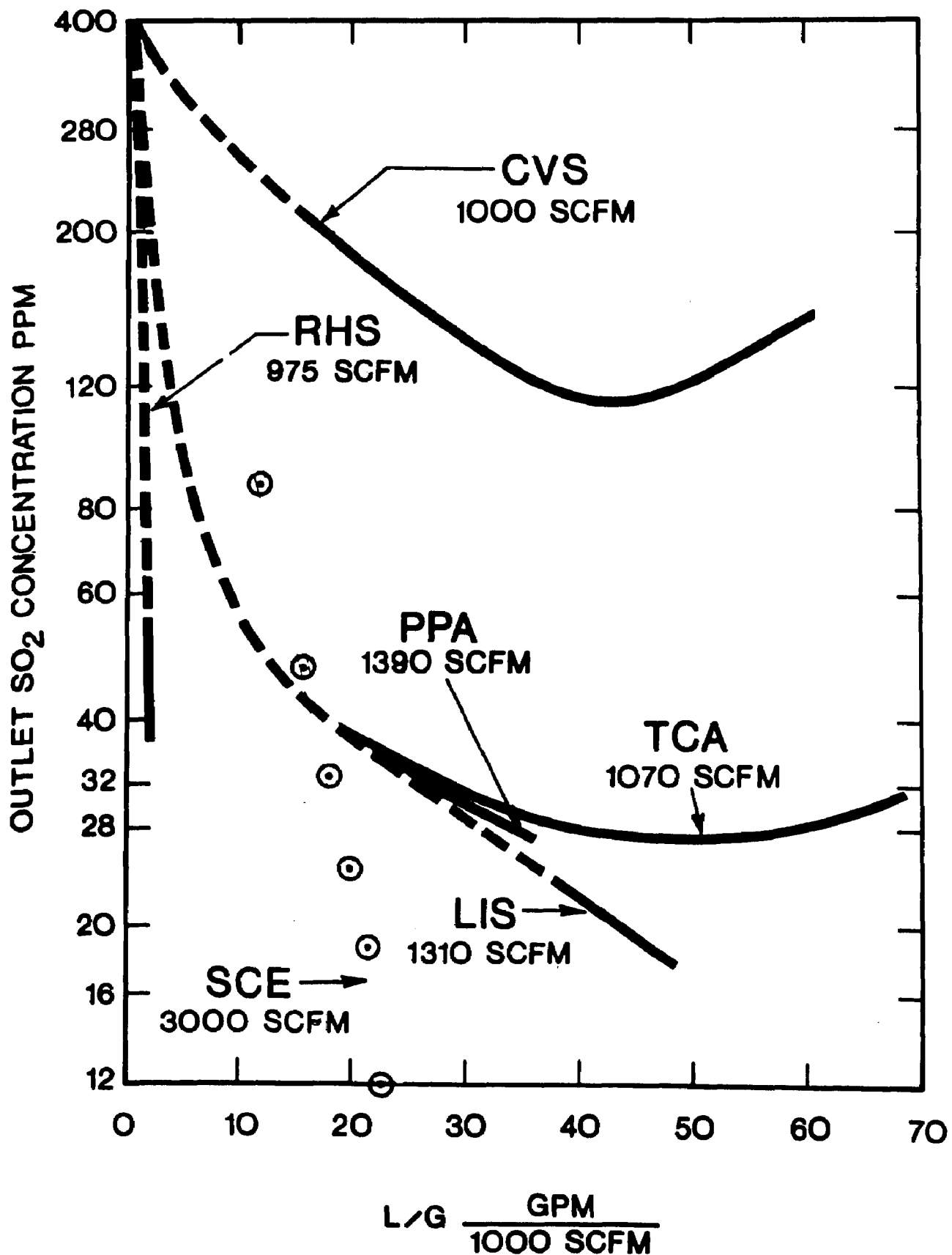


Figure 11
SCRUBBER COMPARISON - LIME



Increasing the suspended solids (i.e. calcium sulfate, calcium sulfite and unreacted calcium carbonate) concentration from 5% to 15% and reducing the calcium carbonate concentration from 1.5 to 0.5% would increase the limestone utilization rate since less unreacted limestone would be lost with the filter cake.

Thus, in the first case

$$\text{limestone utilization} = 1 - \frac{1.5}{5} = 70\%$$

While in the second case

$$\text{limestone utilization} = 1 - \frac{0.5}{15} = 96.6\%$$

Experimental values in the first case were around 66%, while in the second case were around 95% as indicated in Figure 12. As indicated, experimental determination of the degree of reagent utilization is difficult. In this four-day test, five different methods were used, four of them based on time-consuming wet chemical analyses of the cake and the slurry, the fifth based on the SO₂ removal from the gas. As may be seen, this latter method indicated a limestone utilization rate of 117%.

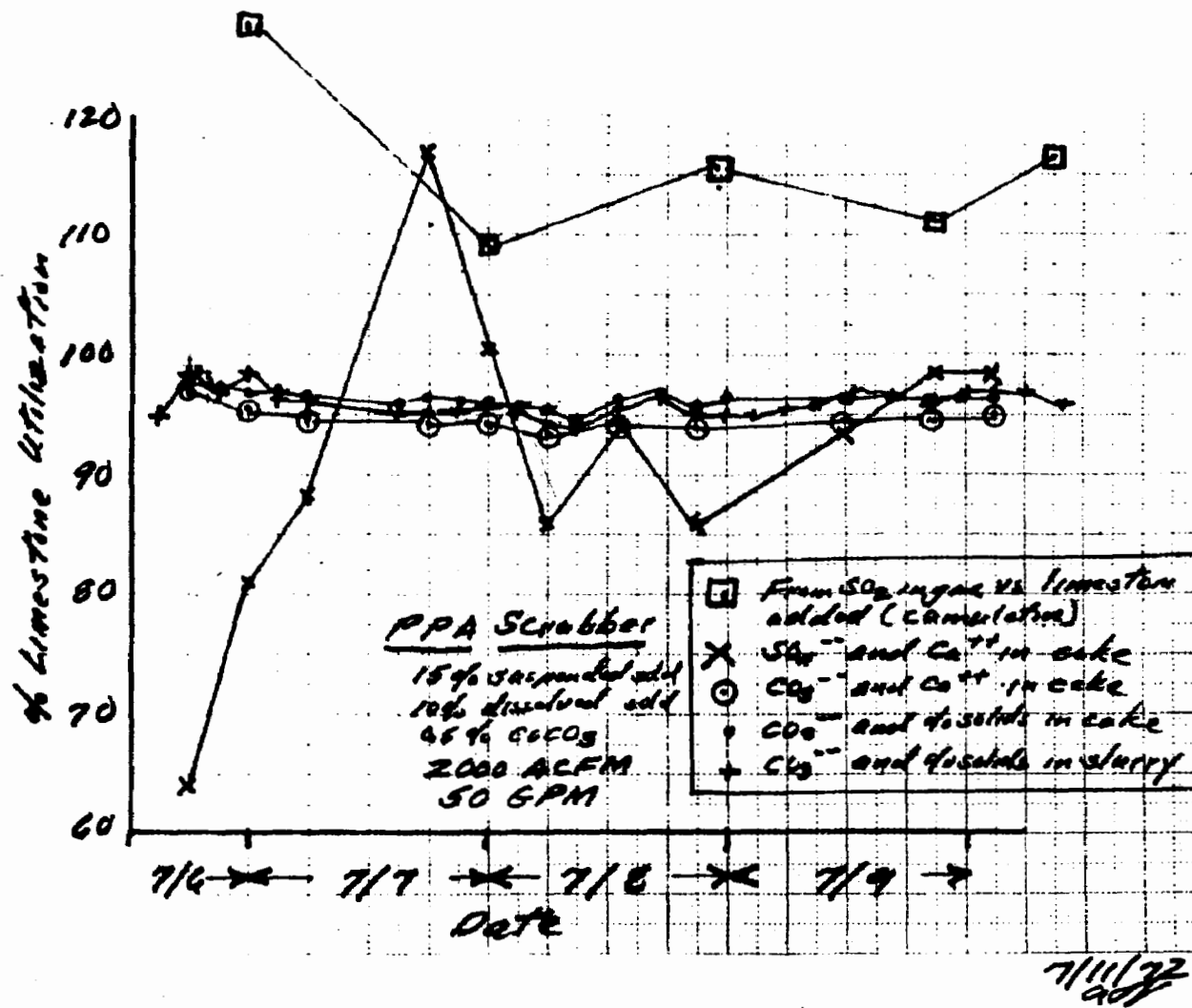
It should be pointed out that, while increasing the solids content in a limestone scrubbing slurry increases the degree of reagent utilization, it also increases erosion of nozzles and pumps as well as increasing the probability of plugging. It was for this reason that our 450,000 scfm Vertical Module is being designed to use a 5% rather than a 15% solids slurry.

Experiments with the SCE scrubber using a soluble lime solution were made to determine the degree of reagent utilization. In one 75-hour test, this was determined to be 93.3% while in a second 159-hour test, the degree of reagent utilization was 92.8%.

Particulate Removal

An objective of the Mohave Test Program equal in importance to SO₂ removal has been that of particulate removal downstream of the 98% efficient electrostatic precipitators. The dust loading downstream of these precipitators, based on two years of operating experience and the manufacturer's guaranteed performance with all sections in service, is 0.05 grains/scf. Optimum precipitator performance has typically met the manufacturer's expected performance with all sections in service of a dust loading of 0.03 grains/scf. Most of the data presented in Figure 13 was based on inlet grain loadings ranging from 0.01 to 0.02 gr/scf. However, with some precipitator sections out of service, due to discharge wire failures, the precipitator manufacturer would

FIGURE 12
DETERMINATION OF LIMESTONE UTILIZATION
BY DIFFERENT METHODS



expect grain loadings as high as 0.095 gr/scf and we have occasionally recorded grain loadings this high. Figure 13 presents a composite of the particulate removal data obtained downstream of these precipitators with five different scrubbers. There are many variables which affect particulate removal performance, for example increasing the gas flow rate (and hence the pressure drop) seems to increase the particulate removal performance on the CVC, PPA, TCA and LIS scrubbers and in the SCE scrubber at gas flow rates above 1750 scfm. Increasing the liquid flow rate on the SCE scrubber is beneficial, at 2500 scfm, the particulate removal efficiency is increased from 75% to 90% by increasing the liquid flow rate from 50 to 66 GPM. At a given liquid and gas flow rate, we have obtained good data correlations (with TCA, PPA, CVS, and SCE scrubbers) on a log-log plot of % particulate removal versus inlet grain loading. A straight line results with increased particulate removal at higher inlet grain loadings.

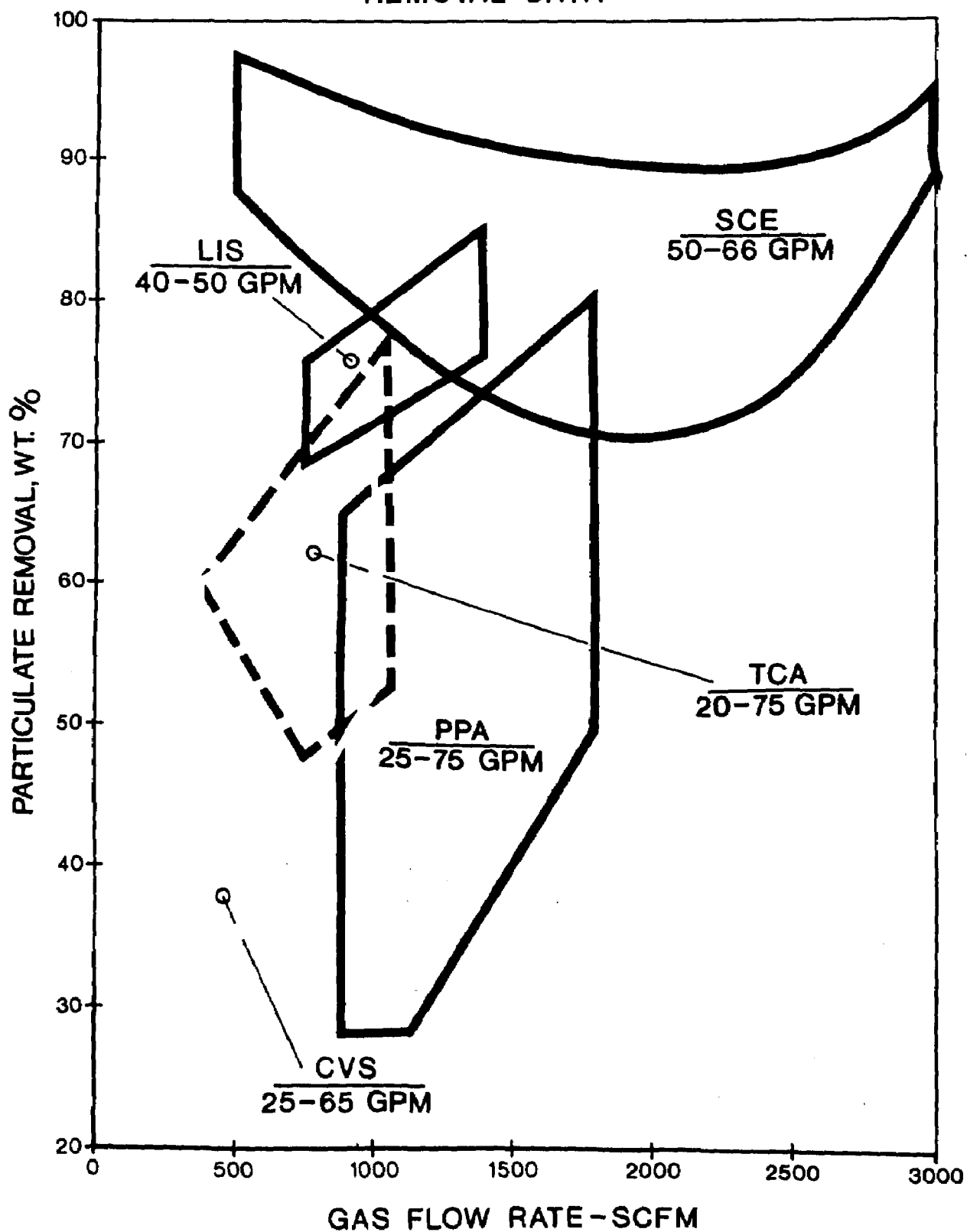
This increased efficiency at higher inlet grain loadings is undoubtedly due to the fact that at higher dust loadings the stack gas is composed of larger diameter particles due to precipitator sections being out of service.

Particle sizes in the stack gas at Mohave are normally very small. About 90 cumulative wt % of the particles are less than 4 microns in diameter with 70 wt % less than 1 micron in diameter, 40 wt % less than 0.5 micron in diameter and about 15 wt % less than 0.3 micron in diameter. With the SCE scrubber, our test data indicated about 75% removal of 0.3 micron diameter particles, 87% removal of 0.5 micron particles, 96% removal of 1.0 micron diameter particles, and 97% removal of 1.5 micron diameter particles.

Pressure Drop

One important characteristic of a scrubber which contributes a great deal to both the capital cost and the operating cost is the pressure drop through the scrubber. The pressure drop is, of course, primarily a function of the mechanical design of the scrubber. Plugging of the scrubber or demister and operation near the flooding point (particularly with the TCA scrubber and the LIS scrubber) caused extremely high pressure drops. Partial plugging occurred with all of the scrubbers tested, particularly with hydrated lime slurries, except with the SCE scrubber. This scrubber also had the lowest pressure drop (ranging from < 0.1 inch of H_2O at 500 scfm to 1.3 inches of H_2O at 3500 scfm) of any of the scrubbers tested. The contribution of dynamic pressure ($\frac{1}{2} \rho v^2$) and L/G ratio to the pressure drop through this scrubber have been quantified and a plot of all of the pressure drop data on a single curve by plotting $\frac{1}{2} \rho v^2$ versus L/G has been obtained.

FIGURE 13
MOHAVE PILOT PLANTS
PARTICULATE
REMOVAL DATA



It was found that the contribution of skin friction and wake contribution of the stage separations was about $7 \left(\frac{1}{2} \rho v^2 \right)$ while that of the liquid spray was about $0.4 \left(\frac{1}{2} \rho v^2 \right) (L/G)$ so that pressure drop could be correlated by the following equation:

$$P = [7 + 0.4 (L/G)] \left(\frac{1}{2} \rho v^2 \right)$$

Comparison of pressure drop through the various scrubbers is presented in Figure 14.

Operating Problems

Insufficient time prevents a detailed discussion of all of the operating problems encountered in the pilot plant program. As previously mentioned, tests with the WPS were discontinued primarily due to plugging, although unreacted ammonia passing through the device also was a contributing factor in this decision. There was an accumulation of solid material at the wet-dry interface with the RHS device, the lime utilization rate was high, and particulate removal performance was marginal.

The planned test program of the AIS was completed but the mode of operation was found to be different than that originally proposed. Initially it was planned to operate the spray drier with a thick slurry feed so that the spray droplets would be "BB sized" particles when dried. It was postulated that this size particle could easily be collected in the downstream cyclone separator. However, when the spray drier was operated in the slurry (as contrasted to solution) mode (about 30 wt % Na_2CO_3) it was found that the soda ash utilization rate was about 25%, making the reagent cost prohibitive. When the spray drier was operated with lower concentration solutions, the droplets formed, and hence the dried particles, were too small to be collected efficiently in the mechanical separator. In many of the experiments, the dust loading leaving the system was greater than the inlet dust loading.

Bechtel's test report on the LIS device stated "The Lurgi impingement scrubber scaled up so badly several times in the lime slurry tests that the desired gas flow rate could not be maintained." Various parts had to be wire brushed, scraped, or acid cleaned. The vanes above the venturi also had to be acid cleaned and the vane demister plugged. In the limestone tests, appreciable build-up occurred on the underside of the impingement trays as well as a considerable accumulation of solids in the bottom of the liquid downcomer trays. Flooding difficulties caused cancellation of the tests at the higher liquid and gas rates.

Figure 14

SCRUBBER PRESSURE DROP

<u>SCRUBBER</u>	ΔP <u>INCHES OF H₂O</u>	<u>GAS FLOW RATE</u> <u>SCFM</u>	<u>L/G</u> <u>GPM/1000 SCFM</u>
SCE	1.0	3000	17
PPA	2.5	1390	54
TCA	6.2	1020	67
CVS	9.0	950	36
LIS	11.5	1300	35

The PPA liquid inlet spray header plugged several times as did the coarse screen and strainer intended to protect this header. A thick scale was also deposited on the egg crate packing. With regard to the demister, the Bechtel test report stated "The PPA absorber demister was completely unsatisfactory for hydrated lime slurry operation." After a ten-day test with limestone, it was found that a hole had been eroded in the fiberglass wall from the force of the slurry spray.

During initial limestone tests with the CVS there was an appreciable buildup of solids (about one inch thick) in the duct from the venturi to the demister. After a ten-day run, the thickness of these solids was between 2 and 3 inches. A slight buildup of solids occurred in the separator. With the lime tests, only a relatively thin scale was deposited in the throat, but thick ($1\frac{1}{2}$ inch) scale was deposited on the vessel walls and the line to the entrainment separator. This scale also plugged the pressure measurement lines, thus explaining some of the erratic BP measurements obtained. The major problem with this scrubber was its relatively low SO₂ removal efficiency.

The major difficulty with the TCA scrubber concerned erosion of the "ping pong" balls. Initial measurements after about 200 hours of operation indicated a wear rate of about 0.5 percent per day. For the ten-day test with limestone, new balls were used and the loss in weight over 10.8 days was 4.45% loss (0.246 grams/ball) or 0.43% per day loss. The problem with ball erosion, in addition to the cost of ball replacement every three or four months, is that when the balls wear through, they fill with slurry and the balls remain immobile. Eventually, the slurry solidifies and if enough balls are immobile the pressure drop increases greatly. This spring, balls constructed of a new flexible soft material instead of the previous hard material were tested. However, in several days of testing so many of these balls split in half that they were all replaced with the old style balls. There were other difficulties with the TCA scrubber; spray nozzle erosion, demister plugging, and some buildup of solids in low velocity areas.

As previously indicated, there were no difficulties with the SCE scrubber itself. There were problems with pump seals, as there were with all of the scrubbers, but the design of this scrubber is such that one pump can be taken out of service and repaired without degradation of the exit SO₂ concentration.

As previously indicated, difficulty was experienced with I.D. fans due to uneven buildup of material on the rotors. More problems were experienced with centrifuges than rotary filters.

Reagent Cost

The annual cost of the reagents is a significant contributor to operating costs. Since each mole of SO_2 required to be removed requires one mole of lime (CaO) or limestone (CaCO_3) or soda ash (Na_2CO_3), the theoretical minimum requirements (100% purity of reagents, 100% utilization) to remove 32 lbs of sulfur or 64 lbs of SO_2 are 56 lbs of CaO or 100 lbs of CaCO_3 or 106 lbs of Na_2CO_3 . Based on supplier quotations for delivery to the Mohave Generating Station, 90 miles south of Las Vegas, Nevada, and including a delivery charge of \$5/ton, the information presented in Figure 15 was prepared. The important fact to note is that if limestone is used in the "non-optimal utilization" system, lime costs on an annual basis are lower. On the other hand, if an "optimal utilization" limestone system is used, maintenance costs could be higher due to the higher solids concentration in the slurry system. Furthermore, this system has a greater potential for plugging and particulate carryover.

Reagent and Scrubber Selection for Full Scale Testing

It should be emphasized at this point that the evaluation made by Southern California Edison of various scrubbers and reagents applies only to the Mohave Generating Station. Different conditions at other generating stations might lead to conclusions different than the ones reached here.

The criteria on reagent cost and operation have been summarized on a comparative basis in Figure 16. The numerical ratings range from 0 to 3, with 3 representing outstanding performance, 2 average, 1 poor and 0 assigned where the minimum required performance was not demonstrated.

Figure 16 compares potential scrubbing reagents in terms of performance, cost and control factors. Based on the pilot plant data, the best reagent system is soluble lime. Except for the potential plugging problems with certain types of scrubbers, this reagent has exhibited overall good characteristics. Without regeneration, the cost and waste disposal problems associated with soda ash are prohibitive. Limestone, the other possible reagent choice, suffers in regard to removal capability and system control. The addition of sodium and/or solids to limestone salts improves performance but increases the waste disposal problem. Ammonia is not recommended at all due to the potential presence of ammonia in the stack gas.

Based on the experimental data, operating problems and the SO_2 and particulate removal needs at Mohave and Navajo Projects, the

FIGURE 15

REAGENT COSTS

	<u>LIMESTONE</u>	<u>LIMESTONE + (NA & SOLIDS)</u>	<u>LIME</u>	<u>SODA ASH</u>
% UTILIZATION	66	95	98	99
REAGENT REQUIRED (LB/LB OF SO ₂)	1.56/1	1.56/1	1.88/1	1.66/1
REAGENT COST (\$/TON TO MOHAVE)	12.50	12.50	21	50
ANNUAL COST	\$1,725,378	\$1,198,684	\$1,090,500	\$4,896,160

Figure 16
COMPARISON OF SCRUBBING REAGENTS

<u>CRITERIA</u>	<u>SODA ASH</u>	<u>SOLUBLE LIME</u>	<u>0.5% LIME</u>	<u>LIME- STONE</u>	<u>LIME- STONE + SODIUM</u>	<u>LIME- STONE + SODIUM + SOLIDS</u>	<u>AMMONIA</u>
SO ₂ REMOVAL	3	2.5	2.5	1	2	2	3
UTILIZATION	3	3	2	2	2	3	1
385 EROSION & WEAR	3	3	2.5	1	1	0	3
MATERIAL COST	1	3	3	2	2	3	1
DISPOSAL	0	3	3	1	1	1	0
LIQUOR CONTROL	2	3	2	1	1	1	2
PLUGGING & SCALING	3	2	1	2	2	1	2
TOTAL	15	19.5	16	12	11	11	12

following conclusions were reached:

1. It is essential that a full scale prototype scrubbing system be constructed and operated reliably before selection and installation of equipment to treat all of the stack gas at either Mohave or Navajo.
2. Construction of two different test module systems would give a higher probability that a workable system for the entire plant could be developed in a reasonable time frame.
3. The scrubber/reagent combinations which seemed to offer the greatest chance of success were the TCA scrubber using limestone and the SCE scrubber using lime.
4. Flexibility should be included in the systems design including provisions to incorporate packing other than ping pong balls in the TCA scrubber and the ability to test this scrubber with lime and the SCE scrubber with limestone.

Although we believe the Mohave Generating Station today is one of the "cleanest" coal burning stations in the United States, with SO₂ emission levels ranging from 200 to 250 ppm and dust loadings from 0.01 to 0.03 grains/scf, Clark County, Nevada District Board of Health believed that an improvement was necessary. Clark County adopted a regulation limiting SO₂ emissions to 0.15 lb SO₂/million Btu after the plant was in operation. In January of this year, the Clark County authorities granted variances for Mohave which require compliance with this SO₂ emission limit. This is intended to provide the time required to carry out the required prototype module test program. This program includes installation and testing of two different scrubber module prototypes each having a capacity equal to one-fifth the stack gas flow for each of the two Mohave boilers. Based on module test results and operating experience, the type and specific design for the full scale scrubber systems would then be selected.

In accordance with this compliance plan and variance, we started construction February 15, 1973, of two 450,000 scfm test modules at Mohave. The time allowed for design and construction of these modules is extremely short, particularly since we believe that a 450,000 scfm scrubber is larger than any operating today in the United States. We are required to start checkout of the Horizontal Module by November 1, 1973 and commence operation by December 1, 1973 with checkout of the Vertical Module to start January 1, 1974 and operations commencing March 1, 1974. However, we are proceeding with this "forced draft" schedule in order to have

time for an abbreviated test program before selecting the final module design. At the conclusion of our test period, we will construct at least ten more modules of similar size at Mohave.

These test modules are based on the results of our pilot plant tests but represent a considerable increase in size. Normally, good chemical engineering practice would be to extrapolate pilot plant data by a factor of 10 when installing a new chemical process. However, with the Horizontal Module, which is based on the SCE scrubber, we also have a new unconventional piece of equipment, the scrubber itself. Considering the difficulties encountered with other large scale scrubbing systems, it required considerable management fortitude to start construction of a new device 150 times larger than was tested on a pilot plant scale. The relative scale up is shown in Figure 17 which is an artist's rendering of the full size scrubber compared to the initial pilot plant.

The Vertical Module is based on the TCA scrubber. Construction of a 450,000 scfm TCA scrubber represents a size factor increase of 450 over the 1,000 scfm pilot plant scrubber data. While TCA scrubbers have been constructed in larger sizes at other locations, operating difficulties informally reported to us by other utilities did nothing to allay our fears. Therefore, provisions are being incorporated in the design of this scrubber to allow us to replace the balls and screens, if necessary, with the PPA type egg crate packing or other packing material or possibly convert the device to a simple spray tower. An artist's rendering of the Vertical Module is presented in Figure 18, compared to the initial pilot plant size. Unfortunately, the man in Figure 18 is smaller than the man in Figure 17 so that a visual size comparison of the two scrubbers is not available.

Some comparative information being incorporated in the test modules design is presented in Figure 19. It is perhaps of interest that an 18 MW transformer is being installed to provide power for these two 160 MW modules. However, the 6000 hp F.D. fan motor for the Vertical Module will obtain power directly from a 13.8 kV source.

Acknowledgement

As indicated previously, testing of the TCA, PPA, LIS and CVS scrubbers was paid for by the Navajo Project Participants (Salt River Project - Operating Agent, Arizona Public Service Company, City of Los Angeles Department of Water and Power, Nevada Power Company, Tucson Gas and Electric Company, and the United States Bureau of Reclamation) and the Mohave Project Participants (Southern California Edison Company - Operating Agent, City of Los Angeles Department of Water and Power, Salt River Project, and Nevada Power Company). Southern California Edison served as Program Manager for these tests while Bechtel Corporation served as the test contractor.

SIZE COMPARISON BETWEEN PILOT AND FULL-SCALE HORIZONTAL SCRUBBERS

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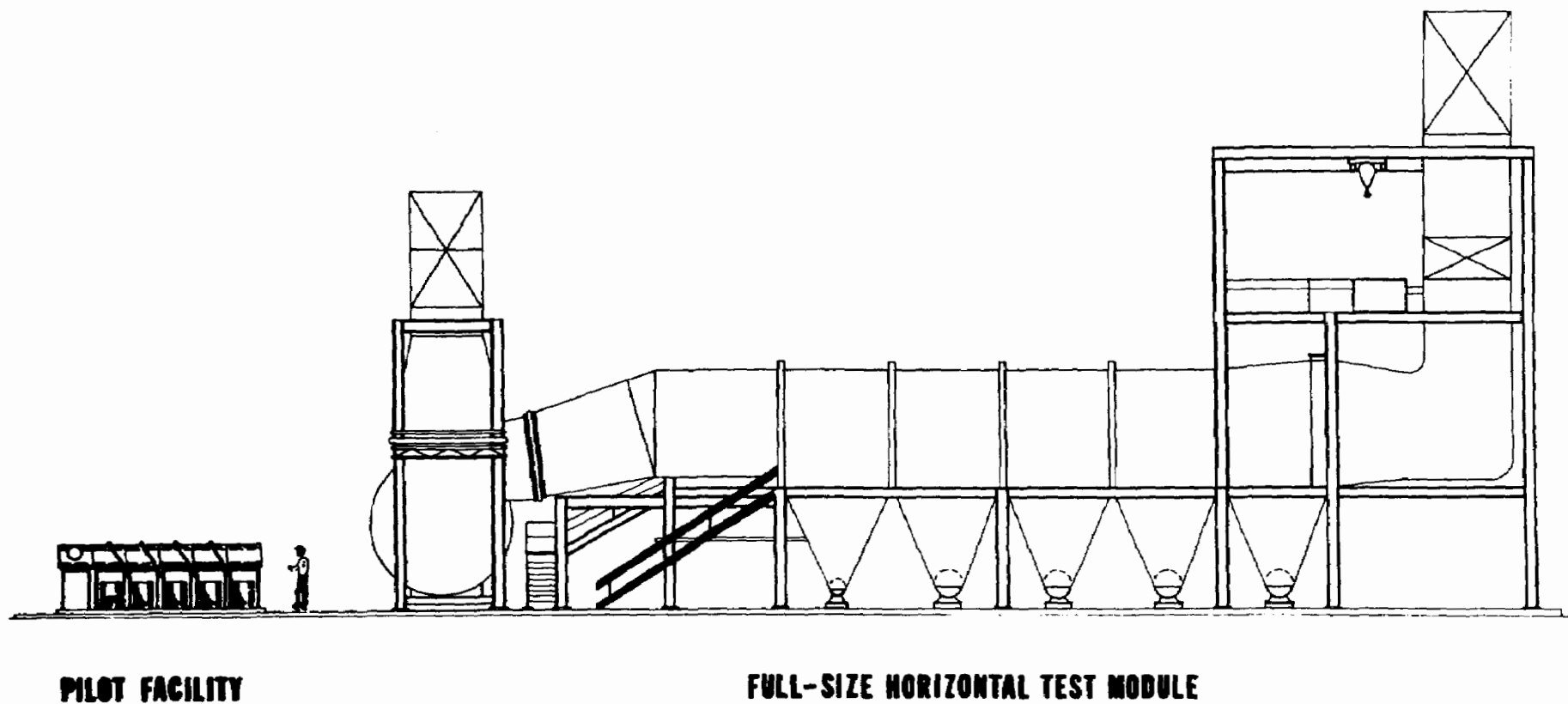


Figure 17

SIZE COMPARISON BETWEEN THE VERTICAL TEST MODULE, PILOT-PLANT AND EXISTING FACILITIES

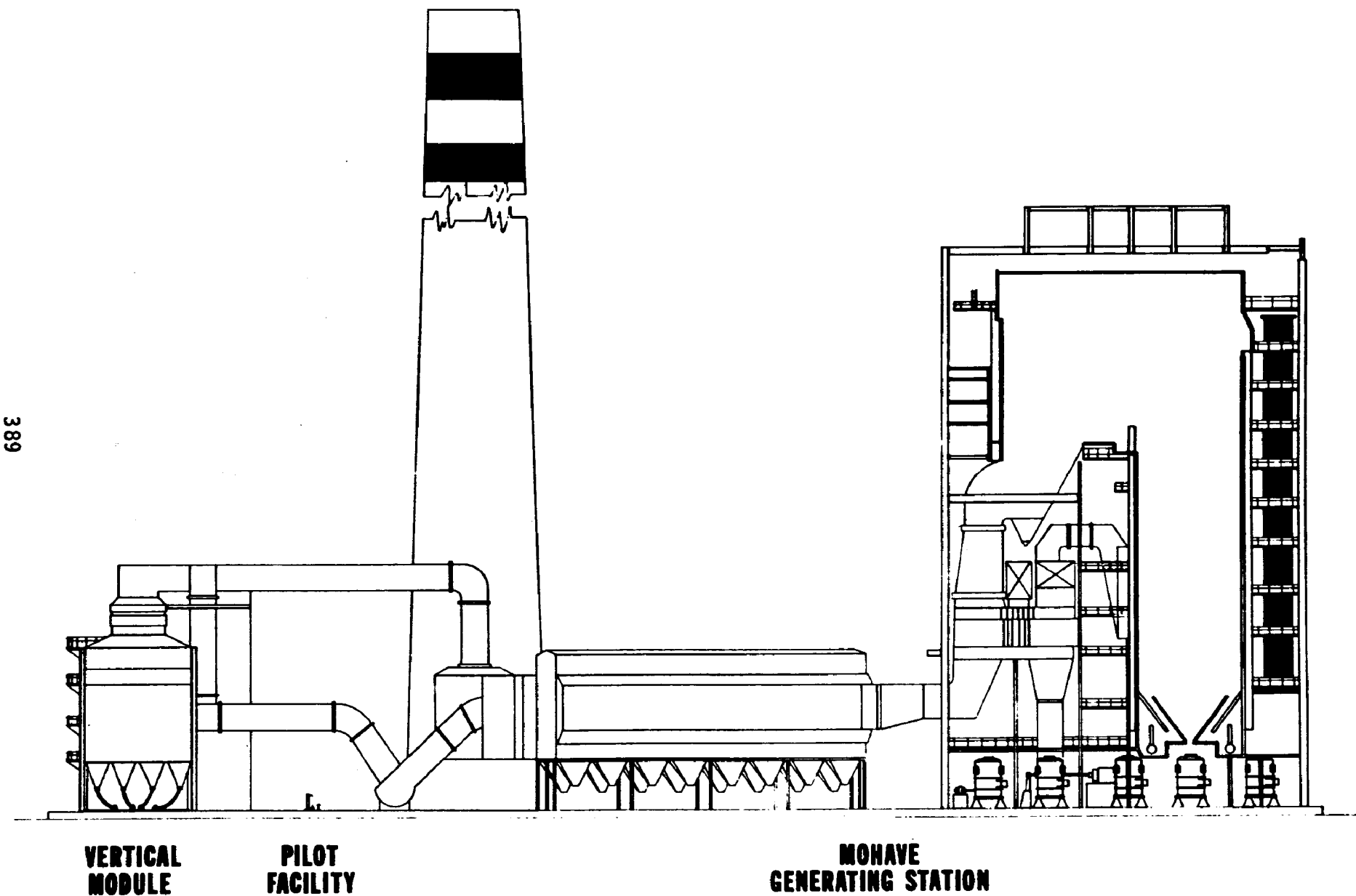


FIGURE 19
450,000 SCFM MODULES
MOHAVE GENERATING STATION

	<u>HORIZONTAL MODULE</u>	<u>VERTICAL MODULE</u>
SO ₂ REMOVAL WITH LIME SLURRY	400 PPM TO 40 PPM	250 PPM TO 40 PPM
SO ₂ REMOVAL W/LIMESTONE SLURRY	250 PPM TO 40 PPM	400 PPM TO 40 PPM
THICKENER TANK	60 FT. DIA. x 16 FT. HIGH	50 FT. DIA. BY 8 FT. HIGH
SCRUBBER DIMENSIONS	15 FT. x 30 FT. x 60 FT. LONG	18 FT. x 40 FT. x 90 FT. HIGH
GAS VELOCITY IN SCRUBBER AT 128 ⁰ F	21.6 FT/SEC.	12.6 FT/SEC.
GAS REHEAT TEMPERATURE RISE	80 ⁰ F	80 ⁰ F
SYSTEM PRESSURE DROP		
NOMINAL	6 INCHES H ₂ O	31 INCHES H ₂ O
MAXIMUM	10 INCHES H ₂ O	40 INCHES H ₂ O
FAN HORSEPOWER		
NOMINAL	1200 HP	4850 HP
MAXIMUM	1750 HP	6000 HP
SLURRY PUMPS		
NOMINAL	8 - 300 HP	4 - 500 HP
MAXIMUM	12 - 300 HP	6 - 500 HP
LIQUID FLOW RATE		
NOMINAL	12,000 GPM FOR EACH OF 4 STAGES	37,350 GPM
MAXIMUM	24,000 GPM FOR EACH OF 4 STAGES	37,350 GPM
L/G RATIO (GPM/1000 SCFM)		
NOMINAL	20	83
MAXIMUM	40	83
ELECTRIC POWER		
NOMINAL	3.0 MW	8.8 MW
MAXIMUM	5.0 MW	10 MW

Testing of the AIS scrubber was paid for by the following members of WEST Associates: Southern California Edison Company, Arizona Public Service Company, City of Los Angeles Department of Water and Power, City of Colorado Springs Department of Public Utilities, Colorado-Ute Electric Association, Inc., El Paso Electric Company, Idaho Power Company, Montana Power Company, Nevada Power Company, Pacific Power and Light Company, Public Service Company of Colorado, Public Service Company of New Mexico, Salt River Agricultural Improvement and Power District, San Diego Gas and Electric Company, Tucson Gas and Electric Company, and Utah Power and Light Company. Southern California Edison Company served as Program Manager for these tests while the Atomics International Division of North American Rockwell served as the test contractor.

Funding for the RHS scrubber tests was primarily provided by the National Lime Association although Southern California Edison Company provided some financial support. Both organizations provided test personnel.

With regard to the WPS, EPA provided advice on instrumentation and test procedures, but the funding was provided solely by Southern California Edison. The test program was conducted by Southern California Edison with assistance from Truesdail Laboratories.

Funding for the SCE scrubber test program described here was provided solely by Southern California Edison Company. The test program was conducted by Southern California Edison and Truesdail Laboratories.

Funding for the two 450,000 scfm test modules is being provided by the Navajo Project Participants (represented by Mr. Tom Morong, Chief Engineer and Assistant General Manager of the Salt River Project) and the Mohave Project Participants (represented by Mr. Jack B. Moore, Vice President-Advanced Engineering of the Southern California Edison Company). Program Management of this Test Modules Program is the responsibility of Southern California Edison Company. Stearns-Roger, Inc. is responsible for the design and procurement of equipment for the Horizontal Module, with the Bechtel Power Corporation serving as the contractor at the site. The Bechtel Power Corporation is also responsible for the overall design and installation of the Vertical Module with Universal Oil Products providing the scrubber and process design under subcontract to Bechtel Power Corporation.

Finally, we feel somewhat embarrassed about taking credit for the work of so many individuals and would like to publicly acknowledge that the individuals listed below made many identifiable contributions to the experiments reported here.

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A REVIEW OF BABCOCK & WILCOX
AIR POLLUTION CONTROL SYSTEMS
FOR UTILITY BOILERS

by

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INTRODUCTION

The Federal Air Quality Act of 1967 was set up in an attempt to deal with air pollution problems in this country on a regional basis. Over 90 air quality control regions were originally designated to be the basis for regional administration and enforcement of the Act. There presently exist a total of 247 air quality control regions through out the nation. The Act also called for the Department of Health, Education, and Welfare (HEW) to develop and publish air pollution criteria that indicate the extent to which pollutants are detrimental to the health and property of people and how emissions can be limited and controlled.

In an effort to speed up progress toward cleaner air, Congress passed the Clean Air Amendments of 1970 that set up the Environmental Protection Agency (EPA), directed the EPA to set national primary and secondary ground level air quality standards, and set a timetable for their implementation. The initial set of standards was issued April 30, 1971, and covered six common pollutants, including particulate matter, sulfur dioxide and nitrogen oxides. Table I lists ground level standards that would primarily affect utility boilers. Primary standards are intended to protect the public health with an adequate margin of safety, and the secondary standards are intended to protect the public welfare, and consider such factors as soiling, corrosion and vegetation damage.

Each state was responsible, by January 31, 1972, to develop and submit an implementation plan for approval by the EPA. The state plans are required to include emission control limits designed to achieve and maintain these national ambient air quality standards. The States have until July, 1975

to achieve air quality equal to or better than the national primary standards. Secondary standards are to be met 27 months later, depending on the availability of adequate control technology, land use and transportation control.

The ammended Clean Air Act of 1970 also has resulted in the establishment of emission standards for new stationary sources. Limits for particulate matter, sulfur dioxide (SO_2), and nitrogen oxides (NO_x) related to fossil fuel-fired steam generators of more than 250 million BTU/hour fuel input are shown on Table II.

This paper will deal with the research and development programs, and demonstration scrubber systems that Babcock & Wilcox has been developing during recent years in an attempt to provide the electric utilities with solutions to their present and future air pollution control problems.

PARTICULATE MATTER

Particulate emissions from most coal-fired and some oil-fired utility boilers have been controlled for many years with mechanical collectors, electrostatic precipitators or a combination of both. In order to meet the stringent particulate collection efficiency required by the EPA for new sources, the engineer today is faced with a difficult problem. Further, many states are adopting particulate emission limits for existing units which are more stringent than the EPA standards for new sources. For example, the state of New Mexico has recently passed an Air Quality regulation that will limit particulate stack emission levels to .05 lb/MKB input by 1975.

Engineers today can choose from four basic types of collection devices when selecting particulate removal equipment. These devices include:

1. Cyclone-type mechanical collectors and classifying hoppers.
2. Electrostatic precipitators.
3. Wet impingement-type scrubbers.
4. Bag filter houses.

1. Mechanical Collectors

Mechanical collectors and classifying hopper devices are typically low collection efficiency components when handling flyash from a coal-fired boiler. Collection efficiencies for these devices will range from 20 to 75%, considerably below the requirements being set by the EPA and state authorities.

2. Electrostatic Precipitators

The electrostatic precipitator has become the principal gas cleaning device for boilers where fine particles cannot be collected in a mechanical device. Properly designed and arranged, precipitators are able to perform at high collection efficiencies over a wide range of particle sizes. However, as these systems age, electrodes corrode and break, hoppers bridge, deposits form on insulators, and more frequent flashover occurs with a resulting increase in the emission rate. To compensate for these malfunctions, and they most certainly do occur, the designer must allow for some redundancy and conservatism in the precipitator design so that design efficiency can be maintained without reducing boiler load or incurring an outage. It is conceivable that a precipitator designed for 92 to 96% collection efficiency can continue to perform near design efficiency with some degree of malfunction; however, the margin of safety becomes very slim when a unit is designed for greater than 99% collection efficiency. These are the minimal efficiencies that are going to be required in order to meet the 0.1 lb/MKB set forth by the EPA. A typical 10,000 Btu/lb fuel with 20% ash will require the precipitator to perform at an average efficiency of 99.6% in order to meet this requirement. It would appear that the

prudent designer may have to provide spare precipitator sections which could be isolated from the operating precipitator modules with the boiler in service to permit routine maintenance, hopper cleaning, etc. if the required emission level is to be met on a day in day out basis. One alternate to providing a modular precipitator design would be for the engineer to select conservative precipitator designs that are less subject to discharge electrode failure.

Precipitator efficiency is controlled by many factors which include dust size and loading, gas temperature, sulfur oxides concentrations, moisture content, ash chemical composition, treatment time and gas velocity. The shift of many power plant operators to low sulfur western fuels is currently having a marked affect on the operation of their existing precipitators, which in many cases, were designed for high sulfur eastern fuels. The immediate result can be a marked increase in stack emission due to many factors not all of which are entirely related to the sulfur content of the fuel. In some cases, the higher moisture content of the western fuel can have a compensating effect on the reduction of the sulfur of the fuel with respect to precipitator performance.

Many operators are redesigning old precipitators, adding on new sections, or installing completely new precipitators to perform on low sulfur fuels based on little operating experience or resistivity data applicable to their specific gas conditions. Also, little is known today to what extent coal composition can be varied without affecting precipitator efficiency. It would appear that considerable effort is required to establish what effect parameters such as coal and ash composition chemistry, mode of burning, flue gas moisture, SO_2 , and SO_3 concentration, temperature, and velocity have on precipitator performance. This will be especially important in designing high efficiency precipitators for low sulfur fuels that are expected to have a wide variation in coal composition over the plant life. It is expected that these plants will be supplying a large portion of our future fossil energy requirements.

3. Wet Impingement-Type Scrubbers

Wet impingement-type scrubbers have been solving a multitude of varied problems for the chemical, pulp and paper and steel industries for many years. Within the past four years, a number of utilities have begun to install prototype and demonstration scrubbers for the purpose of removing particulate and/or SO_2 from boiler flue gas. Particulate removal in these scrubbers is accomplished in a number of ways. Some designs rely on quenching the flue gases to the adiabatic saturation temperature with wetting and/or agglomeration of the particles in a low velocity duct. Their removal from the gas stream is accomplished by gravitational forces and entrainment separators.

Other devices impact the quenched gases on a wetted packing, such as marbles, balls, or bubble caps, and remove particulate by the process of inertial impaction. Particles are removed from the gas stream in this process because the particles are unable to follow the gas stream around the packing, resulting in the particle impacting against the packing. Collection efficiencies for devices of this type are dependent on the particle size distribution of the dust entering the scrubber. Most scrubbers have good collection efficiencies on large particles greater than one micron; however, the collection efficiency for submicron particles can decrease rapidly unless the particles are accelerated sufficiently to cause impaction on the packing surface. The performance of wetted packing can be affected significantly unless the gas and liquor distribution remains uniform over the bed surface.

Removal of submicron particles can be accomplished in a wet scrubber if the particles are accelerated sufficiently and then permitted to collide with or on a droplet surface. This can be accomplished in a high energy venturi scrubber. The smaller the size of the particle to be removed, the higher the velocity and energy required. Most of the energy losses in a venturi result from accelerating the scrubbing liquid. In a venturi scrubber, the

probability of a particle colliding with a water droplet is greatly increased by maximizing the number of water droplets in the throat area. This can be accomplished to a degree by first atomizing the liquid; however, more complete atomization of the liquid droplet can be produced by the shearing action of the gas stream. The accelerated particles impact on the fine liquid droplets which subsequently collide with each other and agglomerate. The gas stream is then decelerated and the water droplets with their captured particles are removed from the gas stream by gravity or inertial separation.

Venturi scrubbers have been used for many years to scrub fine fumes such as the salt cake generated in Kraft recovery boilers where 40 to 50% of the particles are less than one micron in size. More recently, high energy venturi scrubbers have been employed to scrub the iron oxide fume emitted from Open Hearth and Basic Oxygen Furnaces. In this application, where 90% of the particles are less than one micron, the energy requirements amount to a 50 to 60 in. wg gas side pressure loss to obtain virtually a clear stack.

What energy requirements are required in the case of boiler fly-ash? It is first necessary to define the particle size distribution of the fly-ash to be collected. The classical method for obtaining particle size distribution for fly-ash has been to obtain a fly-ash sample according to ASME PTC-27 and determine specific gravity and particle size distribution by Bahco Analyses (ASME PTC-28). Figure 1 is a plot showing typical fly-ash particle size distribution for large pulverized coal-fired or cyclone-fired boilers. Bahco data is usually not reported below a particle diameter of 2 microns because the smallest size fraction determined with this analysis is 1.7 to 2 microns. It can readily be seen from Figure 1 that a significant percentage of the fly-ash (6 to 7%) exists in the fraction below two microns, which may or may not follow the same distribution slope as the larger material fraction. The fraction below

2 microns is the most difficult to collect, regardless of the type of collection device employed.

A venturi scrubber functions much like a sieve; that is, it has a cut-off point, which is a function of gas velocity and recycle liquor rate. These two parameters determine the venturi pressure loss which for a given collection efficiency must be made to vary inversely with dust particle size.

The theoretical venturi grade efficiency curves shown in Figure 2 illustrate how the cut-off point for a venturi can be shifted with energy level. These are calculated curves and assume ideal conditions that do not occur in an actual operating venturi. The collection efficiencies indicated are significantly greater than those expected for an operating unit and can be effected by venturi design. These curves illustrate how the particle size cut-off point in a venturi can be shifted with changes in venturi energy level.

It therefore is quite apparent that submicron particle size distribution for a fly-ash must be determined before the required venturi energy levels for a given collection efficiency can be calculated. Submicron fractions have in the past been examined using light scattering devices, ultracentrifuge techniques, transmission electron microscope, and the scanning electron microscope. These methods, however, suffer from the same shortcoming, i.e., not reproducing the particle size distribution as it exists in the gas stream. It was expected that dust loading and particle size distribution can vary considerably, according to application; therefore, some tool was needed that would measure the actual dust loading and particle size distribution as exist in the gas stream of an intended installation. Such a technique would eliminate the need for expensive and time consuming field pilot plant tests, which only indirectly give particle size distribution and are subject to error in extrapolation to commercial sizes.

To perform these measurements, B&W utilizes a commercial cascade impactor modified to include a cyclone separator in series with from one to seven impactor stages.¹ These components are assembled in a probe that can be inserted in a duct for dust sampling. An iso-kinetic gas sample is drawn through the sample probe, which acts like seven venturis in series. Figure 3 shows the sampling train employed.

Each impactor stage has an orifice and collection cup as illustrated in Figure 4. The orifice diameter and the distance between the orifice and cup determine the particulate collection characteristics of the stage. Some typical particle size distributions for fly-ash determined with this device are shown in Figure 5 along with a typical Bahco analysis for fly-ash. Using theoretical analysis coupled with experimental results, the Research and Development Center of Babcock & Wilcox at Alliance has developed a mathematical model to predict venturi scrubber performance. With this model,² we are able to construct theoretical grade efficiency curves, shown typically in Figure 2 for various venturi design configurations, and apply particle size distribution data determined with the cascade impactor to predict theoretical venturi performance for different energy levels.

Wet scrubbers may not necessarily be the final answer to every dust collection problem especially in water-scarce areas or where visible vapor plumes are objectionable. Large quantities of water are evaporated in cooling the flue gas stream to its adiabatic saturation temperature. This water quantity can be as much as 900 gpm for an 850 MW scrubber unit. Another loss is the dilution water required to remove the ash as a slurry from the system. Some of the dilution water can be recovered with suitable thickening and dewatering equipment; however, some degree of blowdown will be required for these systems due to dissolved solids buildup. The extent of the blowdown will depend on the chemistry of the fly-ash and the make-up water supply to the scrubber.

4. Bag Filter Houses

In applications where extremely low discharge emissions are required, the energy requirements for a wet scrubber may become excessive when compared to that required to obtain the same performance with a bag filter house.

Highly efficient filter houses are commonly used to collect dusts from cement plants, fertilizer plants, metallurgical furnaces, and other applications where collection of submicron material is required. The successful application of a full-scale filter bag house to a 320 MW oil-fired boiler for the control of visible stack emissions was demonstrated in 1968.³ A number of pilot filter houses have been installed in recent years on pulverized coal-fired boilers to determine pressure drop requirements, air to cloth ratios, and operating performance as well as determining the economics of applying these systems to coal-fired units. The performance of a large full-scale filter house applied to a coal-fired unit has not yet been demonstrated. Application of filter houses to coal-fired units in the future will probably be warranted for special situations where extremely high collection efficiencies are required and after taking into consideration site location, fuel source and water availability.

When the engineer today starts to consider the type of particulate collection equipment that will best fit his present and future needs, there will be factors which in the past did not enter into his decision making. Preference may be given by some to wet collection systems since many designs may be augmented in the future with various basic materials, such as limestone for removal of sulfur dioxide. Others may have a ready market for dry-collected fly-ash and will find a combination precipitator for removal of the bulk of the ash and wet scrubbers for removal of submicron dusts and/or SO₂ removal the best overall solution. Some will find that application of a wet scrubber to their particular fuel will result in serious scaling of the slurry lines due to the chemistry of the ash. When more

experience is gained, it may be possible to predict what ashes are likely to cause scaling problems in scrubbers.

SULFUR DIOXIDE REMOVAL SYSTEMS

No processes have received more attention by the different engineering disciplines in recent years than those that are being developed for removal of sulfur dioxide from boiler flue gas. In the mid to late sixties, the primary incentive for their development was the attractive price for sulfur which peaked out at \$40 per long ton in 1968. The price for sulfur in recent years has steadily dropped to levels that have forced the closing of a number of Frasch process mines in the Gulf Coast region. Recent prices for Canadian sulfur, most of which comes as a by-product of natural gas production, have been quoted as low as \$9.50 per long ton delivered to some midwest markets. There will always be a price available for recovered sulfur and sulfur products, but it would appear that this price will be adversely influenced in the future as more crude oil stocks are desulverized and as sulfur is recovered from flue gas sources.

NON RECOVERY SYSTEMS

The development of flue gas desulfurization systems by B&W has been concentrated on both recovery and non-recovery systems. A number of bases can be employed in a scrubber system for removal of SO₂ as a waste product. These bases include lime, high calcium limestone, sodium carbonate, sodium hydroxide and ammonia. A development program was initiated by B&W five years ago to determine the performance for various basic materials in a number of wet scrubber devices. Out of these investigations emerged the B&W limestone wet scrubbing system. Bases such as sodium carbonate, sodium hydroxide, ammonia and lime were found to give better SO₂ removal performance than limestone, but these systems have high raw material costs and many of the bases result in sulfur products that have a high solubility in water and would be difficult and expensive to dispose of.

The chemical costs of lime could be reduced by injecting pulverized limestone into the boiler furnace to accomplish its decomposition to calcium oxide. There are several disadvantages to

this method of operation:

1. Injected pulverized stone increases the dust loading and duty on the scrubber system.
2. Universal application of the injection system was not deemed possible due to possible pluggage in reheater and economizer sections and slagging conditions that could occur due to boiler design or the type of fuel utilized.
3. An injection system could not be applied to oil-fired units due to the tendency for limestone to deposit on the furnace walls or convection surfaces resulting in serious changes to the furnace, superheater, and reheater heat absorption.
4. The problems associated with circulating a lime slurry are well documented in calcium base pulping. The problem of maintaining system chemistry to prevent scaling of piping and other hardware in a lime system was considered more critical than the control required for the limestone system.

Concurrent with determining that limestone was an acceptable base for an SO₂ removal system, a program was initiated for evaluating and determining the scrubber that had the potential for at least 80% sulfur dioxide removal.

This degree of SO₂ removal could not be accomplished in a single or double stage venturi with limestone. A counter current tray absorber did look promising, however, when considering both performance and probable operating problems.

Again, the engineers at B&W's Research and Development Center at Alliance attacked the absorber problem with a fundamental approach. They felt it would be extremely dangerous to scale-up pilot plant test results to a 125 MW size absorber unless the absorption mechanism with limestone was understood. A mathematical model⁴ was developed to determine what effect the significant variables have on scrubber performance. The model was later confirmed in the laboratory pilot plant shown in Figure 6. This model considers the normal operating variables such as flue gas flow, recycle liquor rates, slurry concentration, reaction rates and diffusion constants for the chemical species involved. In addition, the comparative reactivity of various limestones was determined so the prediction of SO₂ absorption could be adjusted accordingly.

Other factors that influenced the decision to proceed on development of limestone wet scrubbing as a first generation system for SO₂ removal were the low cost and high abundance of high calcium limestones in most areas of the United States. The reaction products from this system, calcium sulfite and calcium sulfate, have low water solubilities which reduce the potential for this system to create a water pollution problem from disposal of spent reactants.

In order to evaluate the suitability of various limestones for use in the limestone system, several methods for measuring limestone reactivity were developed. One method involves chemical titration of a slurry sample prepared from a pulverized sample of the limestone. The quantity of titrant is plotted as a function of time, while simultaneously taking into account the change occurring in stone fineness during the titration. This result is compared with the titration rate for the standard stone sample utilized for the pilot plant and model test work. This test is used primarily for screening purposes to determine those materials that should be further screened in the small pilot plant.

This method of laboratory pilot plant testing of stones for use in limestone systems provides for excellent control over all test conditions. In addition, the testing methods are not subject to the many uncontrolled variables that occur when conducting tests with costly field pilot plants.

Confirming tests of limestone performance have been run under closed cycle conditions which are very close to those the stone will experience at the final installation. Closed cycle testing has been conducted in a larger laboratory pilot plant that includes a furnace that can burn 500 lb/hr of pulverized coal, a steam generating bank to cool the combustion gases, a particulate venturi scrubber, a B&W counter current tray absorber, steam coil reheater and ID fan.

The slurry portion of the system includes a limestone preparation and recirculation system, a thickener and a vacuum belt filter. It is possible to operate this system with maximum recovery of water to determine the effects of dissolved solids buildup on scaling and SO₂ absorption for various limestones and fuels. This pilot plant is instrumented with controls, sampling equipment and is capable of continuous round-the-clock operation. Figure 7 is a schematic showing the closed cycle pilot plant which is located at our Research Center.

Waste Disposal

Spent slurry and fly-ash disposal requirements for a coal-fired boiler with a limestone wet scrubbing system will be about double that normally handled for the boiler alone. This will be a severe burden at many locations and could require this material be dewatered and hauled away for disposal. All the problems associated with sludge disposal are not fully known. The possibility of utilizing the waste stream from this process as a useful or valuable product is considered highly remote in this country.

B&W's efforts at waste disposal with this process have been directed toward conversion of the waste stream to a form that will facilitate its disposal, minimize its effects on the environment and reduce, for the customer, the quantity of sludge for disposal. Research efforts currently in progress have not progressed sufficiently to permit a meaningful report at this time.

Demonstration Systems

The first full scale demonstration of the B&W limestone wet scrubbing system is located at the Will County Station of Commonwealth Company. This system is retrofitted on a 163 MW net B&W radiant cyclone - fired boiler that went in service in 1955. Two venturi - absorber scrubber modules treat the entire flue gas flow leaving the unit, 770,000 ACFM.

The expected performance for this system corresponds to an outlet dust emission of 0.0124 grains per DSCF and a sulfur dioxide removal efficiency 81.6 percent. The system and its major components are shown schematically in figure 8.

Each scrubber module consists of a variable throat area venturi that removes the particulate and provides an initial stage of sulfur dioxide removal, followed by a B&W countercurrent tray absorber. Venturi and absorber sprays both drain into separate recirculation tanks that provide for delay time to complete chemical reactions prior to recirculating the slurry back to the module. Three 100 percent capacity venturi recirculation pumps, each rated at 7300 gpm, and four 60 percent capacity absorber recirculation pumps, each rated 5250 gpm were provided for the two modules.

Flue gases leaving each absorber pass through a bare tube steam coil reheater and then to a 2250 hp ID booster fan. Both booster fans discharge into the existing ID fan inlets.

The major control functions for the system, limestone feed rate, venturi spray liquor rate, venturi ΔP , slurry solids concentration and limestone milling system operation are all controlled automatically from the scrubber control panel located in the existing boiler control room. Figure 9 shows the instrumentation and control diagram for the scrubber portion of the system at Will County.

Limestone is received by river barge and stacked with the existing coal handling equipment at Will County. Stone is transferred by conveyor to two storage silos. Each silo discharges on to a gravimetric feeder that supplies one of two 100 percent capacity wet ball mill and classification systems. Each mill has a capacity to grind 12 tons per hour of limestone to a fineness of 95 percent minus 325 mesh. Twenty percent solids feed limestone slurry leaving the milling system is stored in a slurry storage tank from where it is transferred to the scrubber modules.

Spent slurry from the scrubber is pumped to a 65 foot diameter thickener. Clarified recycle water discharges to a 5.5 acre pond and returned to the cycle with the reclaim pumping system. Thickened slurry underflow is pumped to a loading station where fly-ash and other dry additives will be blended with the thickener underflow, to modify the sludge sufficiently to produce a stable land fill material.

Detail engineering for the Will County project commenced in September, 1970. One scrubber module was placed in service on February 23, 1972 with the second module going in service on April 7, 1972.

A second demonstration limestone wet scrubbing system is being supplied for a new electric power generating station located near La Cygne, Kansas. The 820 MW net station is a joint project of Kansas City Power & Light Company and Kansas Gas and Electric Company. The 6,500,000 PPH Universal Pressure Cyclone boiler will be fueled by a low grade bituminous coal obtained from nearby surface mines.

The air quality system, shown schematically in Figure 10, consists of seven venturi-absorber scrubber modules designed to handle the entire flue gas flow of 2,370,000 ACFM. The system is designed for 98.75% particulate removal which corresponds to an outlet particulate emission of 0.10 lb. per million BTU fuel input. Sulfur dioxide removal for the system is designed for 80% efficiency.

Each scrubber module consists of a variable throat area venturi followed by a B&W countercurrent tray absorber. Each module has a 100% capacity venturi recirculation pump, each rated at 7750 gpm and supplied with 350 hp drives. A total of seven, 100% capacity, 10,300 gpm absorber recirculation pumps, were supplied, each with 400 hp drives.

Flue gases leaving the seven modules, are first reheated 25 F with a bare-tube steam coil reheater and discharged by six induced draft fans, 7000 hp each, through a 700 ft. stack.

Limestone consumed by the scrubber system comes from local quarries and is delivered by truck and conveyed with the plants coal handling equipment to two limestone storage silos. Two full size 110-ton per hour wet ball mills grind the limestone to a fineness of 95% minus 200 mesh. Pulverized limestone slurry is then stored in two 200,000 gallon capacity slurry storage tanks.

Spent slurry, containing fly ash and calcium-sulfur-reaction products, is pumped to a 160 acre settling pond, with clarified recycle water returned to the system with two-100% capacity pond return pumps.

This generating unit is currently in the start phase with a scheduled commercial operating date of May 1, 1973.

SULFUR RECOVERY SYSTEMS

It is too early to determine the total magnitude of sludge disposal problems associated with the nonrecovery sulfur removal systems. Some operators may find no economic means for disposal of waste products and will direct their attention to processes that minimize this problem. One sulfur recovery process that can be applied as a retrofit to existing units is a wet MgO system B&W has been developing for the past six years.

B&W MgO System

Scrubbing flue gas with MgO and recovering the sulfur values is not a new system. For over 20 years, many calcium sulfite pulping processes have been converted to an advanced pulping-recovery process developed and patented jointly by Howard Smith Paper Mills Ltd., Weyerhaeuser Company, and Babcock & Wilcox. Over twenty installations

of this type both in the United States and abroad have been installed at both new and existing pulp mills that utilize this process to recover sulfur dioxide from the flue gas leaving chemical recovery boilers. Figure 11 shows a flow schematic for a typical Magnesium Bi-Sulfite Pulping and Recovery process. The scrubbing liquor, a mixture of magnesium sulfite and bisulfite, is utilized as a cooking liquor during the pulping process. Weak liquor from the digester is concentrated to 50 to 55% solids in a multiple effect evaporator and burned in a B&W recovery furnace. Dissolved lignins from the pulping process supply the fuel that maintains the combustion process. Magnesium sulfites and sulfates are thermally decomposed to sulfur dioxide and magnesium oxide. Magnesium oxide is removed from the flue gas stream with mechanical collectors, washed to remove soluble impurities, and slaked to magnesium hydroxide in hot water. The slaked magnesium hydroxide is then added to the sulfite-bisulfite scrubbing solution to remove the sulfur values from the flue gas stream in a venturi or contact tower before exhausted the gases to the atmosphere.

The application of this process to utility boiler stack gas application results in a number of process changes. Most of these are associated with the regeneration portion of the cycle due to the thermal requirements for drying and decomposition which must be supplied from fossil fuels, since the recovered magnesium salts have no heating values. A schematic of this process is shown in Figure 12.

The first step in the process involves quenching of the hot flue gases and removal of particulate from the flue gas stream. Particulate removal can also be accomplished in a high efficiency electrostatic precipitator. Sulfur dioxide removal is accomplished in an absorber of the same design utilized for limestone scrubbing. Magnesium sulfite hexahydrate slurry is removed as a blowdown from the process, concentrated and passed to a dewatering step where partial dehydration of the crystals takes place. Surface moisture and additional waters of hydration are removed in a drier. The dried crystals are decomposed in an oil or gas-fired furnace that discharges a sulfur-rich gas suitable as a feed to a contact acid plant or to an elemental sulfur conversion plant, depending on the desired product. Magnesium oxide formed during the decomposition step is recovered with mechanical collectors, slaked and recycled to the scrubber.

B&W-Esso Dry Sorbent Flue Gas Desulfurization Process

One of the more promising dry flue gas desulfurization processes is the system being developed jointly by B&W and Esso Research and Engineering Company (ERE) with the support of 17 electric utility companies in the United States and Canada. Dry sorbent systems are attractive for many reasons. They avoid plume problems created by wet scrubbing and do not have some of the water disposal problems associated with wet scrubbers. Dry systems which operate in the temperature range of 600 to 700 F places the sulfur dioxide removal equipment ahead of the air heater in a boiler cycle. This should result in reduced maintenance and improved performance for the air heater.

In August, 1967, B&W and Esso Research and Engineering jointly began the study of a dry sorbent flue gas desulfurization process. These studies showed that the development of a good sorbent material that would absorb and desorb sulfur dioxide in the temperature range of 600 to 700 F was feasible. Utility support was solicited and obtained in 1969, and a three-phase research and development program established. The final phase of this program will involve the design, installation, operation and testing of a 150 MW demonstration system. The B&W-Esso process utilizes an electrostatic precipitator for controlling particulate emissions and a dry sorbent for controlling sulfur dioxide and nitrogen oxide emissions.

It provides advantages over existing systems in that the process reduces nitrogen oxide and sulfur oxide emissions simultaneously and also minimizes the problem of disposing of spent material. Product gas from the process is suitable for the production of saleable sulfur or sulfuric acid. Figure 13 represents an 800 MW coal-fired utility boiler with the B&W-Esso system.

SUMMARY

The programs described here are part of a continuing research and development effort that will provide the power industry with some of the answers to their air pollution control problems.

Coal remains as our most abundant fossil fuel, with proven reserves estimated at 830 billion tons, most of which cannot be utilized for future power production without some degree of sulfur removal.

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TABLE 1

National Primary and SecondaryAmbient Air Quality Standards

Pollutant	Ground Level Concentration Not To Exceed	
	Primary $\mu\text{g}/\text{m}^3$	Secondary $\mu\text{g}/\text{m}^3$
Particulate Matter (a)	75	60
Sulfur Oxides (b)	80	60
Nitrogen Oxides (b)	100	100

(a) Annual geometric mean

(b) Annual arithmetic mean

TABLE 2

EPA Standards of Performance for New
Fossil Fuel-Fired Steam Generators

Fuel	Emission Limits Not To Exceed		
	Particulate lb/MKB	SO ₂ lb/MKB	NO _x lb/MKB
Coal	.1 (a)	1.2	.7
Oil	(a)	.8	.3
Gas	(a)	---	.2

(a) Visible emissions will be limited to not greater than 20% opacity.

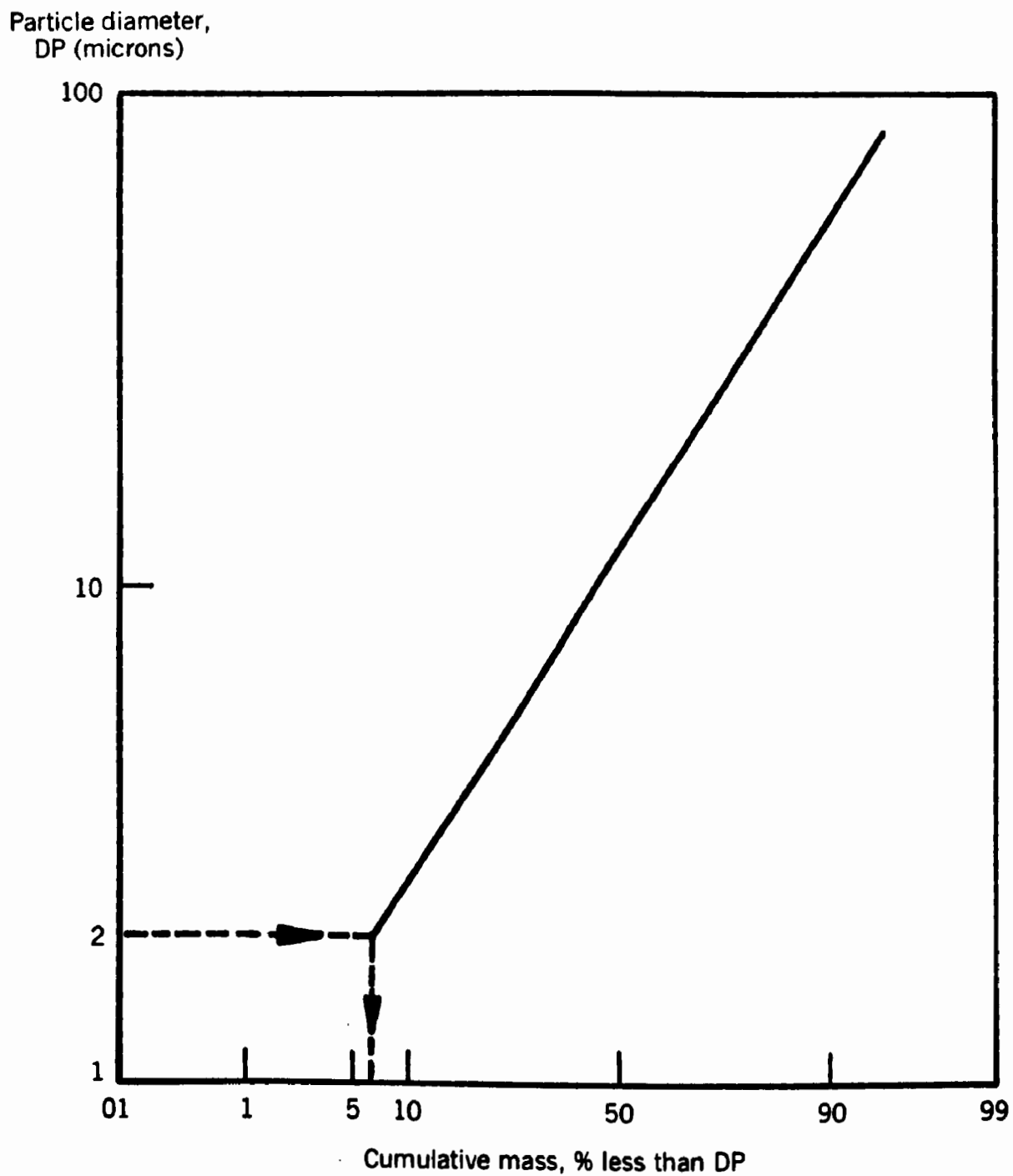


Figure 1
**Typical fly ash particle size distribution
for large PC and Cyclone fired boilers
Bahco-Analysis**

Theoretical
grade efficiency,
%

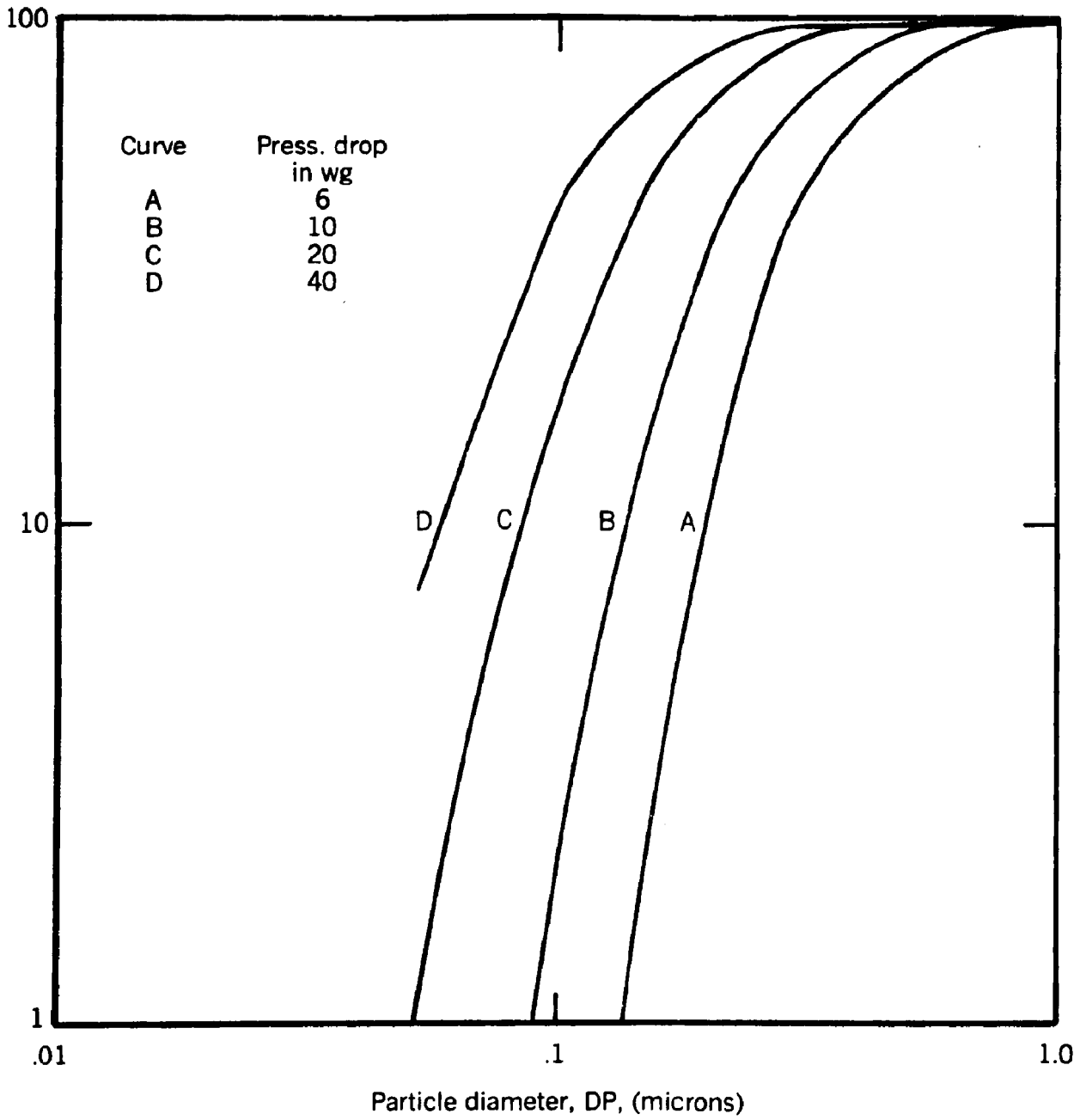


Figure 2

Theoretical venturi grade efficiency curves

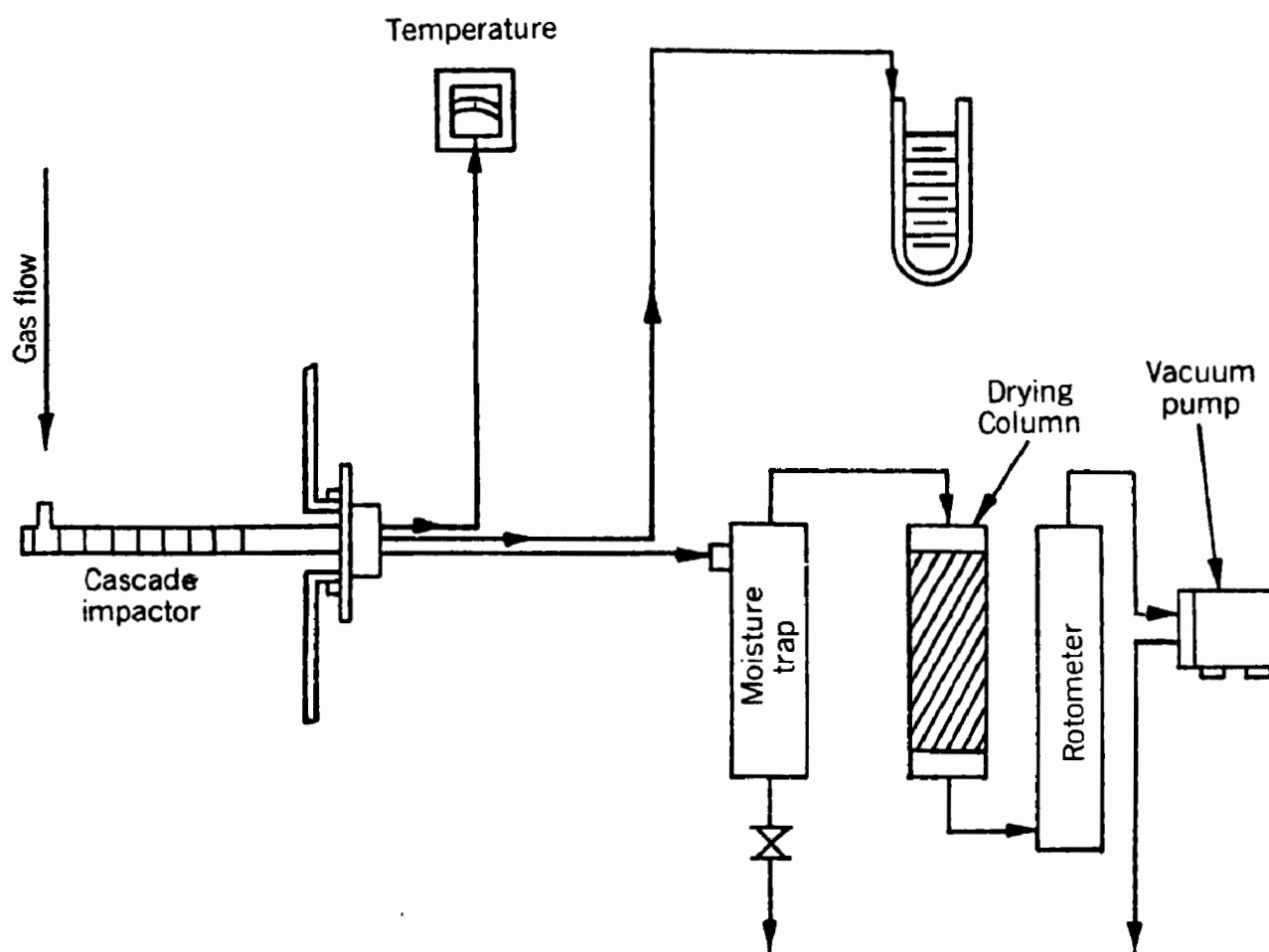


Figure 3
Cascade impactor sample train

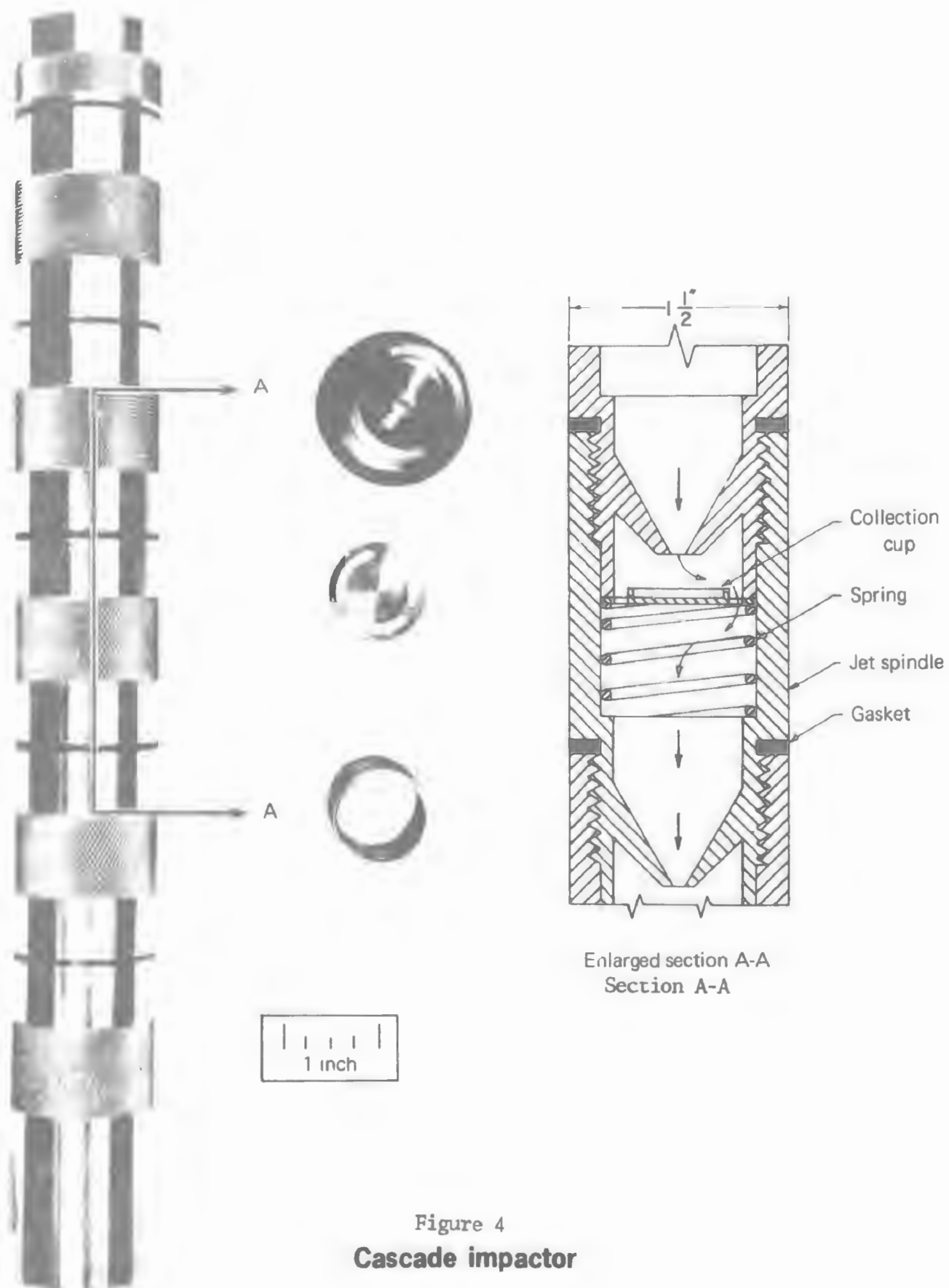


Figure 4
Cascade impactor

Particle diameter,
DP (microns)

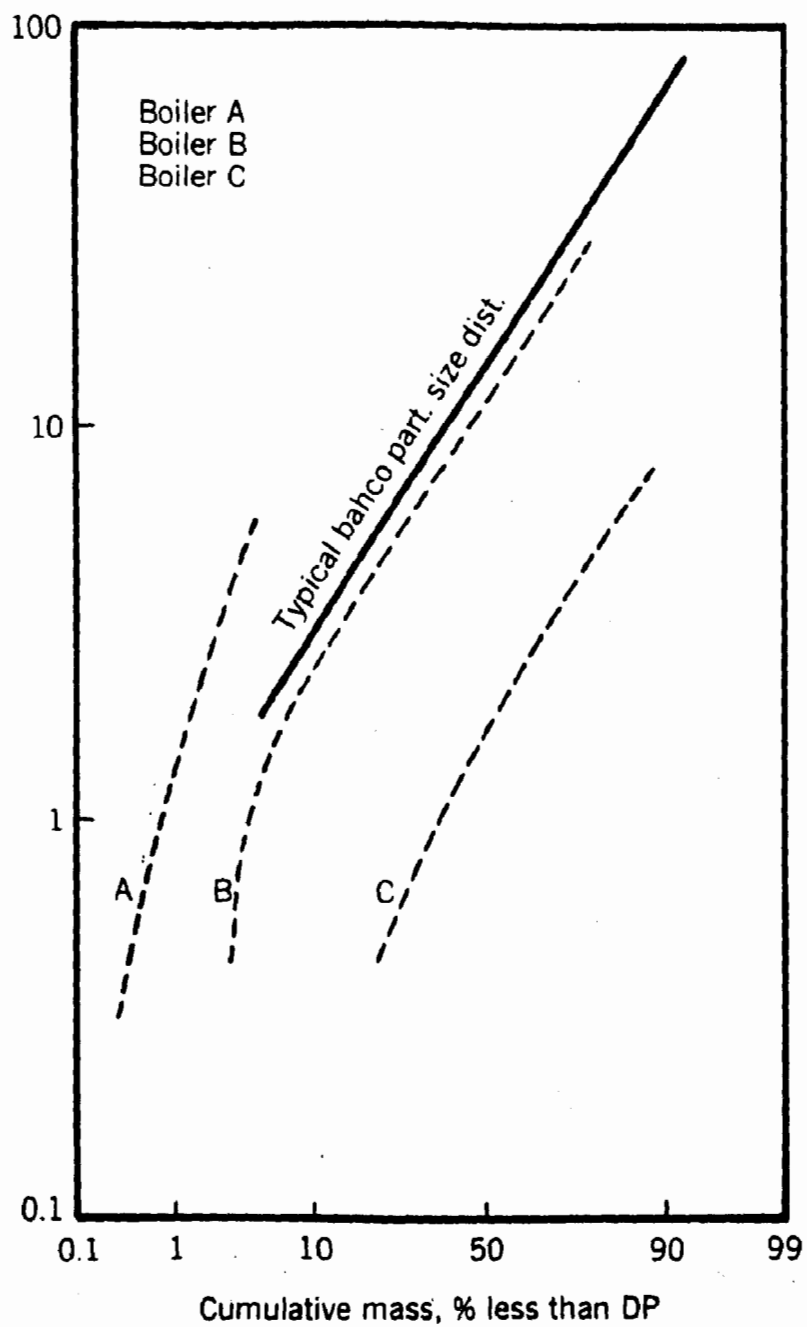


Figure 5
Cumulative particle size distribution

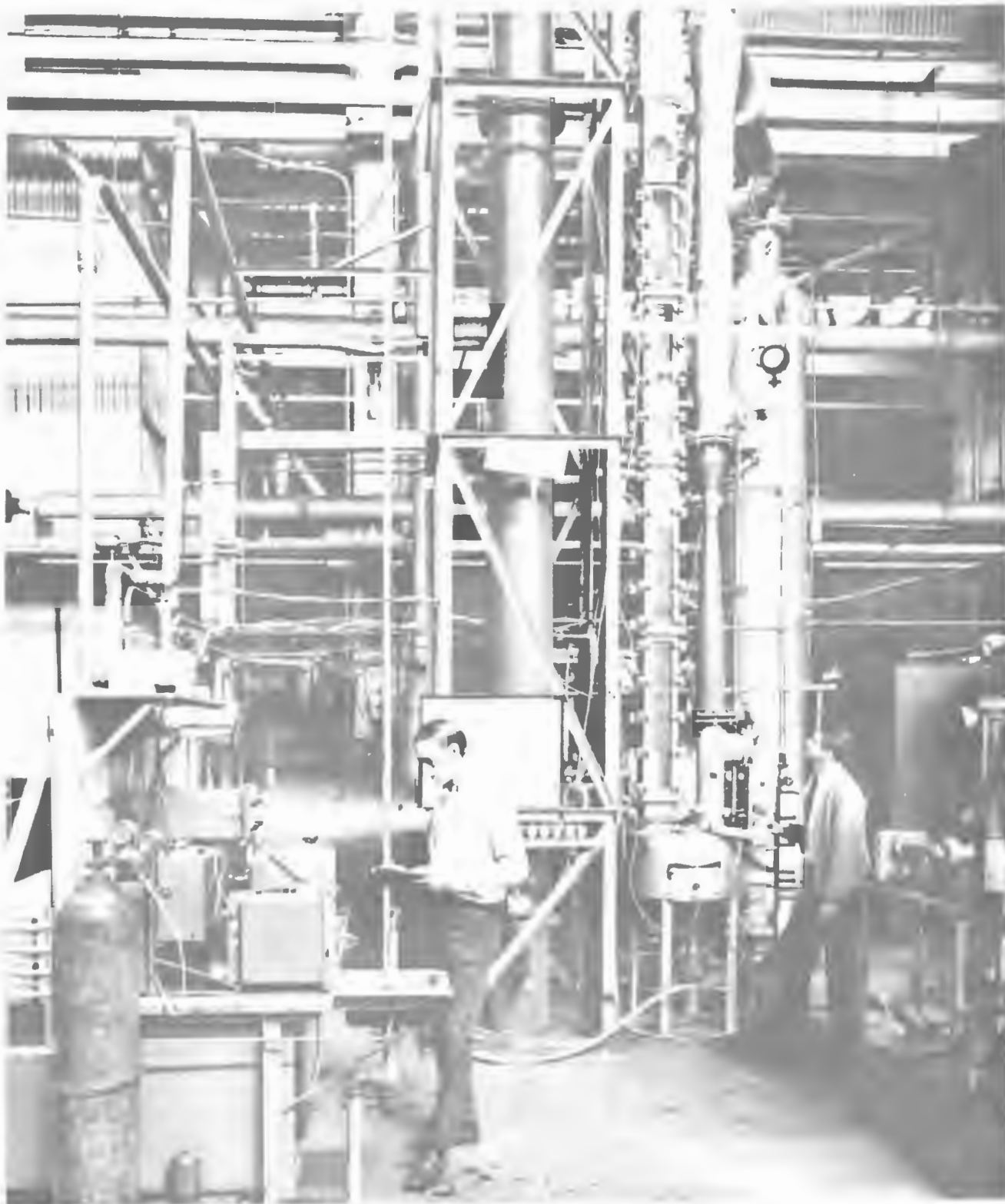


Figure 6
Laboratory pilot plant

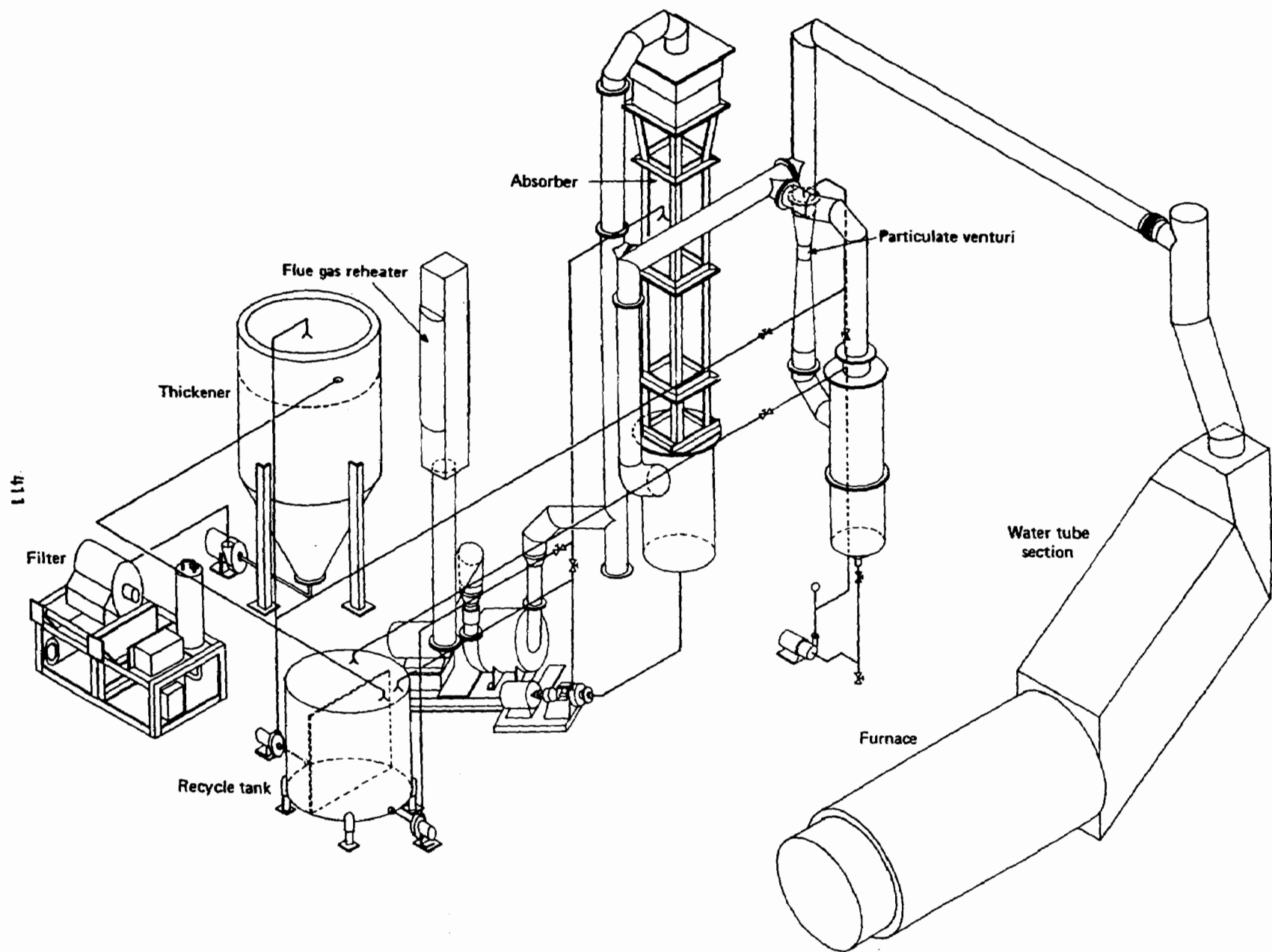


Figure 7
Limestone wet scrubbing pilot plant

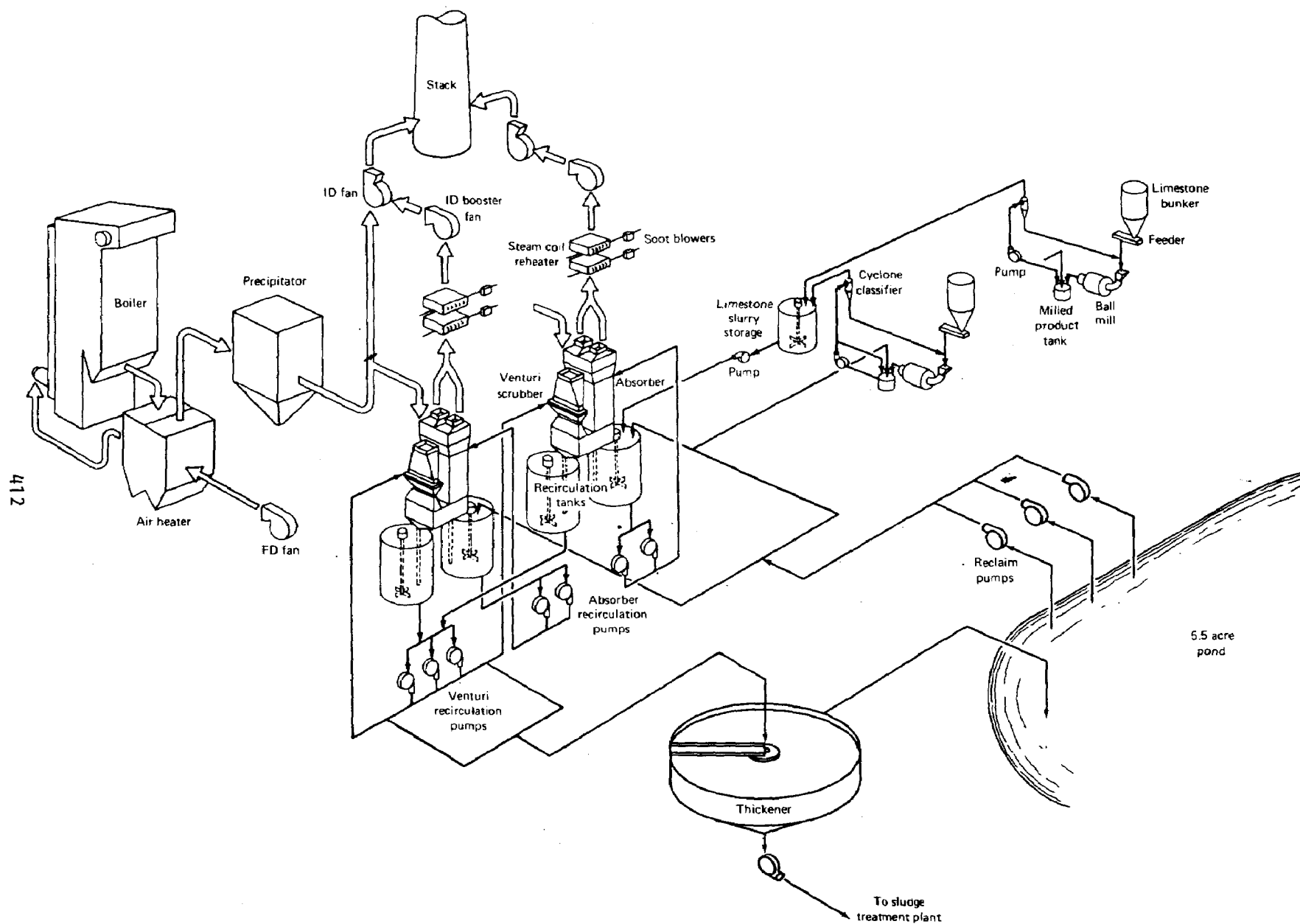


Figure 8
Will County limestone wet scrubbing system

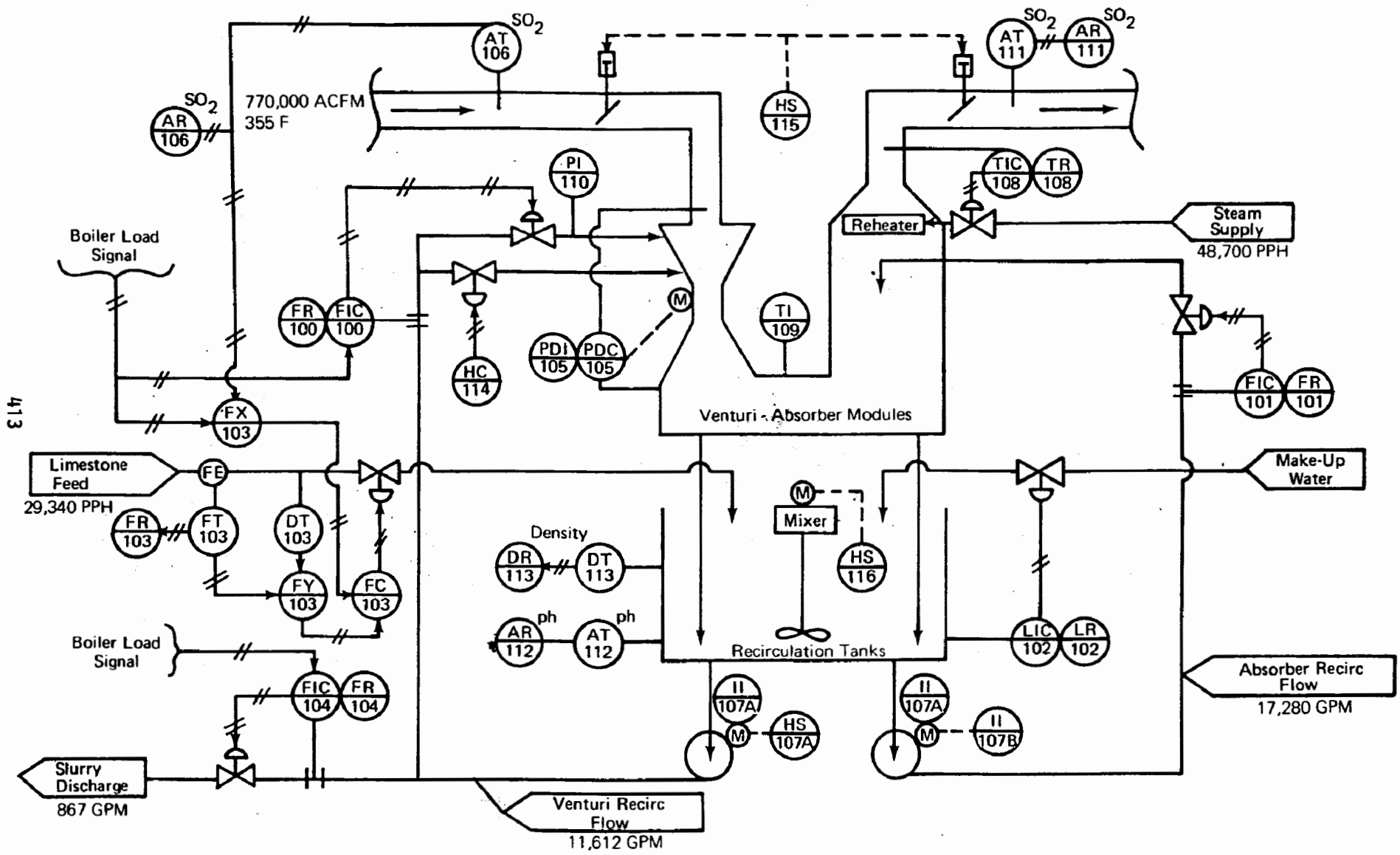


Figure 9

WILL COUNTY INSTRUMENTATION AND CONTROL DIAGRAM

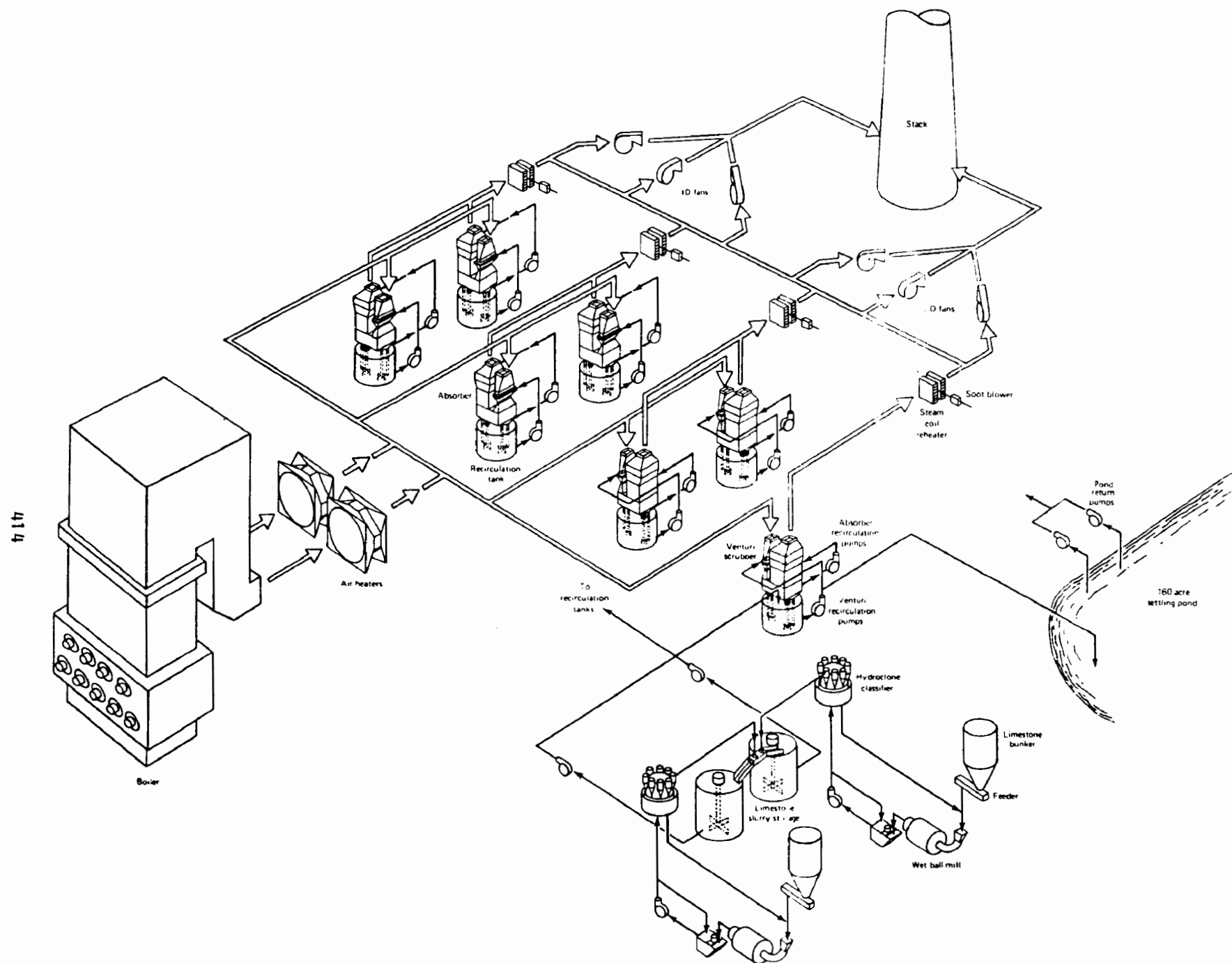


Figure 10
La Cygne Limestone wet scrubbing system

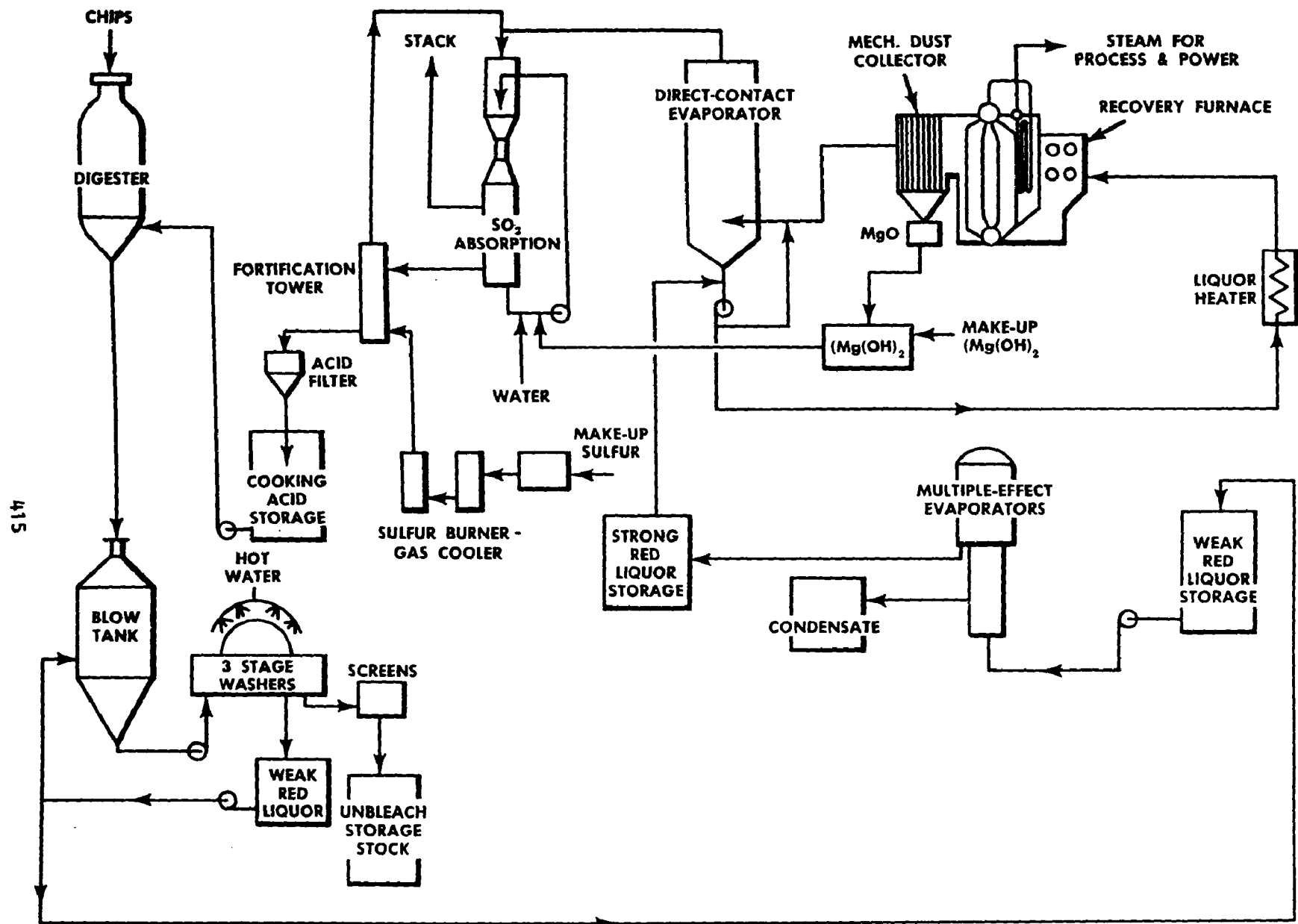


Figure 11
Flow diagram of magnesium base pulping and recovery

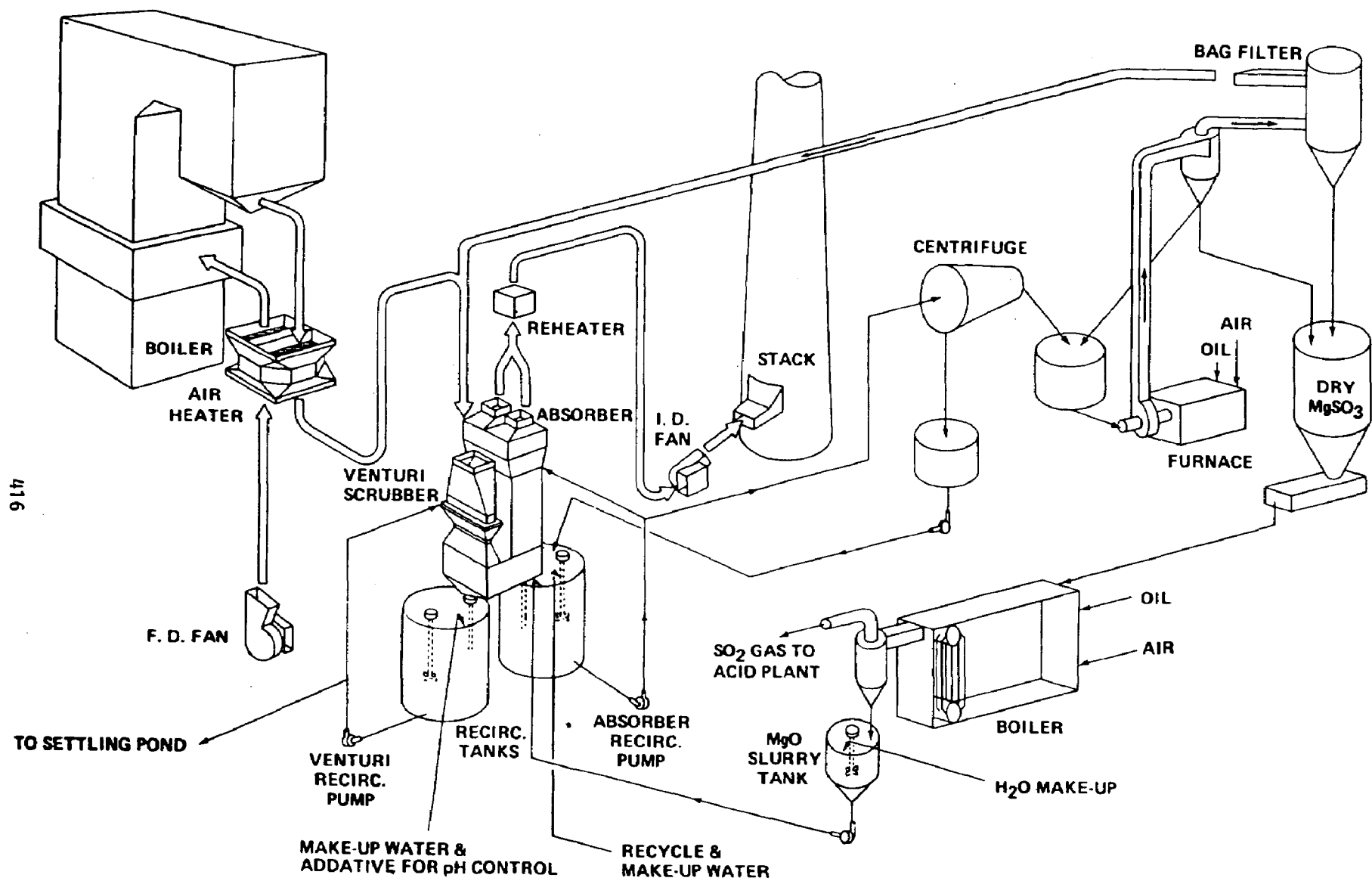


Figure 12
Magnesia scrubbing system

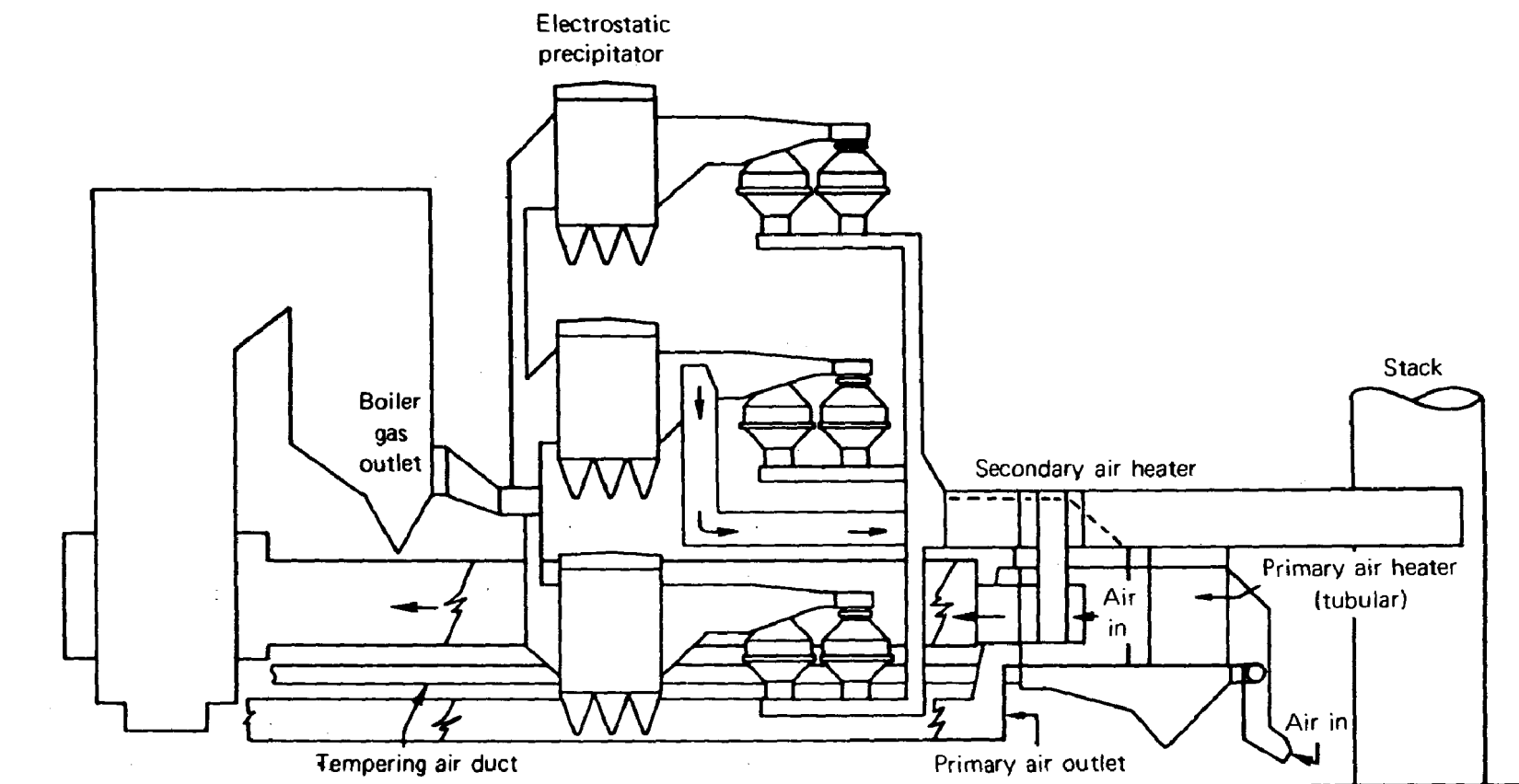


Figure 13
800 MW B&W-ESSO system

ONE YEAR'S PERFORMANCE AND OPERABILITY
OF THE CHEMICO/MITSUI CARBIDE SLUDGE
(LIME) ADDITIVE SO₂ SCRUBBING SYSTEM

at

OHMUTA #1

(156 MW-Coal Fired)

by

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FOREWORD

It is a great honor and pleasure to introduce and participate at this symposium with Jun Sakanishi, General Manager of the Miike Power Station (referred to by Chemico as Ohmuta No. 1, which is part of the Mitsui Aluminum Company Ltd., Japan. Sakanishi San has provided the supervisory leadership necessary to assure the success of this full-scale multi-stage SO₂ Scrubbing System which was retrofitted onto his 156 MW coal-fired boiler.

Sakanishi San's participation has spanned the total history of the project ranging from the basic design and pilot testing phases, through engineering, construction, and start-up; to over one year's operation. It was Sakanishi San who trained his existing power plant operators to thoroughly understand all functions of the system in terms of what had to be done and, most important -- why it had to be done. The interaction of design engineering, comprehensive training and skillful operation has paid off -- the first commercial-sized, successfully operating, highly efficient, totally reliable SO₂ Removal Scrubbing System.

While it is Chemico's pleasure to assume credit for the basic design engineering and the associated process know-how, major acknowledgments must be extended to the outstanding engineering and construction staffs of the Mitsui Miike and Mitsui Aluminum companies who completed the project in the unbelievably short period of nine months -- within budget. Similar work in the U.S.A., taking into consideration problems of work practices and productivity in the construction area as well as the many factors which can adversely affect engineering and procurement schedules, would require a much longer period of time.

The System has been totally reliable and available for all power generation requirements of the Mitsui Aluminum Plant -- a facility which is totally dependent upon a low cost, reliable power supply. Much credit for this reliability must be attributed to the exceptional quality of Japanese equipment manufacturers. The supply of conventional system components such as fans, pumps, controls, etc., and the associated equipment servicing by the Japanese, has proved to be everything which they claimed and more. This is something which American vendor counterparts should note that they need to seriously improve upon.

The success of this installation is indicative of the effectiveness which can be achieved, if required, on American power plants because of the following reasons:

- (a) The inlet SO_2 concentrations at the Ohmuta Scrubbing System are quite similar to most of the SO_2 concentration ranges measured by Chemico during different pilot testing operations at 17 different power plant sites throughout the U.S.A. over the past five years. Only Western coal-fired operations have been different in that these inlet SO_2 concentrations are generally lower than that experienced at Ohmuta.
- (b) Carbide sludge (calcium hydroxide) used at Ohmuta and various grades of lime which are expected to be proposed for most applications in the U.S.A., have sufficiently common properties for SO_2 scrubbing purposes to correlate their mutual successes as additives. Simultaneous SO_2 absorption pilot testing, using both types of materials under similar conditions, has demonstrated these correlations. This is not the case for considerations involving limestone.
- (c) The Ohmuta Plant is essentially a base loaded operation but has been subjected to sufficient load swings and SO_2 concentration variations to demonstrate that the scrubbing system can readily handle various turndown conditions.

Since American applications envision the use of 150 MW modular trains, which is the approximate size of Ohmuta, there are no further scale-up factors involved.

- (d) Fly ash removal at Ohmuta is accomplished by depending upon a relatively efficient, previously existing precipitator. The first stage scrubber/absorption section also acts as a polishing function to remove residual ash in the flue gas and has functioned to provide a system outlet loading as low as 0.001 grains/SCF.

The decision to incorporate a precipitator on American installations versus solely using a wet scrubber for dust collection, will be a function of client considerations for site conditions and the results of associated cost/benefit studies. SO_2 absorption is common to both dust collection techniques.

- (e) The Ohmuta $\text{CaSO}_3/\text{SO}_4$ effluent bleed disposal system is designed to operate, and has operated, as a closed recycle loop between the scrubbers and the disposal ponds. The recycle liquor has been totally saturated with sulfate for extended periods of time (months) without significant scale, build-up or other deposition occurring in the scrubbers.

This success of precluding build-up has been essentially attributed to pH control throughout the liquid system combined with strategic utilization of fresh make-up water which is always required in any scrubber system to compensate for conventional stack evaporative losses.

Some "spokesmen" have attempted to speculate that the pond is purposely "blown down" or "dumped" into an adjacent bay. This is not so. There were periods during the year, however, when extensive rainfall from typhoons created an emergency pond overflow condition. This problem has been resolved by increasing the pond area and building up of higher dike retainer walls.

Pond management of this effluent material is achievable at conditions which are no more or no less complex than that experienced on existing plant sites in this country today.

It is clear that the removal of SO_2 for power plant stacks by the use of any method, is going to significantly increase steam/electric generation production costs in this country. The rationale for or against this SO_2 control has obviously become a matter of multi-opinions on many issues ranging from questionable need for such SO_2 compliance in the first place, cost benefits associated with the various methods, and who should pay for what and how. These issues are subjects, the rhetoric of which, Chemico defers to others. We do say, however, that the SO_2 can be chemically absorbed from the flue gas at high efficiency in a reliable manner, and have demonstrated as such at Ohmuta. Thus, Chemico respectfully submits to this symposium that the criteria, established by an adhoc panel of the National Academy of Engineers concerning demonstrated SO_2 technology for over one year, has been achieved.

There is no technical reason why SO_2 removal via the demonstrated Ohmuta scrubbing technique cannot be achieved in a manner which would not adversely affect availability and reliability of the steam/electric generation facilities.

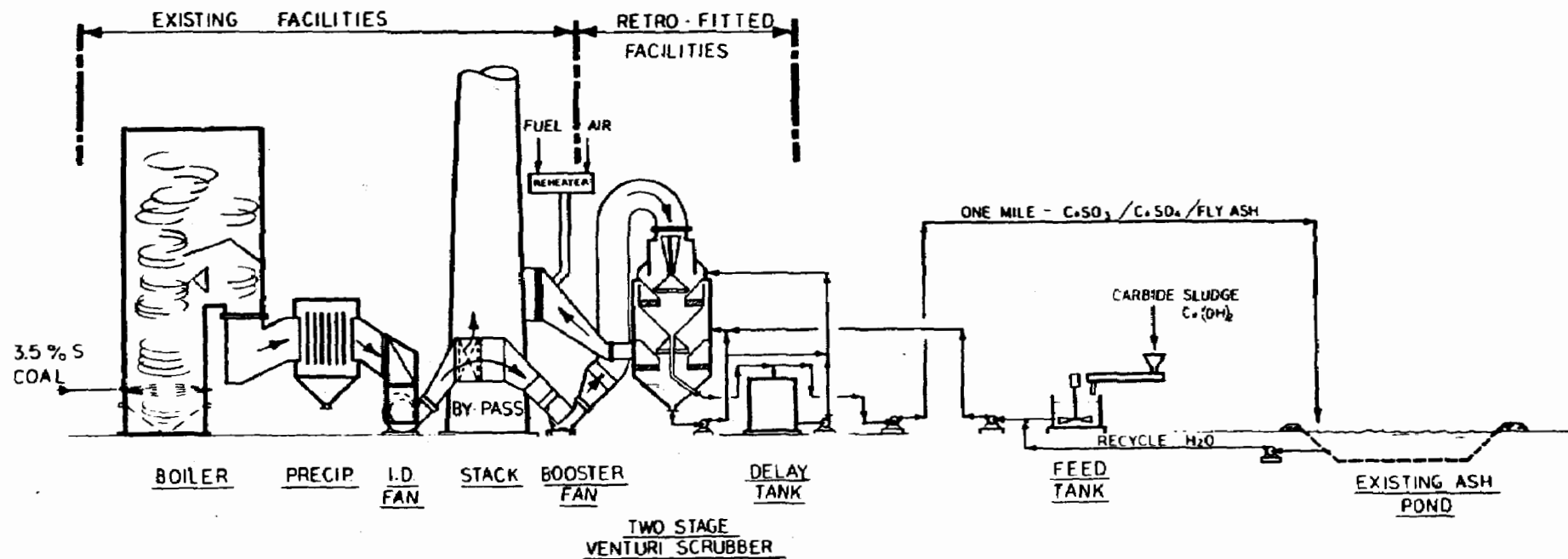
Robert H. Quig, P. E.
Vice President
Chemical Construction Corporation
Air Pollution Control Company
New York, New York
April 26, 1973

RHQ:rg



FLY ASH - SO_2 SCRUBBING SYSTEM
MITSUI ALUMINUM CO
OHMUTA PLANT (156 MW)

SCHEMATIC PROCESS FLOWSHEET



1. Background of project of SO₂ control plant

Mitsui Aluminum Co., Ltd. was established in 1968 with the objectives of 1) to support the local coal industry whose economic base was being weakened due to the drastic change in structure of the fuel source supply and 2) to develop an Aluminum smelting plant which had been planned by Mitsui Group for many years.

We believe that a basic requirement for the Aluminum Smelting Industry is to secure a cheap and stable supply of electricity. Miike Mining Station of Mitsui Mining Co., Ltd. located in Ohmuta City, is enjoying the largest quantity of coal production (6 million t/y) in Japan and produces high quality coal for the Steel Industry. In the process of this production, however, a large quantity of slime coal which is unsalable waste coal is also produced. Under the situation, the basic requirement for Aluminum Smelting Industry has been resolved by utilizing the low-grade slime coal.

Although the coal produced by Miike Mining Station (so-called "Miike coal") is the best in quality in Japan, it has two unfavorable characteristics. First, it is easy to cause clinker problems and second, the coal has a high sulfur content. At the time of commencing the project of the power plant (1967-1968), therefore, our primary efforts in boiler design were "how to avoid clinker trouble" and this was successful. As to the high sulfur content, nobody anticipated at that time the severe pollution control codes which are prevailing today and there were no SO₂ standards to be applied by codes. Under the situation, we thought that it might be acceptable enough to build a 130 meters high stack as a measure of SO₂ control which was also a recommendation of the Japanese MITI (Ministry of International Trade and Industry).

The rapid progress of the Japanese economy has made it necessary to quickly strengthen pollution controls. As a result, power companies and others have been obliged to change their fuel sources. The combination use of low-sulfur oil and high stacks was one of the most prevailing counter-measures at that time. In order to meet the initial objectives of establishing the company in the first place, Mitsui Aluminum Company was determined to continue the use of coal as a primary fuel source and to solve the SO₂ problem through the operation of coal fired boilers with SO₂ control

The power plant was completed in March 1971. At the start of operations coal which was to have a heat value of 9,000 Btu/Lb and 2.1 % of sulfur content as had been originally planned, was changed to coal

with a heat value of 10,300 Btu/Lb and 1.7% of sulfur content. One year later, in March 1972, the SO₂ control system was completed and placed in service. Since then, the power plant with the SO₂ scrubbing system has been operated smoothly without any major trouble, satisfying not only the national government control code, but also the agreements with the local municipal administration.

Attached TABLE I shows the history of the power plant and the SO₂ control plant at Mitsui Aluminum Co.

The work which Chemico had done to date best suited our criteria. Mitsui Miike Machinery executed a license agreement with Chemico and then we began to design the Ohmuta system.

Reasons for selection of Chemico/Mitsui Miike process are as follows:

- First: - We believe that Chemico is one of the most experienced companies in the field of chemical process engineering and construction in the world. They are especially well experienced in applications of the large-sized venturi scrubber which is a critical part of a totally engineered scrubbing system. Accordingly, easy size-up of the venturi absorption tower and reliable process analysis could be expected with Chemico.
- Second: - The process including the venturi-absorption tower is relatively very simple when compared to other SO₂ control technologies. This advantage means relative easier operation and maintenance of the plant which requires a minimum training of operators.
- Third : - The use of venturi vessel scrubber designs allowed that continuous long-period operation and high efficiency would be assured. In addition, the Chemico type SO₂ control plant allowed for a shorter construction schedule which could meet our target schedule of completion of the plant construction by March, 1972 to satisfy the time schedule of MITI's air pollution code.
- Fourth: - The estimate of construction cost was comparatively low, relative to other technologies.
- Fifth : - Mitsui Miike Machinery has had extensive experience

in the supply of chemical machinery. Its factory is located near the site so that the sufficient arrangement could be expected for our various technical requirements.

I wish to note that, in order to assure the success in operation of the first commercial SO₂ control plant applied to a large-scale thermal power station based on the wet Calcium base in cooperation with Chemico/Mitsui Miike, we installed a pilot plant with a gas flow of 1/200 of the commercial plant at the site of the power plant when we placed an order for the commercial plant. The operation of this pilot plant in technical cooperation with Chemico provided much knowledge and experience in construction and operation of the commercial plant.

2. Brief history of selection of Chemico/Mitsui Miike process.

In Japan, the dry type SO₂ control processes had been under development, sponsored by MITI and power companies. Dry type SO₂ control processes were omitted from our selection because there still seemed to be many difficulties to be resolved in both the technical and economical aspects. In addition, these dry processes were considered inapplicable to our coal fired power plant which exhausts so much fly ash.

Since we had to achieve reliable operation of the SO₂ control plant within the limited time of construction, the following criteria were established for process selection after our various investigation and examinations.

First: - Economical requirement.

Relatively low capital and operating costs are critical in order to maintain power generation cost as low as possible. To meet this requirement the wet type scrubbing process using a Calcium basis is more advantageous.

Second: - Simplicity of the process.

Only relative simple developments or improvements to the process could be tolerated in order to achieve reliable operation easily. This requirement is very important since it will result in lower maintenance cost and easier operation of the plant.

Third: - Requirement for the absorbent.

There is a plant of The Electro Chemical Industrial Co., Ltd. (Denki Kagaku Kogyo Co., Ltd.) located in Ohmuta City where a lot of wet carbide sludge was disposed and dry carbide sludge is also being produced. As these absorbents were available at low prices, we planned to adopt a Calcium additive SO₂ scrubber system even if we had a disadvantage of a possible problem of build up of scale - a major concern of all at the time.

Fourth: - By-product from waste disposal.

By-products such as sulfuric acid, elemental sulfur and sodium sulfite were not preferable under the market conditions at that time and the local conditions at the site. In case of Calcium base being adopted, either throw-away system or Gypsum process without the secondary pollution is suitable to our requirements.

Fifth:- Requirement for space available.

Since very small space was available, the system which had the least number of scrubber-absorption towers required was one of our basic requirements. Therefore, we required that the process designer should be well experienced.

Sixth:- High efficiency.

It was imperative that high removal efficiencies of dust and SO_2 at low stoichiometric requirement should be achieved.

Seventh:- Assurance of stable and continuous long period operation.

It was also required that the process should not be too much sensitive in operation, but rather flexible to meet the change in load factor of boiler operation and the fluctuation of sulfur content in coal.

3. Outline of SO₂ control plant and basic specification.

The outline of this Power Plant and the SO₂ control plant is shown in the attached TABLE II.

First:- History of SO₂ scrubbing with many different types of calcium additive processes has shown that build-up of scale is one of the most difficult problems. However, we made the decision to employ this process despite the opinion mentioned above being widely accepted.

The basic resolution was to establish optimum operating conditions which would minimize or eliminate scale by first using a pilot plant. Furthermore, we planned to install spare capacity for respective parts of the system including an extra scrubber vessel. This stand-by scrubber unit and other spare equipment was found unnecessary later when the internal inspection of the scrubber system was carried out in November, 1972 after the system had been in service for six months.

Second:- The project of by-product Gypsum production was postponed in order to first achieve successful performance of SO₂ control project. We selected the throw-away system which enabled us to utilize the existing ash pond for disposal of slurry in a form of Calcium Sulfite (approx. 80 wt.%) and Calcium Sulfate. (Now we are going to start Gypsum production.)

Third:- By the request of The Electro Chemical Industrial Co., Ltd. who supplied carbide sludge to the SO₂ control plant where carbide sludge is used as absorbent, we installed a carbide sludge receiving system to handle either wet carbide or dry carbide whichever supplied.

Fourth:- In order to avoid problems in boiler operation due to rapid pressure change in the duct when an unexpected trouble with a booster fan occurred, we developed a specially designed duct which can handle backward flow of gas without any damper.

Fifth:- In determining the gas flow, we settled K value with a figure of 10 anticipating that it would be strengthened to 5 in the future and we decided to install two units of scrubbers having a capacity of 75% each of total gas flow. Two reasons for the reserve capacity were a possible build-up of scale and the anticipated strengthening of K value in future when two scrubbers will handle total gas flow. The operation of one scrubber is enough to meet the present local code.

We proceed with the project with the basic specifications mentioned now and we succeeded in completion of construction of the SO₂ control plant within a short period of nine months in a limited area of approx. 2,000 square meters (21,500 square feet). In the meantime, the preventive measures against the disposal of waste water was also taken. Flow sheet and arrangement are shown in the attached drawings 1 and 2 respectively.

4. Outline of operation status.

On March 29, 1972, the operation of the SO₂ control plant was started and an excellent record of continuous operation for 202 days until October 17, 1972 was established.

Further continuous operation was assured and no necessity of major modification was confirmed when the internal inspection of the plant was carried out for the first time during the annual maintenance shut-down of the power plant from October 17 to November 10, 1972. The plant has been operated further quite satisfactorily since the plant operation was re-started on November 11, 1972 except a shut-down of the power plant for 4 days in January this year due to mechanical trouble in boiler.

Following is outline of operation status.

First:- Continuous operation for a long period.

Fortunately, the operation was carried out without shut-down although there were several troubles, all of which were just minor and resolved without difficulty while the system remained in service.

Please refer to TABLE III for details.

Second:- Internal inspection during the annual maintenance shut-down of the power plant. Every detail of internal parts was inspected twice, namely during the annual maintenance shut-down of the power plant in October/November last year and at the time of boiler shut-down in January this year, and no major defect was found.

Please refer to TABLE IV.

Third:- One of the major items for daily maintenance work. PH values is being controlled strictly by means of sampling of recycle liquor at each 1st and 2nd stage every hour, measuring pH value with a portable pH meter and then adjusting the quantity of make-up slurry at each 1st and 2nd stage using control valves so as to maintain pH value at a pH with the tolerance of plus and minus 0.2 within the range of preferable pH value.

Fourth:- Basic requirement for operation.

Since it was the first commercial SO₂ control plant in the world and any failure should be avoided, the operation was carried out at lower side of pH value within the range of preferable value where build-up of scale was not noticed during pilot operations. The SO₂ removal efficiency was

sacrificed to some extent at the beginning. We are now trying to raise up the pH value gradually maintaining the smooth operation of the plant.

Fifth;- Ash disposal pond construction.

Please see the attached drawing 3, Ash Pond Layout. Originally the ash pond was constructed for ash disposal, however, it is used now for settlement of waste slurry from the throw-away system. Supernatant is returned to the plant for re-use. The ash pond occupies approx. a million square feet and is located at an area of approx. a mile away from the power plant. The wall of south-western side is lined with a polyvinyl film to seal the leak water in order to avoid a secondary pollution problem. Perhaps because of the heavy rains and mine water which flow into the pond, there is no accumulation of sulfuric acid, and we have had no trouble at all maintaining the plant operation during this one year. The returned water is re-used for spray water, level control and make-up of Carbide slurry.

Fortunately, operation is being carried out quite satisfactorily. The requirements for a large quantity of recycle water had been regarded as one of the disadvantages of Chemico process at the time of process evaluation. Actually, however, this disadvantage was proved later to be one of the biggest advantages because of low solid concentration, high SO₂ removal efficiency with lower pH value resulting in prevention from build-up of scale. The data on operation experience are shown in the attached TABLE V.

Economic Features

Plant cost is about one billion Japanese Yen which is about 3 million dollars and this amount works out at about 6,500 Japanese Yen which is about 25 dollars per KW excluding Gypsum plant.

Actual operating costs greatly underran the originally planned budget of 0.3 Japanese Yen/KWH which is about 0.1 cent/KWh for the past year of plant operation. We can definitely say that we have been able to achieve the goals in our economic evaluation which had been planned as one of the most critical requirements at the time of commencing our project. Our analysis indicates that firstly, 70% of the operation cost is spent for interest, which means that the lower plant cost will greatly contribute to the lower operation and secondly, the low cost of absorbent by use of waste Carbide sludge shows clearly an advantage of wet type Calcium basis SO₂ control process. In addition, the measures taken to protect the plant from the possible build-up of scale have been also very useful to reduce the maintenance cost.

The use of the scrubber system has allowed the increased use of lower cost slime coal in our boiler operation. We have increased the quantity of slime coal from 30% (on dry basis) to more than 80%. This lower cost coal contributed in avoiding an increase of the power generation cost by offsetting the increased cost due to construction and operation of the SO₂ control plant.

The ash disposal pond is presently being filled with the waste slurry consisting of mainly Calcium Sulfite. We are planning to start Gypsum production within this year so that we can expect further reduction of the operating cost by sales of this by-product in place of waste disposal. There is a definite market for gypsum in Japan.

Conclusion

It is almost one year since the plant was completed. In spite of being one of the first large-sized commercial plants in the world, it has shown an excellent result beyond our expectation with great satisfaction. Moreover, to our surprise, so many people concerned not only in Japan, but also in the United States and many overseas countries are very interested in our success.

It is our intention that to further try to attain higher performance and more economical operation of the plant. I believe that our strong intent to maintain coal firing power station brought us the great success in the wet calcium base SO₂ plant.

TABLE I

"Brief history of projects of Miike Power Station
and SO₂ Control Plant"

<u>Year</u>	<u>Miike Power Station</u>	<u>SO₂ Control Plant</u>
1967	Project was started.	
1968	(Nov.) MITI approved project.	
1969	Construction was started.	(Feb.) K value: 29.5 Investigation was started.
1970		Approach to domestic and foreign process owners was started. Research test was carried out at Mitsui Engyo Co., Ltd. (Mitsui Salt Ind. Co., Ltd.) using IHI-TCA test plant. (Feb.) K value: 17.5 (Nov.) First survey team was sent to overseas countries.
1971	(Mar.) Test operation was completed and the power plant operation was started. (Fuel coal: 10,250 Btu/Lb S: 1.7%)	(April) Second survey team was sent. (June) Purchase order was placed to Chemico/Mitsui Miike Machinery Co., Ltd. (July) Test using a pilot plant was started. (1,500 SCFM)
1972		(Jan.) K value: 11.7 (Mar. 29) Operation of SO ₂ control plant was started. (Apr.) SO ₂ control plant passed acceptance test by MITI.

<u>Year</u>	<u>Miike Power Station</u>	<u>SO₂ Control Plant</u>
1972	<p>(June) Installation of an additional pulverized coal dryer was completed.</p> <p>(Fuel Coal: 9,550 Btu/Lb S: 1.8%)</p> <p>(Oct.) Power plant was shut down due to the second annual maintenance and inspection.</p>	<p>(May) Performance test was carried out.</p> <p>(Sept.) Plant performance was checked under various operating conditions.</p> <p>(Oct.) Inspection was made at the first time to check internals of equipment of SO₂ control plant during the power plant shut down.</p> <p>(Oct.) Test operation of Gypsum plant was completed.</p>
1973	<p>(Jan.) Power plant was shut down due to boiler tube leakage (for 4 days).</p> <p>(Feb.) (Fuel Coal: 9,900 Btu/Lb S: 2.2%)</p>	<p>(Jan.) K value: 9.34</p> <p>(Jan.) Inspection was made again during shut down of the power plant.</p>

T A B L E II

"Outline of Power Plant and SO₂ Control Plant"

1. Electric power plant

- | | | |
|-----|-----------------------------|--|
| (1) | Generator: | 174,000 KVA, 15,000 V, 60 HZ |
| (2) | Turbine: | 156,250 KW 3,600 rpm |
| (3) | Boiler: | 490 T/Hr, Manufactured by
F.W. - I.H.I., Single drum natural
circulation type. |
| (4) | Combustion system: | Pulverized coal firing, Front
burners arrangement type. |
| (5) | Coal treatment: | Two slime coal dryers, having
a capacity of 24 T/Hr and 45
T/Hr. each. |
| (6) | Electrostatic Precipitator: | Dust removal efficiency: 98.7%
Outlet dust loading: 0.25 Gr/SCFD |
| (7) | Stack: | 425 ft high, concrete outer shell. |

2. SO₂ control plant

- | | | |
|-----|------------------------|--|
| (1) | Process: | Chemico/Mitsui Miike Machinery
process, wet type and Calcium base. |
| (2) | Capacity: | 2 units of gas flow of 241,000 SCFM
each.

One unit only is operated for the time
being to handle 75% (241,000 SCFM)
of total gas flow (319,000 SCFM)

Two units will be operated simultan-
eously when required to handle to
total gas flow in future. |
| (3) | Performance guarantee: | SO ₂ removal efficiency: 90% or more
Dust " " : 90% or more
Stoichiometric requirement of
absorbent 120% or less
Continuous reliable operation. |
| (4) | Equipment details: | Boost-up Fans : 1,000 KW x 2 units

Recycle Pumps: approx. 200 KW x
6 units. |

Scrubbers : 241,000 SCFM x
2 units.

Reheat Furnace : 1 unit incl. Fan etc.

SO₂ Analyzers : 2 units.

(5) Disposal system:

Throw-away system.

Waste slurry is transferred to ash pond and supernatant is returned from ash pond to SO₂ control plant.

(6) Gypsum plant:

Under planning.

T A B L E III

"Report on minor troubles occurred in operation of SO₂ Control Plant"

- | | | |
|----|---|---|
| 1. | Modification for improvement of carbide sludge receiving system: | 1) Protector was installed to protect Agitator from damage caused by various foreign matters contained in wet carbide sludge. |
| | | 2) Dry carbide sludge contains approx. 3% of carbon particles and other foreign matters. Cyclone separator was installed to avoid possible troubles of piling-up in a slurry tank and erosion caused by carbon particles and foreign matters. |
| 2. | Improvement of ash pond water return pump: | Wooden chips flowed from timber yard into ash pond by heavy rain of typhoon in June, 1972 and plugged suction side of ash pond water return pump. Use of substituted water caused increase of pressure drop of gas at 1st stage mist eliminator due to insufficient pressure of water for mist eliminator washing and may have caused build-up of scale. Improvement was made and strainer of pump was installed. |
| 3. | Improvement of flushing schedule of washing spray at mist eliminator: | Flusing schedule was improved. |
| 4. | Change of make-up point of Carbide slurry: | Feed point at 2nd recycle line was improved to avoid build-up of scale. |

5. Improvement of connecting tubes for tangential nozzles of recycle liquor of scrubber:
 - 1) Scrubbing liquor ran out due to loose fitting of chemical tubes. The tubes were changed to rubber tubes.
6. Improvement of rubber lining arrangement after butterfly valve:
 - 1) Rubber lining of pipe inside was damaged at a part after butterfly valve due to turbulence. The trouble was resolved by installation of orifice.

T A B L E IV

"Status of equipment and internal parts of SO₂ control Plant inspected during annual maintenance shut-down of the power plant"

- | | | |
|----|--|---|
| 1. | Carbide Sludge receiving system: | Piling-up of carbon particles was found in slurry tank. |
| 2. | Scrubber: | No defect was found at glass flakes lining. No build-up of scale was also found. |
| 3. | Recycle liquor piping: (rubber lining) | No defect was found in general. Thin deposit of scale (1/25" to 1/12" thick) was found but the plant was operated without trouble. Slight damage of rubber lining was found at a part of piping after butterfly valve. |
| 4. | Mist eliminator: | Partial build-up of scale was found at the parts of:

1) area affected by trouble with ash pond water return pump at the time of typhoon in June, 1972.

2) outer area water coverage of spraying water was not sufficient.

No trouble is anticipated in future operation because of minor modification in mist eliminator sprays. |
| 5. | Piping to disposal pond: | No erosion, corrosion and build-up of scale were found. |
| 6. | Recycle water pipeline: | Muddy scale was found, but removed completely without trouble. |

- | | | |
|----|-------------|---|
| 7. | Pumps: | No trouble was found. |
| 8. | Ducts: | Slight damage was found at expansion joint. |
| 9. | Delay tank: | Piling up of carbon particles contained in slurry was found.
Exhaust gas containing a very small quantity of SO ₂ was connected with a stack thru, vent gas piping. |

T A B L E V

"Operation Data"

Most of figures were
obtained in operation
during January/February
1973.

1. Characteristics of coal.

Heat value:	9.800 Btu/Lb
Moisture:	6%
Ash content:	2.91%
Volatile matter:	35.44%
Fixed carbon:	36.86%
Moisture content:	1.59%
Sulfur:	2.2%
Ash fusibility:	S.P. 2330° F

2. Characteristics of carbide sludge:

	<u>Moisture</u>	<u>Consumption</u>	<u>Purity</u>
Wet carbide:	55%	approx. 80 T/D	85% as $\text{Ca}(\text{OH})_2$
Dry	6%	" 30 T/D	90%
Total:	-	110 T/D (wet base)	

	$\text{Ca}(\text{OH})_2$	CaSO_3	CaSO_4	CaCO_3	SiO_2	Al_2O_3	Fe_2O_3	200 mesh thru.
	wt. %	$1/2\text{H}_2\text{O}$	$2\text{H}_2\text{O}$				wt. %	%
Wet Carbide:	84.3	1.8	1.0	6.9	1.7	0.7	1.1	99.72
Dry "	87.8	3.9	0.3	4.9	2.7	0.7	0.7	87.12

3. Main operation data (as of October, 1972)

Output:	156,000 KW	
Coal:	9,700 Btu/Lb	S: 1.9%
Gas load to handle:	75%	

SO ₂ concentration	Boiler outlet	1,900 ppm
	Scrubber outlet	180 ppm
	Stack	610 ppm
Gas temperature	Boiler outlet	315°F
	Scrubber outlet	130°F
	Stack	212°F
	Reheated gas	172°F
K value:	7.84	
Ca(OH) ₂ :	Stoichiometric requirement:	
	105 to 110%	

4. Return liquor from ash pond.

pH 8.2
 Ca⁺⁺398 ppm Mg⁺⁺70 ppm Cl⁻ 728 ppm NO₂⁻0.28 ppm
 SO₄⁻⁻1,012 " Fe⁺⁺0.45 " Mn⁺⁺-
 SS 5.2 " COD 6.4 "

5. Slurry analysis.

	<u>Ca(OH)₂</u>	<u>CaSO₃</u>	<u>CaSO₄</u>	<u>CaCO₃</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>
Make-up	87.3	0.5	0.7	2.3	1.9	0.24	0.8
Bleed	6.0	69.5	12.2	1.02	5.8	2.6	0.3

TABLE VI

Explanation of "K value"
which is used as the SO₂
emission standard in Japan

K value

Constant ranging from 5.26 to 29.5 according to the area stipulated by the Air Pollution Control Law of Japan and is shown in the following equation concerning SO₂ allowable emissions.

$$Q = K \times 10^{-3} \times H_e^2$$

Where	Q:	Quantity of SO ₂ allowable emissions from the stack. *(NM ³ /HR)
		* Cubic meters at 0°C and 1 atm.
	H _e :	Effective height of stack (Meter) calculated by the following Bosanquet's formula. $H_e = H_o + 0.65 (H_m + H_t)$
	H _o :	Actual height of stack (Meter)
	H _m :	Equivalent height of stack (Meter) effected by discharged flue gas momentum.
	H _t :	Equivalent height of stack (Meter) effected by discharged flue gas temperature.

Both H_m and H_t are calculated by the following formulas

$$H_m = \frac{4.77}{1 + 0.43 \frac{V}{V_g}} \times \sqrt{\frac{Q_1 V_g}{V}}$$

$$H_t = 6.37 g \times \frac{Q_1 - t}{V^3 T_1} (\log_e J^2 + \frac{2}{J} - 2)$$

$$J = \frac{V^2}{\sqrt{Q_1 V_g}} (0.43 \sqrt{\frac{T_1}{gG}} - 0.28 \frac{V_g T_1}{g \Delta t} + 1$$

Where

Q_1 : Quantity of wet flue gas discharged from
(M^3/SEC)

V_g : Discharge velocity of the above gas (M/SEC)

V : Wind velocity (M/SEC)

T_1 : Temperature at which density of discharged
flue gas becomes equal to that of atmosphere ($^{\circ}K$)

Δt : Difference between temperature of
discharged flue gas and T_1 ($^{\circ}C$)

G : Temperature gradient ($^{\circ}C/M$)

g : Gravity constant 9.81 (M/SEC^2)

T_1 and G are usually assumed to be $288^{\circ}K$ ($15^{\circ}C$) and
0.0033 respectively.

In case of Ohmuta city, (where Miike Power Station is located.)

$K = 9.34$ usually employed

$K = 5.26$ employed in an emergency when
judged by the local government.

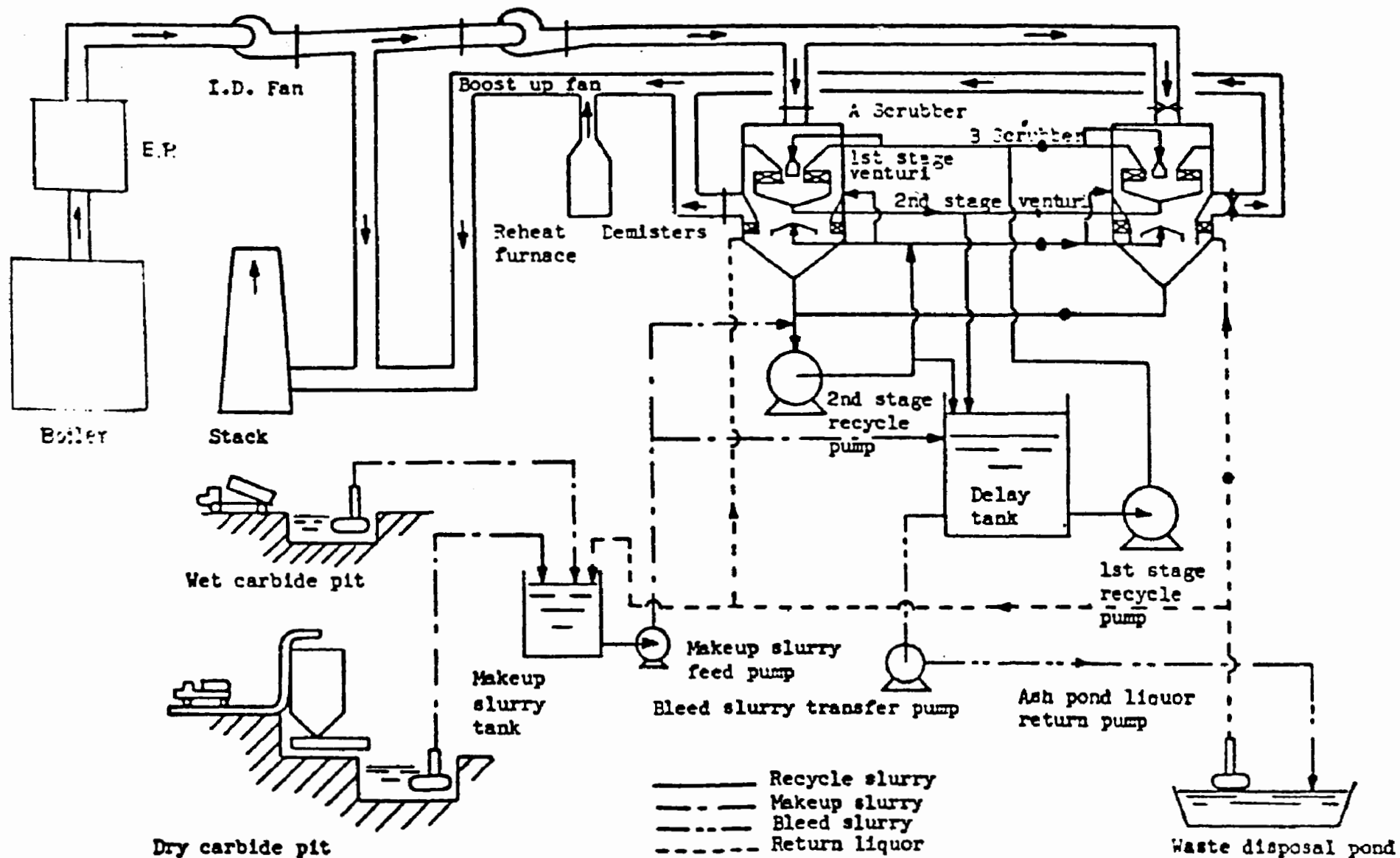
For the Ohmuta area, the K-value has been progressively decreased, leading
to more stringent emission limitations with time, such as

1968: $K = 29.50$

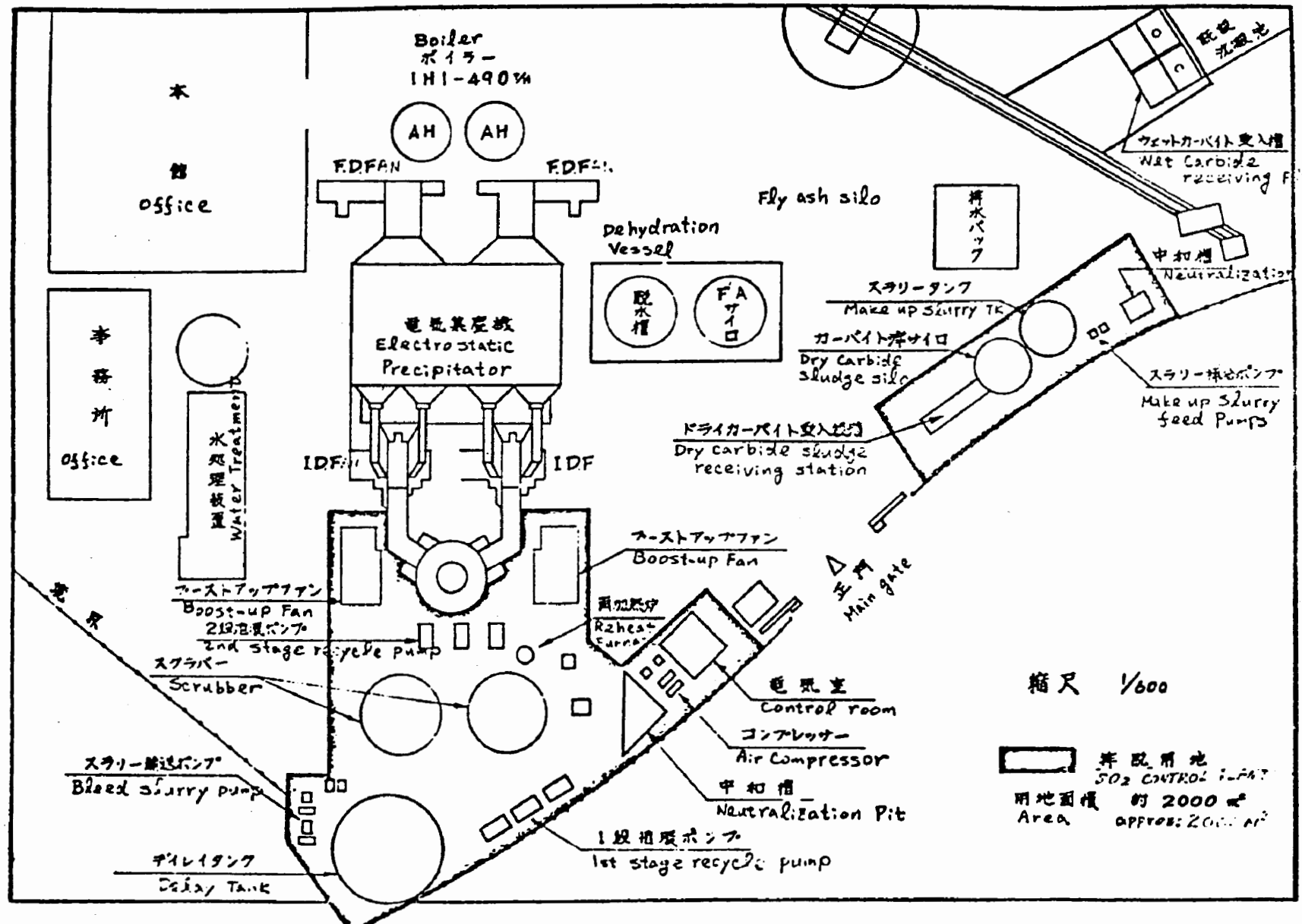
1970: $K = 17.50$

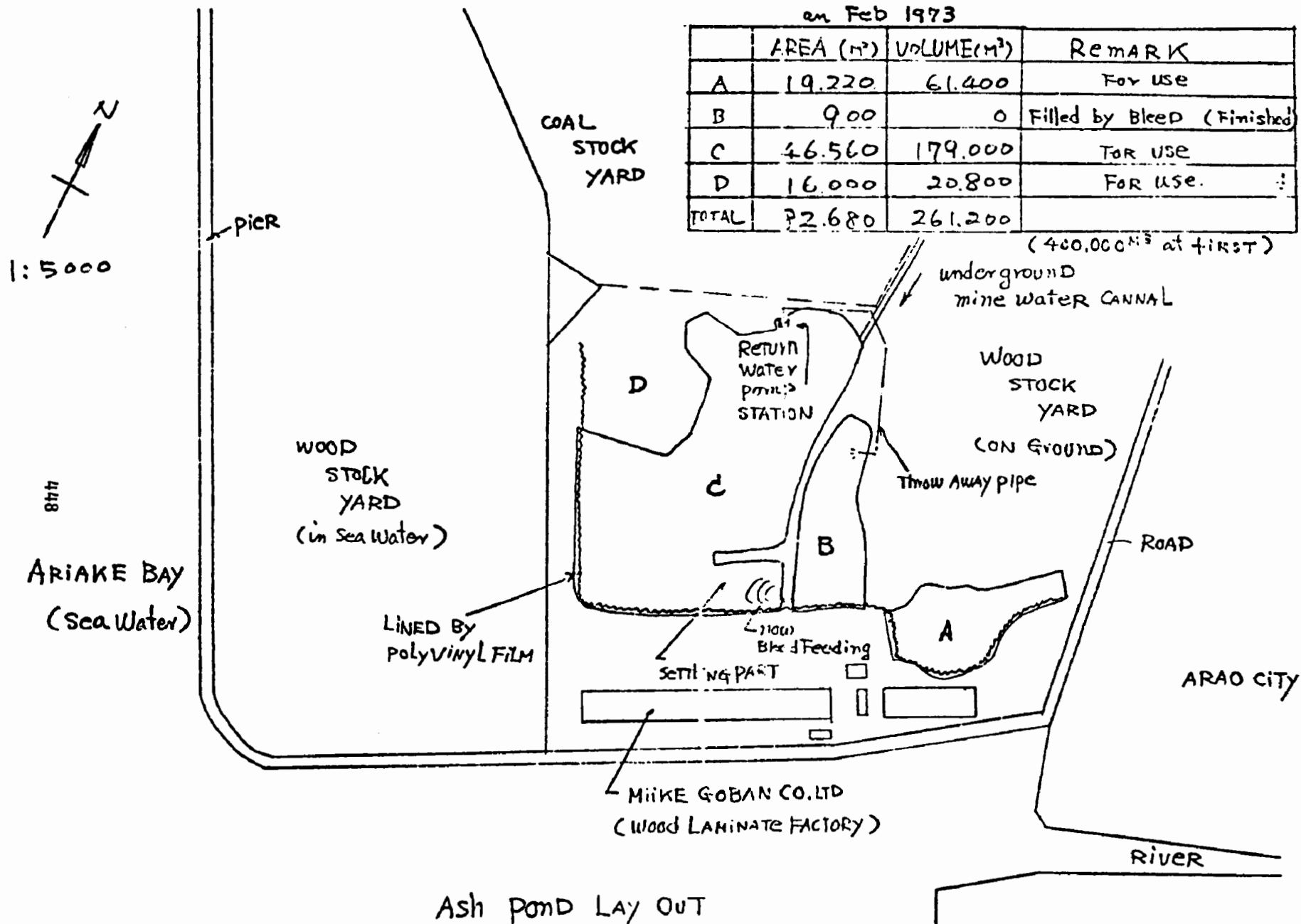
1972 $K = 11.70$

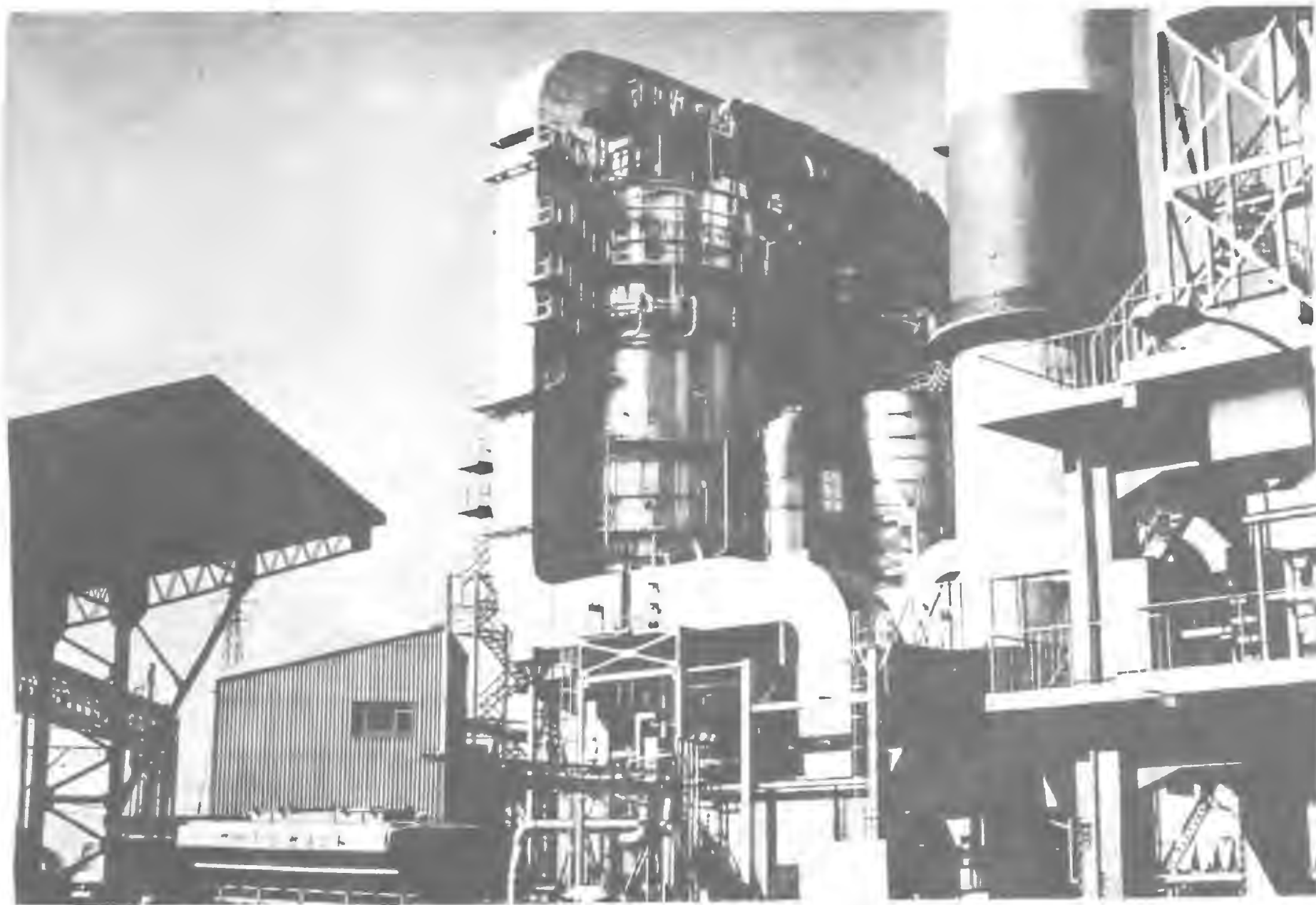
1973 $K = 9.34$



Process Flow Sheet







#1 Ohmuta scrubber



#2 Ohmura pond system

PANEL DISCUSSION:

SIGNIFICANCE OF OPERATION TO DATE
OF 156-MW CHEMICO/MITSUI LIME SCRUBBING SYSTEM

PANELISTS

P. Wechselblatt - Chemical Construction Corporation

J. Craig - Southern Services

H.W. Elder - TVA, Muscle Shoals

F.T. Princiotta - EPA

Pond Saturation

P. Wechselblatt— In the questions that were raised perhaps the one that everyone was most interested in was the degree of saturation of the pond. And I think that in order to view this, it is necessary to understand exactly what is happening in the system. A great amount of liquid is being recycled (perhaps 90 gal/1000 cfm in total), and there is a huge storage of liquid. The amount of liquid going to the pond and coming back from the pond is very low. In fact, if the liquid coming back from the pond were boiler feed water, it would change the degree of supersaturation by only 4 percent in the scrubber. Therefore, except for the fact that Bob Quig took a walk on it—and I am sorry there was no picture of just a hard hat where he sank—the pond was completely irrelevant to the degree of saturation or supersaturation in the scrubber. And when we argue about the pond points, I would suggest that if you looked at the points in the scrubber recycle loop you would find invariably that the liquid is saturated or supersaturated; therefore, the only line in question on the job is the return line from the pond to the scrubber. That line, of course, could scale if you had supersaturation, but all other lines in the system are operating in the supersaturated mode.

Lime/Limestone Buffering

The second thing that I would comment on is the buffering action of limestone and the buffering action of lime. There really is very little black magic in this. The numbers are reproducible. Everyone has done a great deal of work in the last 5 or 6 years. When I was at the startup of the plant in Omuta and helped with the performance tests, we altered the carbide sludge to the system because our guarantee to Mitsui Aluminum was a more severe guarantee than their requirement from the State, from the municipality. So it was necessary to run the system at times for guarantee purposes for the period for the guaranteed tests at a stoichiometry where we could obtain better than 90 percent SO_2 removal. Under most of the yearly conditions, since the code requirement is not that stringent, the plant operates between 80 and 85 percent removal with a lower utilization of carbide sludge. The system was remarkably responsive to alterations in the carbide sludge feed. For example, if you wanted to raise the pH of the system from 7 to 8.5 (which might have a stoichiometric change of perhaps 0.9 to 1.2), it was possible to watch the pH change with the change in lime feed. The response time of the system is excellent. Now you try to balance the response time of the lime system against the buffering action of the limestone system. I really do not want to get into a hassle about it, but this rapid response really is a tremendous aid. Particularly when putting the system on automatic control (which would necessitate sulfur dioxide measurements, gas volume measurements, and things of that sort), you want the system to respond very quickly. This system responds almost instantaneously. And I might say that with a change in feed you can

watch the SO₂ out of the stack increase as you change the hydroxide feed. It is almost instantaneous. You can watch it take place.

Mist Eliminators

Another comment that was made this morning had to do with mist eliminators. Chemico operates mist eliminators very successfully. We have had problems on other jobs, but we have never had a problem with mist eliminators. We operate them on a rotating cycle and at a higher velocity than anyone talked about this morning. In fact, if you take a look at the design, you will find that usually about 20 percent (15 to 20 percent) of the cross-sectional area is taken up by supporting structure. Therefore, the mist eliminators in general operate at about 20 percent higher superficial velocity than anyone calculates when they calculate a cross-sectional area of the vessel.

Japanese Versus American Results

I was impressed when I saw the plant in operation. I have seen plants of various sorts in this country, and I would just like to say this, and I feel very strongly about it: it is kind of a challenge. I am disheartened when I see a system designed in this country that was erected by the Japanese in 9 months. We started at the same time in this country, doing the same design work, and the first unit we will have operational in the United States will be in another 2 to 3 months—almost a 30-month schedule compared with their 9-month schedule. They take our design sheets and process flow sheets, which they pay for; they build a plant; and they start operating a plant. They have no particular problem, and if they can do it there, we can do it here. And I think it is a challenge to the industry. There is no reason why the Japanese can do it better than we can.

H. W. Elder - Okay, the subject is of significance and I think we will all have to agree that in Japan the significance is unquestionable. It has been an excellent installation. The Japanese have done one fantastic job of installing equipment and making it run. And it is a real credit to the initiative and fortitude of the Japanese that they had this large measure of success. We have a problem now in translating that technology to application in this country, and this is in no way taking a shot at what has been done in Japan.

Transfer of Technology

I think there are some questions that must be raised about transfer of technology from one application to another. I hate to beat this horse some more, but this closed-loop business is important, I think; and Pete (Wechselblatt), I am not sure I agree with your total conclusions on that point. Number 1, it is too bad we have to talk about closed-loop systems. We need some guidelines on quality of water that can be discharged from any plant, not only limestone scrubbing power plants, but any situation. And that would give us some guidelines then as to how much blowdown we could take and how much fresh water we can add. Therein lies the important point, because if you can add no fresh water, I can practically guarantee that you will have scaling. Based on TVA's pilot plant operation and my conversations with experienced persons, I believe that use of saturated and supersaturated solutions for washing mist eliminators (or for points where dilution is required) is absolutely essential if you are going to avoid scaling. So I think that you have to use at least some makeup water to make the system run. So then it is just a question of the amount. For your situation or for the Mitsui

situation, particularly with the low solids concentration in the recirculated stream, the sulfate concentration can be rather critical. I think that the accepted (well, it is pretty well agreed) way to control sulfate scaling is by recirculation of calcium sulfate to provide precipitation sites. And the lower the solids concentration, of course, the lower the sulfate concentration. So if it becomes saturated with sulfate, I would expect scaling to occur. The low solids in the loop coupled with the clarifier liquor returned from the pond with a high sulfate concentration could be dangerous it seems to me. A couple of other points of uncertainty, and again I am just raising questions, the fact that the waste material settles in a fashion that is a little bit unusual based on our experience is a little perplexing. I think that if the sulfite/sulfate ratio in the reacted solids is similar to that which we have experienced, you would expect it to settle very poorly. So this says to me that maybe there is something different about the carbide sludge as compared with freshly calcined lime—differences in particle size or differences in surface characteristics, for example. But if the sulfite/sulfate ratio is the same and if the particle size is the same as freshly calcined lime, you would expect the reacted product to behave the same way. As far as flyash removal from the system, I am not sure how important this is. If I were personally putting in an order for a system for control of SO_2 from a new power plant, I would certainly want to take the flyash out as well as avoid the expenditure for a precipitator. What effect the dust has in admixture with the calcium reaction products is really not clear, but it is worth raising the question. It affects both the chemistry of the liquor and, of course, it affects the erosion or

mechanical considerations in the scrubber system itself. So there are really four main points that I am raising relating to the transfer of technology: the amount of fresh water and how it can be added; the question of low solids; the effect of sulfate on precipitation; and the effect of flyash in the recirculating slurry loop. As I say, I am not throwing rocks. I am just raising questions.

J. Craig—I will keep my discussion pretty brief. I feel there will be a number of questions from the audience and probably some discussion on the panel. Apparently, the installation is meeting Mitsui's design criteria and operating goals. Mr. Sakanishi (J. Sakanishi, Mitsui Aluminum Co.) and all the employees at his station are to be commended on a well run and well maintained operation. Now, as to what I saw there: I saw a station operating base-loaded, with apparently very little variation in the flue gas flow rate. We observed operating logs for 8 days; based upon that, there was probably plus or minus 2 MW variation from around the 156-MW capacity of the unit. In comparing that variation to our stations, where we can go from probably 40 percent to 110 percent of the flue gas flow rate in a matter of 24 hours, it leaves some question in my mind whether you can just extrapolate Mitsui's operation to a typical plant in our system. We also observed that sulfur content in the coal was pretty constant at Mitsui; this is because of where they get their coal and how it is processed. Again, if you look at our sulfur content, it could vary as much as 2 to 4 percent sulfur in a relatively short period of time. I believe both of these favorable operating conditions allow Mitsui to run a chemical plant the way a chemical plant should be run—either at or near steady state conditions. I am not fully convinced myself that we can run

our typical units in this same kind of mode. I, too, walked on the pond, but that is a little bit misleading—I am not a Sumo wrestler. The pond has a crusted surface approximately 6 inches thick. It held me up, but Mr. Sakanishi warned me not to go too far out. We penetrated the crust very easily with a stick; below the crust was a very pasty material. I might indicate that the top layer was thixotropic in nature. As a consumer, we would like to buy a system that includes a solution to the problem of waste disposal. Mitsui apparently has solved their problem for a short operating time; they are going to a gypsum final product. Again, I am not sure that is the best solution for our needs. In addition, there is some question regarding the water balance. Members of the group walked around the pond and could not find any visible overflows from the pond. That was on one given day and I cannot say that that was the way it was for a year. We were not able to resolve the question of open-loop versus closed-loop operation.

Areas of Commonality

F. T. Princiotta — First of all, I think we should discuss areas of commonality and areas of difference, with perhaps the first statement being that I do not think any one plant in the United States, for that matter, is completely representative of all other coal-fired plants; it is an impossibility. We tried to do it at Shawnee, I might add, and it is just impossible. Everybody has a different sulfur content in the coal, a different ash content, and different sludge disposal logistics. So I think it is unreasonable to expect one particular plant, particularly in

a foreign country, to answer all questions regarding this technology. However, I think anyone who has studied the system carefully has seen that there are really amazing parallels to many U. S. applications, many areas of commonality. In the first place, it is a lime-based American system utilizing American-based technology. And, as everyone knows, much potential exists for these systems in the United States due primarily to the low cost of the input alkali. In my opinion (based on discussions I have had with Combustion Engineering people, Chemico's pilot plant experience, and the English experience 40 years ago), there is no reason to believe, well there is no hard evidence, that there is any difference in the characteristics of carbide sludge as opposed to calcium hydroxide. The major difference that I see is that it is a pure form of calcium hydroxide. Other areas of commonality include unit size, percentage of sulfur in the coal, and use of a precipitator. The 156-Mw unit can be easily scaled up without any increase in size of the basic module which can handle this amount of flue gas. The system uses 2 percent sulfur coal, whereas many coals in the United States may have higher sulfur content. Yet, if you averaged out the sulfur content of all the coals in the United States, I suspect it would be close to 2 percent. Admittedly, it would be nicer if that plant happened to have 3,4, or 5 percent sulfur coal; but it is relatively close to many U. S. coals. Regarding the precipitator upstream of the scrubber, as you well know from several discussions so far, many utilities plan to employ a precipitator. The Navajo/Mohave experiments will have a precipitator upstream of the scrubber. And it is not necessarily any dramatic, in my opinion at least, cost advantage

to go in with an all-scrubber system as opposed to a precipitator/scrubber. I think Gary Rochelle (G. T. Rochelle, EPA) treated this in one of his earlier papers. So again, it is not representative to all cases, but a reasonable case.

Areas of Difference

In my mind, the major areas of difference that are really significant were brought out by John Craig; they are in the areas of the system being base-loaded with relatively constant coal. Again, of course, there are many systems in the United States that approximate this condition but there are also many plants, particularly the older units, that do not. They do have wide swing loads, as we heard for the Will County unit. This is an area of difference and could affect the control of the system. I think we should also mention that within several months, Pete Wechselblatt referred to it informally, there will be a Duquesne Light scrubber on the line. This will be very similar to the Japanese Chemico scrubber and will, I think, answer quite a few questions about relating this technology to the U. S. situation. I believe that much of the success did relate to the use of Japanese equipment and Japanese construction personnel. I think there is no question (based on Shawnee experience, and experience of chemical plants, refineries, and other chemical operations) that the reliability and quality control of American equipment leaves a lot to be desired. There is no question about that in anyone's mind, really. Regarding the blowdown situation, my own belief is that it is not very relevant because the model proposed for sulfate

scaling, which is what is at issue here, indicates that the degree of supersaturation of calcium sulfate is the significant parameter. Now this has not been proven, but it is the most widely held theory and I think that Pete Wechselblatt is right in the calculation that there is only a minimum of 4 percent difference in this degree of supersaturation in the scrubber itself. So I am not worried about whether the pond leaches or not. Of course, it presents a water pollution problem that is certainly serious in the U. S. But, as far as operability is concerned, that may not be significant. I think I should briefly mention the settling differences. Based on the results presented yesterday in the sludge discussions, I think it should be mentioned that probably what we are seeing here is not any difference in sludge. What we are seeing is drying of the top layer of sludge. Based on everything that I have seen and heard, I would suspect that, in times of rain, this would probably end up reslurrying again and forming the boggy type sludge materials that have plagued other installations, like Will County. So in my mind, there is nothing magical about the sludge. And I think we heard earlier that, given the right weather conditions, people have walked on Will County Sludge.

Open Discussion

We are now open for discussions and anyone who wants to challenge anyone else on the panel, go right ahead.

P. Wechselblatt — I am not picking points. I recall one fact which has not been stated and that is that the sludge going to the pond contains approximately 15 percent calcium sulfate and, therefore, 85 percent calcium sulfite. And the significance of that is that calcium sulfate must be

coming out of solution because 15 percent is too high a number for SO₃ collection. So there is calcium sulfate coming out of solution and this is a demonstration that the solution is in fact over saturation.

H. W. Elder — Frank (Princiotta), I would like to question one of your points. You say that the average sulfur in U. S. coals is about 2 percent, but the system does not operate on a national average sulfur level, you know. It operates on what you have to burn. I think you will have to agree that there is a significant difference in removing 1000ppm and 5000ppm of flue gas. I think that the level certainly must influence the liquid-to-gas ratios and other important design considerations. So differences between the levels operated at Mitsui and those that we face in the TVA system, for instance, are important differences.

F. T. Princiotta — Yes, and I agree. But 2 percent, in my opinion, is not very far from many high sulfur coal problems, the average probably being around 3 percent.

I. S. Shah (Combustion Equipment Associates, formerly with Chemico) — I was part of the successful installation at Mitsui/Miike. Last year we were talking about whether to use lime or limestone, and I think there is only one system in the world that is operating successfully without mechanical problems of any kind and that happens to be Mitsui Aluminum. We have a lot of installations with limestone, regardless of equipment problems or process problems, that are not still operating successfully. So now here we see a successful operating unit. Instead of asking questions about why it works, let us start asking how it works. And let us learn something from that and make the technology better, rather than fighting

with "My lime system works and my limestone system does not work." The second question regards the saturation solubility. Everybody has talked about solubility of sulfur/sulfite, in the presence of all the components. Everybody is theorizing. It should be this because that is what I have. TVA got some that they say is the sulfite/sulfate ratio. Maybe they have a unique oxygen, unique coal, unique flyash. Maybe, then, nobody else has it. We talked about the saturation solubility within the scrubber just like Pete (Wechselblatt) said. It is 90; it must be almost beyond supersaturation because the amount of bleed that you are taking out from the scrubber loop is practically, I would say, within 5-10 percent of the total recycled liquor. Now we talked about the ponds. The next installation that is going to come on line and which is under design, I think, is TVA's Widow's Creek.

Open - versus Closed-Loop Operation

Can I ask you a question, Bill (Elder)? Have you designed that pond for no leaching, no overflow, or complete recycle loop? And if not, why?

H.W. Elder — Because we cannot control scaling if we operate in a completely closed loop.

I.S. Shah — So you said open-loop is required for reliability of operation.

H.W. Elder — Well, you will hear more about this during the Widow's Creek discussion, but basically we are. . . .

I.S. Shah — I was asking a question. Is open-loop necessary for reliable operation of the SO₂ systems or not? In my opinion it may be necessary.

H.W. Elder — I was trying to answer the question. The system does have a horizontal mist eliminator and that mist eliminator is washed with once-through water. The scrubber loop itself is closed-loop except, of course, for the makeup required for evaporator of that that goes with the solids. But the design of the mist eliminator loop itself is open-loop. We would like to learn how to put that back into the scrubber system. Based on some of the progress we have made at Shawnee, that may happen. But right now, it is designed for the mist eliminator to have a blowdown from it. You are right, we probably do not know exactly what the sulfite/sulfate levels are. But we know what happens when it gets too high: we have grown some mighty nice gypsum crystals in the mist eliminator by trying to use saturated (or at least high sulfate level) liquor for wash. So we know the effect even if we do not know the reasons.

Alex Weir, Jr. (Southern California Edison) — We have been able to operate, in essence, a closed-loop system for about 3 months, and have washed with lime slurry mist eliminators without any really serious problems.

Bob Sherwin (Bechtel Corporation) — There is one point that is not clear to me. I would just like to ask what is being done with the precipitator ash at the Mitsui aluminum plant. Does this go out to the lime pond?

F.T. Princiotta — I do not believe it does, but why not ask Pete (Wechselblatt)?

P. Wechselblatt — Well, I do not know where it goes. Mr. Sakanishi would. But it does not go the lime pond because Mitsui is trying to keep the calcium sulfite as pure as possible for gypsum.

A. Weir — Okay, it does not get mixed.

P. Wechselblatt — No, it does not.

Joe Selemczi (Dravo Corporation) — I also had the pleasure of the congenial hospitality of Mr. Sakanishi. There are two points I would like to contribute to this discussion. One is that when we are talking about sulfur content of coal, we have to look at the Btu value, which was somewhat lower for Japanese coals than for the Eastern coals in the United States. So that coal would calculate out to something like 2.5 to 2.7 percent sulfur based on Eastern coals. There is also a lot of varied thinking about the sludge and why somebody can walk on the water of Gethsemane there. Actually, what Mitsui has going into the pond is a lean slurry of calcium sulfite sludge containing about 3 to 4 percent solids. You can compare this with a horizontal, long settling tank. The heaviest fractions settle out first and build up close to the discharge points. That is what you can walk on; nobody walked out to the section of the pond that is farther away from the discharge point. Now I can say this with confidence because we have examined the sludge from Japan as well as many dozens of other sludges. When you operate the thickener with 3-4-5 percent solids content in the sludge, you are in the free settling zone. Correspondingly, your discharge will behave entirely differently in your pond. When you have a 20 percent or higher solids content thickener underflow, settling is going to be hindered. The discharge is not going to settle preferentially. You are not going to have the larger particles settle out close to the discharge point and the fine particles travel maybe a few hundred feet or maybe a few thousand feet if you happen to have that kind of distance. These are the

comments I wanted to make.

Ab Saleem (Peabody Engineering) — My comments are related to the L/G's which are used and the SO₂ removal that can be obtained. I would like to submit to the panelists and the audience: if you sprayed all that water to an open shell with no internals you will get removal of 90 percent or more. And to me the 300-mm system pressure drop is excessive and unnecessary.

F.T. Princiotta — Sounds like you may be selling a spray unit. I might add that, although it was not brought out, there is some particulate removal requirement in the venturi scrubbers. As I recall, it is approximately 0.007 gr/scf of particulate outlet of that system. As far as I know there is nothing in the United States that can match that right now. So keep in mind pressure drop does buy us some particulate removal.

J. Ando (Chuo University) — Mr. Sakanishi wants me to explain something for him. There is a variation of the operating load. As I said, the operating load is fairly uniform for the Mitsui aluminum plant. But he has the experience that on a few occasions the operating load could amount to nearly 50 percent of the usual operating load, but he could not follow up the variation. It is not very often, so they operated very carefully and they have done it without any problem.

J. Craig — Let me go a little bit further then. It is not often and for what time period did this occur?

J. Ando — (after conferring with Mr. Sakanishi) - Several times in 1 year.

J. Craig — But not on a daily basis?

J. Ando — Just for one day he dropped, and then backed up.

J. Craig — For one day?

Question — I would like to ask Pete (Wechselblatt) a question. Pete, how critical is water makeup at various locations in the scrubber and mist eliminator? And if it is extremely critical, what would happen if that loop were closed and how, when you talk about the pond's being supersaturated, does it take a little bit of water to drop the supersaturation in order for it not to scale?

P. Wechselblatt — Our newest jobs in this country are designed to utilize fresh water makeup; that is, the liquid lost by evaporation. This water is used preferentially for pump seals, for fan spray wash water (if in fact there is a wet fan), and for mist eliminator wash water. Of course there are differences. I am sure different equipment suppliers and different designers have different rates at which they wash mist eliminators, for example. But the rate set at Mitsui is such that the normal evaporation loss of the system (and therefore that concomitant makeup) is satisfactory to use all the fresh water makeup to wash the mist eliminator and allow you to have approximately 50-75 gal/min left over for fan spray wash water and 5 gal/min per pump seal. So in our view, the quantity of evaporation down to about 50 percent load is satisfactory to add the fresh water to where we think it is most important.

Paul Cho (EPA Region V) — I would like to answer one of the questions that John (Craig) brought up. That is, your worry about some of the plants which are operated under a fluctuating load condition. I think that is not a technical problem in itself. And secondly, people are concerned

about open-loop or closed-loop. I think this is a little bit confusing here without defining what percentage of makeup water we are talking about: if operating loss itself were defined, you could see an absolute closed-loop system. And I further suggest that a power plant in this country has cooling water operations and there is some border proton water available. I was wondering if anyone has looked into this area as makeup water.

J. Craig — Well, the discussion really is the applicability of Mitsui and what Mitsui demonstrates to the U.S. Regarding the ability to bypass gas, are you saying you bypass a certain percentage of untreated flue gas to the stack? If so, will the regulations in Japan allow you to do this?

P. Cho — No, I think that the bypass I am talking about is that instead of using one scrubber, probably you can use two. This is perfect application in terms of your fluctuating load condition. If you have two modules and bypass you can vary the stoichiometric ratio as well as the amount of flue gas introduced into the scrubber.

J. Craig — Well, we are talking about probabilities versus what we saw at Mitsui and the probability is an expensive gamble.

F.T. Princiotta — I think it is a good point though. To some extent, John (Craig), would you not agree, that costs can help you buy reliability; having extra scrubbers, I do not think one can argue, does improve reliability.

H.W. Elder — I think the important point here on turndown though, Frank (Princiotta), is that with variation in gas flow rate or variation in sulfur level, the trick is to absorb a certain amount of sulfur in a given volume of liquor and to precipitate part of it and accommodate some as soluble solids until it gets out of the scrubber. And if the ratio of

absorbed sulfur per unit volume changes for any reason, it can upset this balance between solubility in the scrubber and, therefore, precipitation in the scrubber. And that is the key point, really.

A.V. Slack (TVA, Muscle Shoals) — There have been a great many postulations here. I wish we had a little more in the way of hard data. Pete (Wechselblatt), as I understand it, you consider that it does not make any difference, as far as operation of the scrubber is concerned, whether one operates with saturated liquor return or not. Is that a correct interpretation of your remarks?

P. Wechselblatt — Yes.

A.V. Slack — Well, this does not agree at all with not only data at TVA and EPA, but it does not agree with data in Europe. I have seen a plant there in which the lime system is being operated closed-loop with saturated return liquor, and there was scaling. And I cannot see much difference in data, really, between your operation and the other. So I think this is a postulation on your part. Now if you have pilot plant data in which you have actually operated a saturated return liquor, I would like to see it. I think, though, that at Mitsui the data that Gerry McGlamery (TVA, Muscle Shoals) showed indicates or proves that the return liquor is not saturated and until you do saturate it you cannot say that you would not have trouble either in Japan or in this country under such an operating mode.

P. Wechselblatt — In answer to that, I would point out the very small quantity of liquid going to and from the pond. If the liquid coming back from the pond is, for example, at 50 percent of saturation, this system is a more closed system than if you operated a pilot plant with a thickener

and underflow at 35 percent solids.

Pat Rapier (Burns & Rowe) — In continuance of the question that came up regarding the 300-mm pressure drop as being excessive, I have some experience. It was many years ago, but it is directly related to this. If you take out the mist eliminators; if you take out all the impingement baffles in the collector, whatever it is; if you use, as a substitute, a 316 stainless cyclonic collector; if you precede the collector with a 316 stainless fan and keep the tip speed of the fan blades at over 12,000 ft/min (I believe that will correspond to a 4- to 6-inch pressure gain through the fan); and then if you put the slurry in through the fan itself and let the fan do the contacting, you create an extremely high collision rate between the particles in the air stream and with the water, which indeed the fan itself can accelerate and atomize. We tried this using a 30,000 ft³/min unit, which is much smaller than we are talking about here, but the same type of operation could be done on the larger units. It would scrub out about 100 percent of the dust particles that were available down to the micron range, and down probably about as low as 0.25 micron. The pH of the liquor was not regulated because in those days we were not interested in trying to remove sulfur, but it was removing sulfur dioxide. My recollection is that the pH of that liquor was coming out at about 5.5. The circulation rate going in for 30,000 ft³/min scrubbing was 72 gal, a large portion of which was recirculated. We were furnishing a moderate amount of evaporation water for makeup, but the main portion was recirculated.

P. Wechselblatt — Commercially, a device such as that might be repre-

sentative of a Typson disintegrator, which I believe is commercially available for particulate removal.

Del Ottmers (Radian) — I have a question to be directed to Mr Wechselblatt. As I understand it, you have a scrubber with a hold tank. You are operating with two feeds, two scrubbers with a total L/G of 90. I was interested in the supersaturation and how you control this. In that regard, I wondered about the volume of the hold tank that you are using and the size of the stream of slurry that you are taking to your pond.

P. Wechselblatt — Well, the size of the hold tank provides approximately 30-min residence time, and the bleed from the system to the pond I believe is 3 percent of the liquid rate. But again, it is the kind of number I would rather give you after the meeting. It can be made available to you; I just do not recall the number.

R.H. Quig (Chemical) — Bill (Elder), I direct a question to you. You and I have had a running commentary from time to time on this recycle loop. I just want to put a couple of things in perspective. Do you essentially feel that this problem of closed-loop saturation falls into two areas of concern? One is that you are concerned that, if you have a saturated return system, you will plug and scale the scrubber vessels regardless of the different geometries or shapes or what they are - spray towers, ping pong balls, venturi, whatever. Is that a major point of concern? The second point is, and I agree with you for sure on this one, the concern for overall pond management and the impact of water quality standards. But could you first comment on your concern for plugging and scaling as related to this problem of saturation. How fast do you plug and scale your pilot units when you truly have saturated liquor in terms of sulfate

coming back?

H.W. Elder — Well, you know, I can not say flatly that if it is saturated it will scale. What I do say is that if you can not add any fresh water in the system, it would certainly scale. Now it becomes relative then, and the less saturated the recycle water the more fresh water you can add. And that has to be in the right direction. Now the other point, how long does the pilot plant operate before it scales up? You know, we have scaled it up at 4 hours and we have used lime. And we have run for 1000 hours with limestone without scaling it up.

R.H. Quig — Saturated?

H.W. Elder — Yes, well saturated to the extent that the purge from the system is a slurry with 40 percent solids, 60 percent water. That goes out and does not come back. That simulates what would happen if you put it in a storage pond. But under those conditions, yes, we have operated without scaling for a continuous run of 1000 hours. We, I think, have a pretty good understanding of the system, the chemistry, and the techniques with limestone. I do not understand the lime system that well and perhaps if I did I would be less concerned about some of these points that I have raised. Again, it gets back to the reactivity of the absorbent. I talked about that yesterday: the difference in stoichiometry and its effect on scaling in the scrubber itself. Now what we are saying really is that the reactivity changed. More calcium was available to react with the SO_2 that was absorbed. Lime is a more reactive material than limestone. Therefore, the amount of calcium available with the lime system is higher than with limestone. I would expect the tendency to precipitate sulfite

in the system is greater with lime. As I say, there are some questions in my own mind about the difference between lime and limestone chemistry that sort of confound our conversation.

R.H. Quig — Well, yes, perhaps so. But I would like to refer to this chart that you fellows prepared here. It has several points of data you have grabbed, based on information from visitors to the Omuta system. And that chart (which we do not really agree with, but just let us assume at the moment that it is correct) shows a saturation condition of several weeks. We did not plug and scale, and I know the unit was operating at full load with the impact of the changing SO₂ concentrations due to the different coals. Now your chart says in effect that the scrubber system operated saturated for about 6.5 weeks, if we look at the chart, under a saturated or supersaturated condition. And then your chart says that, for the rest of the year, it operated at less than that. So I submit that if your data are correct (and it is not because you only have partial information due to returning visitors) it operated for 6 weeks totally saturated. I think that in itself has significance. We happen to know that it operated much longer than that. But giving you credit for you assumptions, it still operated.

H.W. Elder — Well, of course, you know the obvious question. If it operated a few weeks, why not a few months, or a few years? We would have had a lot more confidence in the performance had it operated 6 months rather than 6 weeks with saturated conditions.

R.H. Quig — Well, I would just like to conclude our position on that issue: we have gone through ranges of saturation and we find no impact there.

F.T. Princiotta — I think we are running out of time, and I am sure

people are anxious for a break, so we would like to conclude discussions on the panel. I would like to thank all the panel members.

THE
TVA WIDOWS CREEK
LIMESTONE SCRUBBING FACILITY

PART I
FULL SCALE FACILITY

by

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Power Research Staff
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ABSTRACT

The design of a limestone slurry scrubbing system for TVA's Widows Creek Unit 8 (550-MW; plant located in Northeast Alabama) is discussed. Basic design premises on which the design is based are presented. Descriptions of major components of the scrubbing facility are described.

Estimated capital and operating costs are contained in this paper. The estimated capital cost of this installation is \$42,000,000 not including a portion of the solids disposal costs. The estimated capital cost is \$43,636,000 if the full initial scrubber effluent ponding costs are included. The estimated operating cost is approximately 2.9 mills per kilowatt hour generated.

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In mid-1970 TVA made a decision to install a full-scale demonstration limestone scrubbing SO₂ removal system on generating Unit 8 at Widows Creek Steam Plant (in Northeast Alabama, near Chattanooga, Tennessee). The primary objective is to work out design and operating problems that affect both SO₂ removal efficiency and process reliability, with emphasis on the latter.

Since late 1970 considerable small scale, pilot plant and prototype developmental work has been done on the limestone scrubbing process in an attempt to establish design parameters for the full scale demonstration unit. The results of the developmental work are described in a separate paper. A draft environmental statement covering the full-scale demonstration SO₂ removal system and waste disposal pond was prepared and issued on June 30, 1972. Following receipt and resolution of various state and federal agencies' comments, the final environmental statement was issued January 15, 1973.

Following finalization of the environmental statement, the project authorization was submitted to and approved by TVA's Board of Directors in February, 1973. Since engineering had commenced prior to the project authorization it enabled construction to begin in March, 1973. The engineering for the project is about 50 percent complete. Equipment bids have been received and contracts awarded on most of the long delivery equipment items. Specifications and requisitions for other material and equipment are at various stages of completion.

The mechanical completion date for the facility based on the present project schedule is mid-1975. Pre-operational testing is scheduled to be conducted in the third quarter of 1975.

An attempt is made in this paper to discuss the design of the facility and the estimated capital and operating costs. The design areas of the facility to be discussed are: basic design premises, limestone handling and grinding system, scrubber system, and solids disposal system.

Figure 1 is a general plot plan of the Widows Creek Steam Plant showing the general location of the scrubber facility, limestone storage, handling and grinding facilities, and the solids disposal area with respect to existing facilities.

Basic Design Premises

The following design premises were established for the scrubbing facility during the planning stages of the project:

1. Coal analysis (as fired basis)
 - a. Ash content, 25%
 - b. Sulfur content, 4.3%
 - c. Moisture, 10%
 - d. Heating value, 10,000 Btu/lb
2. Capacity
 - a. Maximum power generation rate for Unit No. 8, 550-MW
 - b. Stack gas rate at capacity,¹ 1,600,000 acfm at 280°F
(5,325,000 lb/hr)

¹ Based on a total of 33% excess air including air heater leakage.

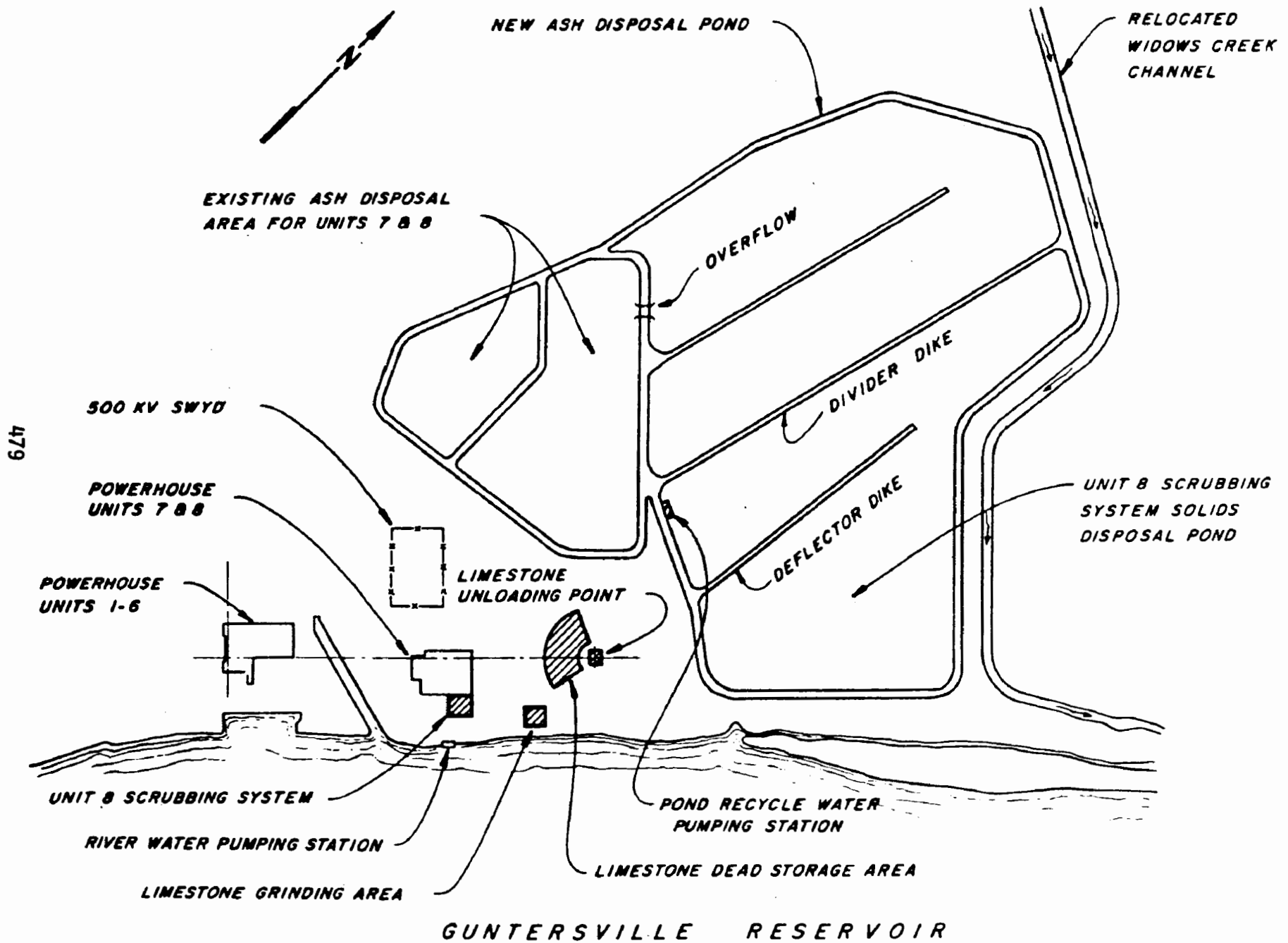


FIGURE 1
GENERAL PLOT PLAN

3. Sulfur dioxide removal
 - a. Percent removal, 80
 - b. Inlet concentration, 3440 ppm (wet basis); 3740 ppm (dry basis)
 - c. Outlet concentration, 650 ppm (wet basis); 750 ppm (dry basis)
4. Particulate removal
 - a. Inlet particulate loading,² 5.6 gr/scf (dry); 5.1 gr/scf (wet; 3.6 gr/acf (280°F)
 - b. Particulate level at scrubber exit,² 0.020 gr/acf (125°F saturated); 0.022 gr/scf (wet); 0.026 gr/scf (dry)
5. Stack gas reheat temperature, 175°F (50°F rise)

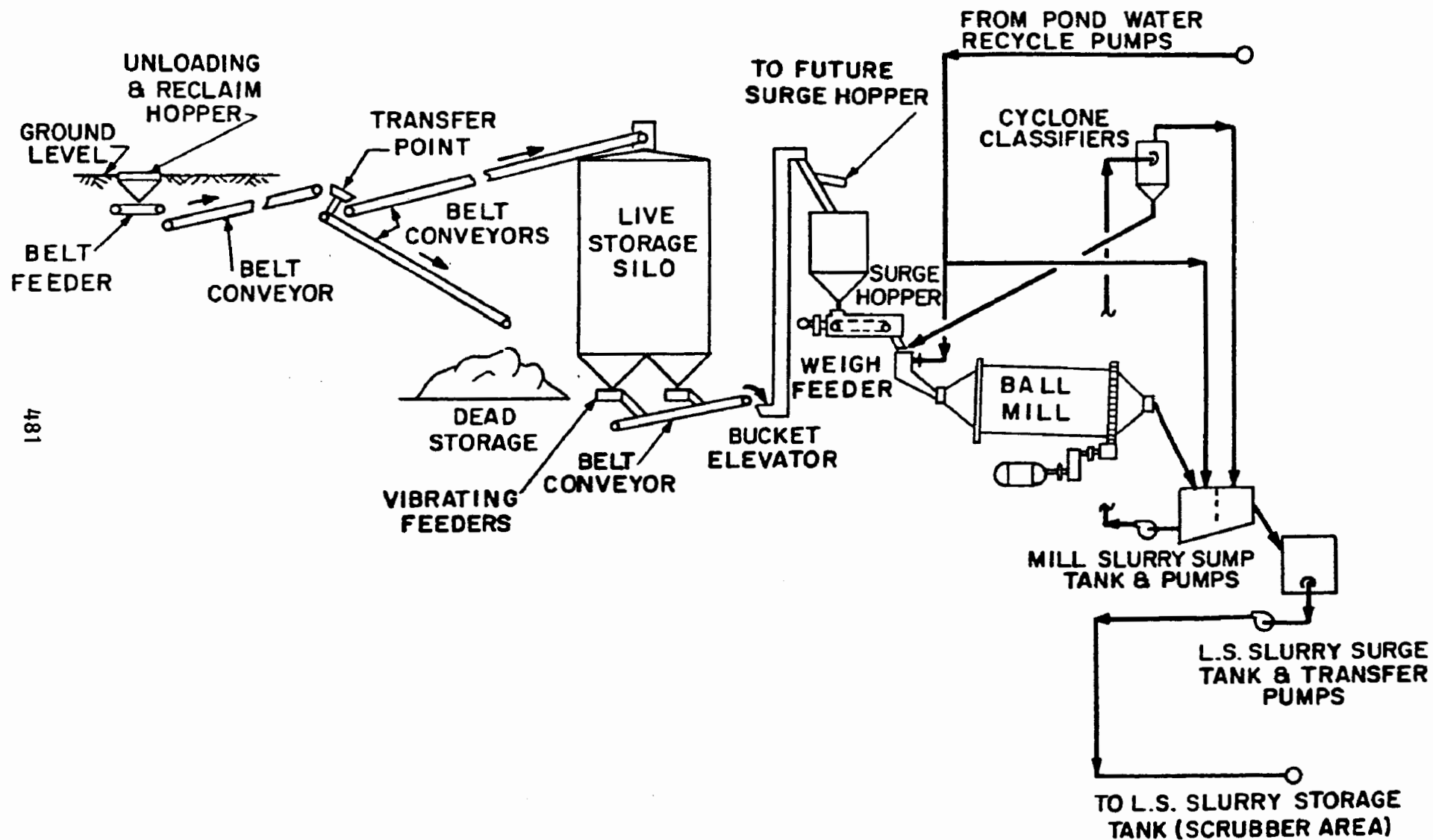
Limestone Handling and Grinding

A wet grinding system for limestone was chosen over dry grinding because it is less expensive and does not produce a dust problem. Even if dry grinding were used, the ground limestone probably would be slurried before feeding to the scrubber.

A schematic drawing of the limestone handling and grinding system is shown in Figure 2. The facility is designed for receiving limestone by both rail and truck from the quarry. The limestone is conveyed from an unloading hopper to either the live storage silo or the dead storage area. Material will be reclaimed from the dead storage area as required to maintain an adequate level in the live storage silo.

Limestone is conveyed from the live storage silo to a wet ball mill where it is ground from the purchased size (3/4 by 0 in.) to the desired size. The resulting slurry is pumped from the ball mill through a classifier where the oversized particles are separated and recycled to the ball mill. The product slurry (40% solids) from the classifier goes to a surge tank from which it is pumped to the scrubbing area limestone slurry storage tank.

² Based on the conventional ASME sampling technique.



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FIGURE 2
LIMESTONE HANDLING AND GRINDING SYSTEM

The grinding system is designed to produce a ground particle size of 90 percent minus 200 mesh at the design rate of 50 tons per hour dry limestone. The 50 tons per hour limestone rate corresponds to a limestone feed stoichiometry of 1.5 at full load and design conditions. Pilot plant work indicates that little or no improvement in SO_2 removal is obtained by using limestone quantities above 1.5 of stoichiometric amounts.

The unloading and conveying facilities up to the live storage silo are designed for a 900 tons per hour limestone rate. The live storage silo has an effective capacity of 6400 tons. The unloading and storage facilities up to and including the live storage silo are designed to accomodate a future limestone scrubbing facility on Widows Creek No. 7 generating unit which has a maximum rated capacity of 575-MW. The dead storage area is designed to accomodate 120,000 tons of limestone corresponding to approximately 50 days capacity at maximum limestone requirements for Units 7 and 8. The live storage silo will have about six days' capacity initially and about three days if used to supply the maximum limestone requirements for both Units 7 and 8. The design of the unloading and conveying systems will permit the use of only day-shift personnel for the limestone unloading and reclaim operations.

The belt conveyor and bucket elevator conveying limestone from the live storage silo to the limestone surge hopper are designed for 200 tons per hour to accomodate both the Unit 8 scrubbing facility and a future Unit 7 scrubbing facility. The limestone surge hopper has a 50 ton limestone capacity and is designed only for Unit 8 as are all the limestone facilities downstream of it.

A weigh feeder is used to feed limestone from the surge hopper to the ball mill at controlled rates. The grinding system is a closed circuit wet ball mill system with cyclone classifiers. The ball mill has a 11'-0" inside diameter shell 20'-0" long and is equipped with a 1250 horsepower motor. The ball mill and cyclone classifiers are equipped with rubber liners. A rubber liner was selected for the ball mill rather than a steel liner because it provides a longer wear life, less maintenance, and a lower noise level.

The mill discharge slurry (about 65 percent solids) goes into the primary compartment of a two compartment sump tank from which it is pumped to the cyclonic classifiers. Sufficient pond water is added to the primary sump compartment so that the overflow or product slurry from the classifiers is a 40 percent solids slurry. The overflow from the cyclonic classifiers goes to the secondary compartment of the mill slurry sump. The product slurry overflows from the secondary compartment of the mill slurry sump tank into a limestone product slurry surge tank which has about five minutes capacity.

At reduced rates slurry underflows from the secondary compartment into the primary compartment of the mill slurry sump tank for recirculation to the classifiers to maintain a constant feed rate to the classifiers. Three 50 percent capacity cyclonic classifiers are provided with one being an installed spare.

Underflow from the classifiers containing oversized particles is fed back to the ball mill for regrinding. Sufficient pond water is also added to the ball mill to maintain a 65 percent solids slurry in the mill discharge.

The product slurry (40% solids) is pumped from the product slurry surge tank to a limestone slurry storage tank located adjacent to the scrubber facility about 300 yards from the grinding facilities. The slurry storage tank has a capacity of about 181,000 gallons corresponding to about eight hours storage capacity based on the maximum limestone slurry requirement.

Scrubber System Design

A simplified flow diagram of the scrubber system is depicted in Figure 3. The scrubbing system consists of four identical trains each handling 25 percent of the flue gas from Unit 8. The flow diagram shows the major components typical for each train and those components common to the four trains.

The flue gas after exiting the existing electrostatic precipitators passes through a fan, venturi, liquid-gas separation chamber, absorber, entrainment separator, and a reheater for each train into an existing stack. Flue gas bypass ducts are provided around each scrubber train to prevent an undue amount of boiler downtime because of scrubbing system malfunctions, particularly during the initial shakedown operation of the system. A plenum connecting the inlet ducts to the four fans is provided to permit operation of up to 75% load with one of the scrubbing trains out of service.

Limestone slurry, pond water recycle, and make-up river water are added to an absorber circulation tank. Slurry is pumped from the absorber circulation tank into the absorber and drains back into the tank. The recycle pond water is regulated to maintain the solids concentration level, about 10% by weight, in the absorber circulation tank. The absorber circulation tank overflows into a venturi circulation tank from which slurry is pumped to the venturi and drains from the separation chamber back into the circulation tank. The solids concentration in the venturi circulation tank is dependent upon the inlet flue gas flyash loading but will normally run about 15 percent.

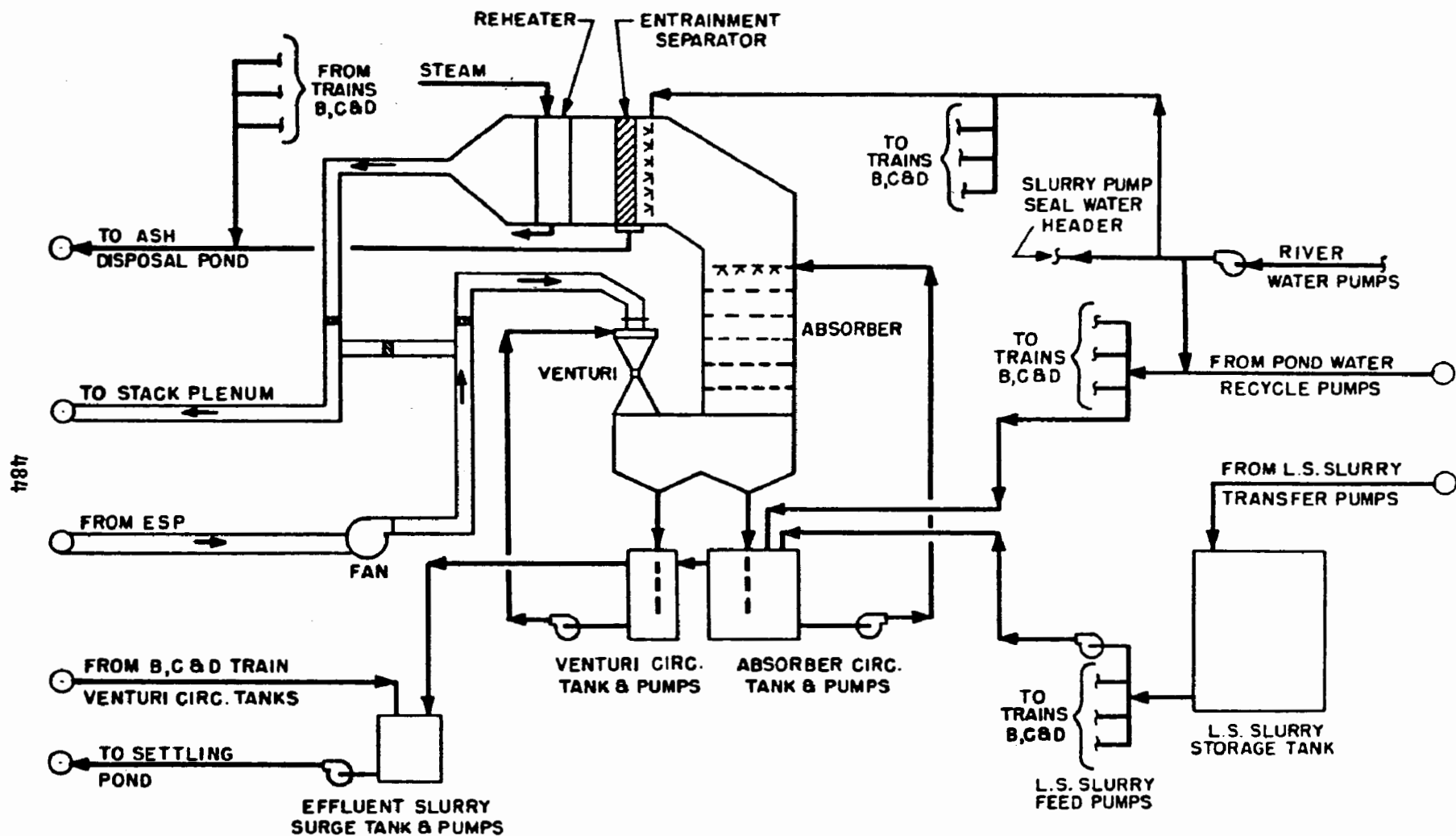


FIGURE 3
SCRUBBER SYSTEM FLOW DIAGRAM

The venturi circulation tanks on each of the four trains overflows into a common effluent slurry surge tank from which the effluent is pumped to a settling pond. Supernatant pond water is recycled to the absorber circulation tanks and to the limestone grinding system.

Four flue gas fans are provided, one per train, to supply the static pressure for the system losses. The design capacity for each of the fans is 400,000 acfm (280°F) with a test block capacity of 460,000 acfm (280°F). The fans will be equipped with induction motors and variable speed fluid drives to permit flue gas flow regulation. The static pressure will be sufficient to convert the Unit 8 furnace from a forced draft furnace to a balanced draft furnace. The fans are a double width, double inlet and radial tip blade design with an A-242 steel casing and impeller with high strength alloy wear plates. After investigating and evaluating the advantages and disadvantages of locating the fans upstream of the venturis versus downstream of the reheaters, it was decided to locate them upstream of the venturis. It was concluded that the dry fly ash erosion problems would be less severe than corrosion and solids build-up problems with the fans located downstream of the reheaters.

The venturi is used to cool, saturate, and remove flyash from the flue gas. It is designed to operate with a differential pressure of five inches of water at full load conditions; however, higher differential pressures may be used at reduced loads. The venturi is a rectangular throat design equipped with a motor operated variable throat mechanism. The venturi housing material is 316L stainless steel and the convergent section is lined with castable silicon carbide (2 inches thick). The throat damper blades are lined with fired alumina brick. The venturi throat is 23'-0" wide (inside), and has an effective throat depth of 28" (2-14" sections). The expected SO₂ removal in the venturi is about 10 percent.

Constant speed elastomer lined centrifugal slurry pumps will be used to pump slurry from the venturi circulation tank to the venturi. A total of six venturi circulation pumps are provided, one operating pump per train and a common spare for each two trains. The pumps are designed to supply a liquid circulation rate to the venturis corresponding to an L/G of 10 gal/Mcf of saturated flue gas at the design flue gas rate. At reduced flue gas rates the L/G will be higher.

The venturi circulation tanks have a capacity of 40,000 gallons and are 18'-0" in diameter and 25'-0" high. The retention time in the tanks is about 12 minutes based on the venturi circulation rate. The tanks will be provided with agitators to maintain solids suspension.

The absorber is a grid type absorption tower. It is designed for a superficial gas velocity of approximately 12 feet per second at the design gas rate. Its dimensions are 30 feet wide, 16 feet deep, and 34 feet high. The absorber has five grids, 65-70 percent open area, spaced either four or five feet apart. A final grid selection has not been made, but preliminary plans are for them to be of the floor grating type and made of 316 stainless steel (top and bottom grids) and fiberglass reinforced polyester (intermediate grids). The expected SO₂ removal efficiency for the multi-grid absorber is about 70 percent and the pressure drop is expected to be about 2 inches of water with clean grids. The corresponding overall expected SO₂ removal including the venturi is about 80 percent. The slurry is distributed in the absorbers using 316 stainless steel distribution headers equipped with low pressure drop (5 psi) spray nozzles. The use of turning vanes in the venturi-absorber sump to give better gas distribution in the absorber is being studied.

The absorber circulation pumps will be elastomer lined centrifugal slurry pumps designed to supply a maximum slurry rate to the absorbers corresponding to an L/G of 60 gal/Mcf at the design gas rate. A total of 10 pumps are provided, two operating pumps per train and a common spare for each two trains. The pumps are equipped with variable speed drives for varying the slurry rate to the absorbers.

The absorber circulation tanks have a capacity of 148,000 gallons and are 33 feet in diameter and 25 feet high. The retention time in the tanks based on the maximum absorber circulation rate is seven minutes. Agitators are provided in the tanks to maintain solids suspension.

The entrainment separator is a chevron vane type (4 pass) located vertically in a horizontal shell. The vanes will be 316 stainless steel, 12 inches deep and spaced on 1½ inch centers. The superficial gas velocity in the entrainment separator is approximately nine feet per second at the design gas rate. The face of the eliminator blades are washed continuously with once through river water at a rate of 1 gpm/ft.² The wash water drains from the entrainment separators to the ash disposal pond. The environmental statement may be referred to for the water quality considerations for the ash pond overflow which will consist of ash sluice water from all Widows Creek generating units and the entrainment separator wash water from the Unit 8 scrubbing facility.

The venturi liquid-gas separation chambers, absorber shells, venturi circulation tanks, and absorber circulation tanks will be constructed of Corten A steel and coated or lined inside. Although a final coating or lining selection has not been made, the primary considerations are for a polyurethane elastomer base coating (50 mils) for the separation chamber and absorber shell, and flakeglass reinforced polyester resin (60-80 mils) for the tanks.

Indirect tubular exchangers (one pass) are used for reheating the flue gas from the saturation temperature of about 125°F to 175°F (50°F reheat) to desaturate and provide buoyancy for the gas. Steam at approximately 500 psig and 650°F from Unit 8 is used as the heating medium. The material of construction to be used for the tubes has not been defined. Corrosion specimen are being evaluated in pilot plant tests to determine the material of construction for the reheater tubes.

Slurry piping four inches and larger in diameter will be soft rubber-lined carbon steel. Smaller slurry piping will be PVC-coated aluminum or 316L stainless steel. A decision has not yet been made on the type of slurry block valves but they will likely be either an elastomer lined plug type valve or a knife gate type valve.

Steam operated soot blowers will be provided at the locations in which solids deposition is expected to occur based on research and development experience. The locations where soot blowers are to be provided include the inlet ducts to the venturi, the elbow between the absorber and the entrainment separator, and the reheater section.

A perspective drawing of the scrubber area is given in Figure 4 which shows the general arrangement of the equipment. The controls for the system are located in the existing Unit 8 control room to minimize operating personnel requirements. Adequate controls and instrumentation are being provided to minimize operating personnel, to monitor and control the system performance, and to provide the necessary data for studying system variables.

Provisions have been made in the design of the scrubber system to make the system as flexible as practical. The absorber is being designed so that it can be operated as a multi-grid, turbulent contact or spray tower absorber. The base case for design is the multi-grid absorber which has been discussed above.

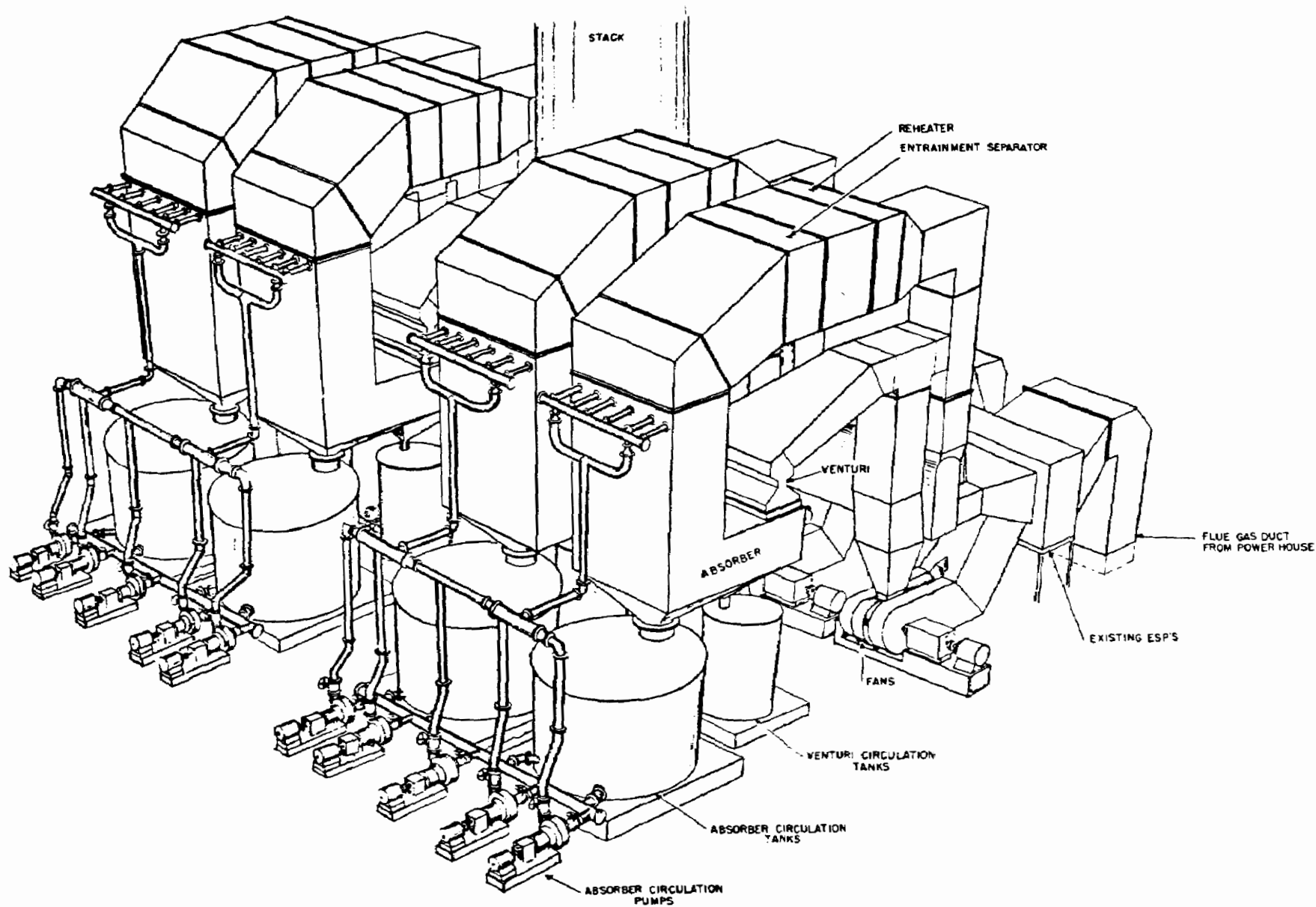


FIGURE 4
SCRUBBER AREA PERSPECTIVE VIEW

Provisions are made in the absorber design so that it can readily be converted to a mobile bed type absorber should it prove desirable in the future to obtain improved SO₂ removal. The variable speed absorber circulation pumps permit the use of lower L/G's required for mobile bed absorbers. Also the flue gas fans are designed with sufficient static pressure head to accomodate the higher pressure drops associated with mobile bed scrubbers.

Another back-up which is being investigated is the changing of the limestone scrubbing process to a double-alkali process. Investigations have been conducted which indicate that the conversion to a double-alkali process is feasible. Pilot plant tests are planned in late fiscal year 1973 to further define a double-alkali process for the Widows Creek Unit 8 scrubber facility. Hopefully pilot plant testing will show that a double-alkali system is a possible and practical back-up process for the limestone scrubbing process being installed.

Solids Disposal System Design

Ponding was chosen as the most feasible method of disposing of the waste by-product solids from the Widows Creek scrubbing facility. The by-product solids consisting of flyash, reaction products (hydrates of calcium sulfite and sulfate) and unreacted limestone are pumped to the pond as a 15-16 percent solids slurry. The supernatant liquor from the pond is recycled to the limestone grinding area and the scrubber area.

Thickeners could be used to concentrate the surge slurry and reduce the pumping rates to and from the ponds. However, the savings in pumping costs do not justify the additional capital investment for thickeners. Also there is doubt as to how effective thickeners would be in concentrating the purge slurry because of the very poor settling characteristics of the reactant products in the slurry.

The poor settling characteristics of the solids in the bleed slurry to the pond result in large pond volume requirements for solids disposal. Based on the TVA pilot plant data, the weight percent water in the settled solids after settling for extensive periods (up to 240 days) ranges from 57 to 66. For planning the solids disposal pond requirements for the scrubbing facility 60 percent water in the settled solids was assumed. This corresponds to a pond volume requirement of about 1.4 cubic yards per thousand pounds of solids pumped to the disposal pond. Based on the expected average coal analyses with regard to sulfur and ash content the solids disposal rate in terms of settled solids corresponds to about 150 cubic yards per hour at full load conditions.

The initial scrubber effluent solids disposal pond will have an effective volumetric capacity of 4.5 MM cubic yards. The area of the pond including dikes is about 100 acres and the dikes average about 30 feet in height. The life of the pond is estimated to be about seven years based on projected capacity factors. The pond dikes are designed so that they can be raised 10 feet to increase the pond capacity to 5.8 MM cubic yards (increase of 1.3 MM cubic yards). The total estimated pond volume required over the remaining life of the plant, based on the above settled solids density data and the projected capacity factors, is 9.3 MM cubic yards and thus an additional storage volume of approximately 3.5 MM cubic yards would be required for which no provisions are made. Due to the developmental nature of the project and the possibility of developing means of enhancing the settling characteristics of the solids, it was not deemed justifiable to provide for the total estimated pond requirements for the remaining life of the Unit 8 generating unit. TVA is continuing research and development work on means to increase the compaction of the settled solids to reduce the pond volume requirements for solids disposal.

Estimated Capital Costs

In Table I, the estimated capital costs for the wet limestone scrubbing facility at TVA's Widows Creek Unit 8 are summarized. These costs are based on cost estimates prepared by TVA, which are based on detailed layouts and firm prices for much of the major equipment. The estimate is based on construction beginning in March, 1973, and with completion in August, 1975. The estimated direct cost for the scrubber facility is \$22,360,000 not including a portion of the solids disposal costs. If the additional cost of solids disposal is included, the direct capital cost is \$23,640,000. The total field construction costs are \$31,400,000 and \$33,018,000 respectively. The total project costs are \$42,000,000 and \$43,636,000 respectively. The cost estimates do not include the cost of land which is associated with the pond or the other parts of the scrubber facility.

Estimated Operating Cost

The estimated operating costs are summarized in Table II. The estimated total operating cost is approximately 2.9 mills per kilowatt hour generated. For an investor-owned utility, the capital charges portion of the operating cost would be higher for the same total investment due to differences in cost of money, income taxes, and so forth. The estimated total operating cost for an investor-owned utility, based on the same parameters (capital investment, operating life, capacity factor, etc.) except for capital charges, is approximately 3.5 mills per kilowatt hour generated based on capital charges of 15 percent of the total investment per year.

TABLE I

Widows Creek Unit 8Limestone Wet Scrubber FacilityCapital Cost Estimate Summary

<u>Item</u>	<u>Estimated Cost, M\$</u>
Grading, landscaping, yard drainage, surfacing	177
Roads, sidewalks, bridges	608
Power house modifications	35
Electrical equipment building	100
Ductwork	2000
Fans	960
Reheaters and soot blowers (includes steam & condensate piping)	1525
Railroad facilities	320
Ball mill building	200
Limestone grinding facilities	255
Limestone conveying facilities	919
Limestone storage facilities	562
Mobile equipment for limestone handling	155
Scrubber area foundations	350
Scrubber area steel structures	1110
Scrubbers	1280
Pumps	765
Tanks (including linings and agitators)	390
Entrainment separators	150
Piping	2471
Elevator	80
Painting	30
Instruments and controls	550
Electrical work	2821
Electrical transmission plant	1526
Cranes and hoists	92
Solids disposal area	767
Construction facilities	<u>2162</u>
Total direct cost subtotal	22,360
Field general expense	2670
Allowance for shakedown modifications	2000
Contingencies	<u>4370</u>
Total field construction subtotal	31,400

Table I, Continued

<u>Item</u>	<u>Estimated Cost, M\$</u>
Indirect Costs	
Engineering design	2500
Managers office - Office of Engineering Design & Construction	100
Office of Power (research, development, & coordination)	2480
Initial limestone supply and preoperational testing	1200
Employee compensation benefits	300
Administrative and general expenses	400
Interest during construction	3380
Other	<u>240</u>
Total indirect cost subtotal	10,600
	<hr/>
Total project cost excluding supplemental pond costs	42,000
Additional supplemental pond cost allocations	
Direct costs	1280
Field general expenses	128
Contingencies	210
Indirect costs	<u>18</u>
Subtotal	1,636
	<hr/>
Total project cost including supplemental pond costs	43,636

Notes

1. The total project cost with additional pond cost allocations from separate authorization contains a total of about \$2.8 million (\$2.2 million direct cost) for scrubber effluent solids disposal pond. The pond will have an effective capacity of 4.5 million cubic yards which will last about seven years at projected Unit 8 load factors based on present expected settling characteristics. The pond dikes are designed so that they can be raised in elevation to obtain an additional storage capacity of 1.3 million cubic yards at an estimated cost of about \$ 1.6 million (\$1.2 million direct costs).
2. The estimate includes about \$2.1 million (\$1.2 million direct costs) for solids disposal over and above the pond costs.
3. The estimate includes about \$7.0 million (\$4.0 million direct costs) for limestone handling, storage and grinding facilities.

TABLE II

Estimated Annual Operating CostTVA Widows Creek Unit 8Limestone Scrubbing System

<u>Item</u>	<u>Estimated Annual Cost, M\$^{1/}</u>			
	<u>Limestone Processing^{2/}</u>	<u>Scrubber Area</u>	<u>Solids Disposal</u>	<u>Total</u>
Direct costs				
Raw material - limestone ^{3/}	--	821	--	821
Conversion costs				
Operating labor & supervision ^{4/}	27	105	27	159
Utilities	42	986	5	1033
Analyses	10	30	10	50
Maintenance ^{5/}	220	1390	130	1740
Subtotal conversion costs	299	2511	172	2982
Subtotal direct costs	299	3332	172	3803
Indirect costs				
Capital charges ^{6/}	700	3170	770	4640
Overhead				
Plant, 20% conversion cost	60	502	34	596
Administrative, 10% operating labor	3	10	3	16
Subtotal indirect costs	763	3682	807	5252
	=====	=====	=====	=====
Total annual operating cost	1062	7014	979	9055
Operating cost, mills/kWh generated	0.34	2.24	0.31	2.89

Notes

- 1/ Based on capacity factor of 65 percent (3135 x 10⁶ kWh/year generated).
- 2/ Limestone handling, grinding and storage facilities.
- 3/ 273,600 tons limestone at \$3 per ton delivered.
- 4/ Operating labor and supervision at \$6 per hour.
- 5/ Annual maintenance costs are based on 4.0, 6.0, and 3.0 percent of total field construction of \$5.6 million, \$23.1 million, and \$4.3 million, respectively, for limestone, scrubber and solids disposal areas.
- 6/ Annual capital charges based on 10 percent of total investment (25-year life) except capital charges on \$2.8 million for pond costs in the solids disposal area are based on 20 percent (7-year life).

It should be noted the effect which capital investment has on the operating costs. The capital investment is approximately 50% of the operating costs. The second largest contribution to the operating cost is maintenance and the third largest contribution is utilities.

Also, the capacity factor (65 percent) used in this estimate may be high for a unit approximately 10 years old. A decrease in the capacity factor would increase the operating cost substantially.

THE
TVA WIDOWS CREEK
LIMESTONE SCRUBBING FACILITY

PART II
PILOT-PLANT AND PROTOTYPE OPERATING EXPERIENCE

by

J. J. Schultz, T. M. Kelso, J. L. Graham, and J. K. Metcalfe
Division of Chemical Development
Tennessee Valley Authority
Muscle Shoals, Alabama
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ABSTRACT

The Tennessee Valley Authority (TVA) has been engaged in a limestone - wet-scrubbing pilot-plant test program for the past 2 years. The purpose of the program is to provide information for the design and operation of a demonstration-scale (550 mw) scrubber system now under construction at TVA's Widows Creek power station in northeast Alabama.

The pilot-plant testing program consisted of two phases. The objective of the first phase (1 year) was to select a scrubber type for the Widows Creek project. Four different types of scrubber systems were evaluated. As a result of this evaluation, a venturi (for particulate removal) followed by a multigrid scrubber was selected as a basis for the design of the Widows Creek system.

The objective of the second phase was to closely duplicate the Widows Creek design in the pilot plant and evaluate the following.

- Process equipment and construction materials.
- Mist eliminator system.
- Scrubber operation during simulated changes in the operation of the boiler.
- The effect of the scrubber grid configuration and the temperature of the scrubbing slurry on SO₂ removal efficiency.

The following conclusions can be drawn from the pilot-plant studies.

- Limestone wet scrubbing provides an effective method for removing SO_2 from boiler flue gas.
- An SO_2 removal efficiency of 70% can be expected using the multigrid type of scrubber with a scrubbing liquor recirculation rate (L/G) of 50 to 60 gallons per 1000 cubic feet of gas and a $\text{Ca}:\text{SO}_2$ mole ratio of 1.5. The efficiency can be increased to about 90% if a two-stage mobile-bed scrubber is used.
- Techniques for adequate long-term disposal of the spent solids from the scrubbing slurry (including fly ash) have not been developed. Initially, ponding of the spent solids will be used for the Widows Creek system.
- The long-term operating reliability of the limestone - wet-scrubbing system will be largely determined by proper design and selection of suitable construction materials to cope with the erosive and plugging characteristics inherent in slurry scrubbing.

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Introduction

TVA has been engaged in a limestone - wet-scrubbing pilot-plant test program for the past 2 years. The program is designed to provide information for the design and operation of the full-scale (550 mw) limestone wet scrubber which is being installed on unit 8 at the Widows Creek generating station. The information obtained from the pilot-plant program includes the following.

- Selection of scrubber type.
- Selection of optimum operating conditions.
- Evaluation of scrubber performance during simulated changes in boiler operation.
- Identification of suitable process equipment and construction materials.

The program was performed in pilot plants located at TVA's Colbert Power Plant near the fertilizer research and development facilities at Muscle Shoals, Alabama.

The first pilot plant, a temporary unit located near the unit No. 3 boiler, was operated for 1 year before it was dismantled to make room for the installation of an electrostatic precipitator. The evaluation of four basic scrubber types was done in this pilot plant. The

second one is a permanent unit located near the unit 5 boiler, designed to closely duplicate the system planned for Widows Creek. It has been operated for 1 year and is still being operated. Except for changes in the scrubber type, the same general mode of operation was used in both pilot plants; a discussion of the work performed in both follows.

General Description of Process

Flue gas for the pilot plant is obtained from a pulverized coal-fired boiler in which coal containing about 4% sulfur and 15% ash is burned. The boiler is normally operated with 20% excess air. The flue gas contains about 6% oxygen (including air heater leakage) and 2800 ppm SO₂. It can be withdrawn from the boiler outlet duct on either side of an electrostatic precipitator; fly ash loadings are about 4 gr/scf or 0.1 gr/scf. The temperature of the gas entering the pilot plant is about 300°F.

In the pilot plant the flue gas is scrubbed with a limestone slurry containing 15% undissolved solids (combined limestone reaction products and fly ash). This level of solids is optimum for maintaining the stability of the slurry pH and SO₂ removal efficiency. Spent scrubbing slurry is continuously bled to a series of settling tanks where the solids settle. The settled solids contain from 55 to 65% water by weight. The supernatant liquor from the settling tanks is returned to the scrubbing loop to maintain the solids content at 15%. The liquor system is operated on a closed-loop basis; no liquor is overflowed to waste. This mode of operation is planned for the Widows Creek system. The only liquor lost from the system that must be replaced with fresh makeup water is (1) the water required to humidify the hot (300°F) flue gas and (2) the free and chemically combined water in the settled solids. This loss is equivalent to about 1 gpm of makeup water in the 1-megawatt pilot plant. With this mode of operation, the liquor phase of the slurry system contains about 10g/l total dissolved solids and is supersaturated with calcium and sulfur salts.

Pulverized limestone (normally 75% minus 200 mesh) is mixed with water (part of the makeup) to give a 60% solids slurry. Slurry of this concentration has excellent storage characteristics and requires only mild agitation to maintain homogeneity. The fresh slurry is fed to the scrubbing slurry retention tank at the required rate (usually 1.5 moles of Ca per mole of SO₂ in the inlet flue gas).

Work Performed in the First Pilot
Plant (Temporary Unit at Boiler No. 3)

The following types of scrubbers were tested in the unit 3 pilot plant.

- Ventri-Rod¹ followed by a packed-bed Crossflow scrubber.
- Ventri-Rod/open spray tower.
- Mobile-bed scrubber (TCA)².
- Ventri-Rod followed by a multigrid scrubber.

The objective of the evaluation was to determine which system would give the best combination of SO₂ removal efficiency and operational reliability. Pilot-plant operating experience and data for the first three scrubber types were presented last year at the Second International Lime/Limestone Wet Scrubbing Symposium ("Scrubber-Type Comparison," by T. M. Kelso, P. C. Williamson, and J. J. Schultz).

The present paper will cover the testing and development of the Ventri-Rod multigrid scrubber system which ultimately led to its selection for the commercial-size installation at Widows Creek.

All of the scrubbers tested gave acceptable SO₂ removal efficiencies at approximately the same liquid to gas ratio (L/G, gallons/1000 ft³). The TCA and multigrid scrubbers could be operated at higher gas velocities than the Crossflow or spray tower (12 ft/s vs. 8 ft/s). These data are shown in Table I.

The Crossflow scrubber was abandoned for slurry scrubbing because of rapid plugging of the packed bed. The Ventri-Rod spray tower, although nonplugging, did not give acceptable SO₂ removal efficiency at allowable pressure drop (less than 15 in H₂O) if the gas velocity exceeded 5 ft/s. The lack of sufficient space for fitting to the Widows Creek unit precluded the use of a low-velocity scrubber.

The TCA and multigrid scrubbers were nonplugging and reliable. The TCA scrubber (containing two or three 1-foot beds of spheres) had excellent gas-liquid contacting characteristics and gave the best SO₂ removal efficiency (90%). The major disadvantage of the TCA scrubber was erosion of the packing spheres (polypropylene). A 25% weight loss of the spheres occurred during 1000 hours of operation and failures due to puncturing began to occur. Universal Oil Products (manufacturer of the TCA scrubber) has a program underway to develop a more erosion-resistant sphere material; thermoplastic rubber has shown promise.

¹ A type of venturi scrubber manufactured by Environeering, Inc.

² Turbulent Contact Absorber manufactured by Universal Oil Products Company.

TABLE I

Typical Operating Characteristics
of Scrubber Systems Tested in TVA Pilot Plant

<u>Scrubber system</u>	<u>L/G, gal/1000 ft³</u>	<u>ΔP, in H₂O</u>	<u>Velocity, ft/s</u>	<u>SO₂ removal efficiency, %</u>
Ventri-Rod/Crossflow	55	10	5	80
Ventri-Rod/spray tower	65	15	5	75
Three stage mobile bed (TCA)	55	10	12	90
Ventri-Rod/multigrid	50	8	12	75

The multigrid scrubber, while not as effective in removing SO_2 as the TCA, has the advantage of having few internal parts. The pressure drop across the multigrid scrubber (containing five 65% open grids spaced on 5-foot intervals) is only about 2 inches of H_2O ; consequently the particulate (fly ash) removal efficiency is poor. To remove the fly ash, a venturi (Ventri-Rod) was installed upstream of the multigrid scrubber. The Ventri-Rod, operated at an L/G of 10 and a pressure drop of 5 inches of H_2O , was effective in removing the fly ash from the flue gas and also providing a sharp wet-dry junction in the inlet gas duct.

Selection of Scrubber for Widows Creek

As a result of this evaluation, the venturi/multigrid scrubber system was selected as the basis for the design of the Widows Creek system. A Ventri-Rod type of venturi was used in the pilot plant; however, a standard venturi with similar operating characteristics may be used in the Widows Creek installation. The expected SO_2 removal efficiency using the multigrid scrubber is about 75% (700 ppm SO_2 in the gas exhausted to the atmosphere). If higher SO_2 removal efficiency is required, the scrubber can be converted to a two- or three-stage TCA type. A new pilot plant was built to continue the evaluation of this system.

It should be noted that a venturi or some other type of scrubber effective for particulate removal is necessary at Widows Creek because the present electrostatic precipitator is not very efficient. The ash collected in the precipitator is slurried to the ash disposal pond and that collected in the scrubber goes to the scrubber solids disposal system.

Work Performed in the Second Pilot Plant (Permanent Unit at Boiler No. 5)

A perspective view and flow diagram of the unit 5 pilot plant are shown in Figures 1 and 2. The gas capacity is equivalent to 1 megawatt (2400 acfm at 120°F), and the design closely duplicates that planned for the Widows Creek installation. The objective of the new pilot-plant test program was to evaluate the following:

- Mist eliminator design and operation.
- The effect of grid configuration and slurry temperature on SO_2 removal efficiency.
- Scrubber performance during simulated changes in power plant operation.
- Process equipment and construction materials.

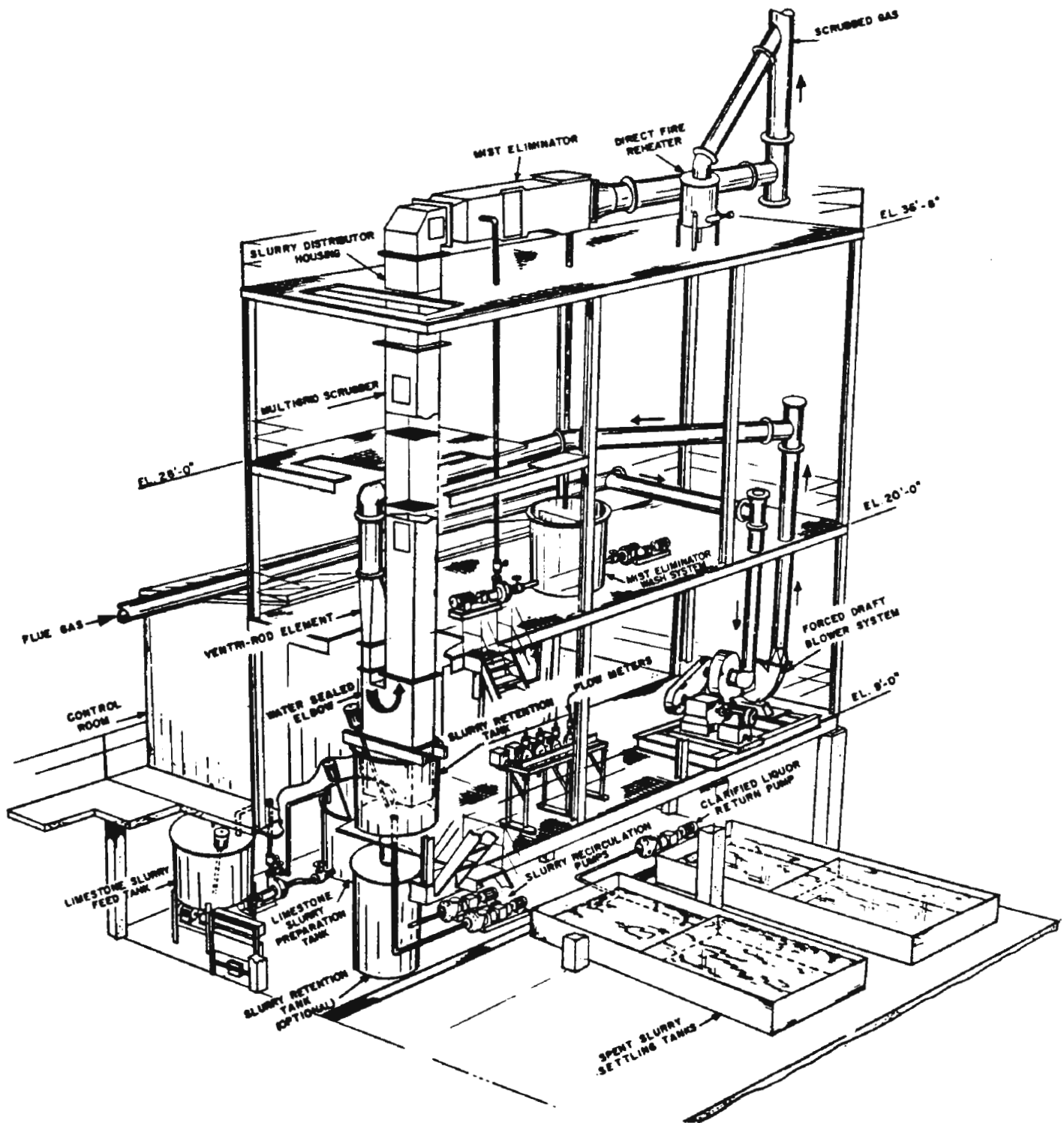


FIGURE 1

Limestone - Wet-Scrubbing Pilot Plant at Colbert Power Plant (Permanent Unit)

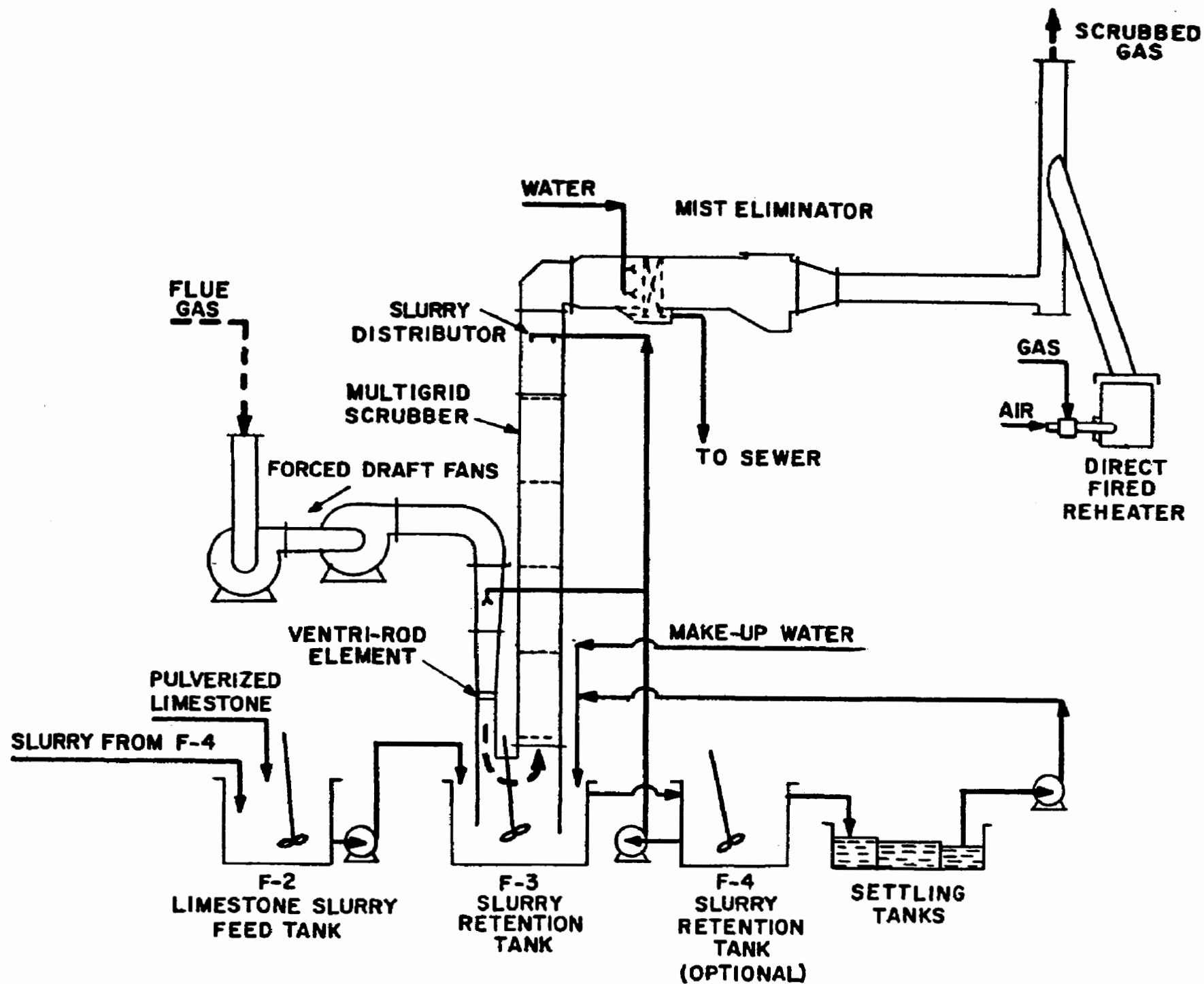


FIGURE 2

Flow Diagram: Limestone - Wet-Scrubbing Pilot-Plant (Permanent Unit)

A discussion of these items follows.

Mist Eliminator Design: Removal of entrained scrubbing slurry, and consequently particulate, from the gas leaving the scrubber was a major problem identified during the unit 3 pilot-plant program. Commercially available mist elimination systems installed in the vertical scrubber housings were inadequate. The most severe problem with this type of system was plugging of the mist eliminator element by accumulation of solids from the entrained slurry. The plugging occurred because there was not a sufficient amount of fresh water available to continuously wash the mist eliminator when the scrubber slurry system was operated on a closed-loop basis. A total of only 1 gpm of fresh water was required for makeup in the 1-megawatt pilot plant, whereas most vendors recommend a continuous wash of about 2 gpm per square foot of mist eliminator face area. This is equivalent to about 8 gpm in the 1-megawatt pilot plant, or 8 times the required makeup rate. In some tests a blend of 3 parts clarified liquor from the slurry settling tanks and 1 part fresh water was used to wash the mist eliminator intermittently (twice an hour) at the vendor's recommended rate of 2 gpm per ft². This method was not satisfactory because of scaling (calcium sulfite and sulfate) caused by the supersaturated clarified liquor (Figure 3).

An effective mist elimination system was ultimately developed and is now in use. It consists of a horizontal housing connected to the outlet of the vertical scrubber tower. The superficial gas velocity through the horizontal housing is 9 ft/s. A 4-pass chevron element is installed in a vertical position in the housing. The element (Type 316 stainless steel blades spaced on 1-1/2-in centers) is 12 inches deep and has a face area of 4 ft². It is washed continuously with fresh water which is discarded to the fly ash disposal pond separate from the limestone slurry disposal system. Fly ash pond effluent water, used in a few tests for washing, was as effective as fresh water. The particulate loading of the gases exhausted to the atmosphere averaged 0.04 gr/scf.

Tests were made to determine the minimum effective wash rate with this configuration. A wash rate of 0.25 gpm/ft² (1 gpm total) was effective, but was marginal in regard to uniform coverage of the chevron element. At this rate (1 gpm total) the wash water was drained into the slurry system as makeup. Maximum effectiveness was obtained with a wash rate of 1 gpm/ft² (4 gpm total). Since this was approximately 4 times the makeup required for the slurry system, the excess water was routed to the fly ash disposal pond rather than to the limestone slurry disposal system. The composition of the discarded wash water was monitored in the pilot plant at various wash rates to determine the environmental impact caused by this mode of operation (Table II). Based on these data a wash rate of 1 gpm/ft² is planned for the Widows Creek installation. The excess wash water not required for makeup will be discarded to the ash disposal pond.

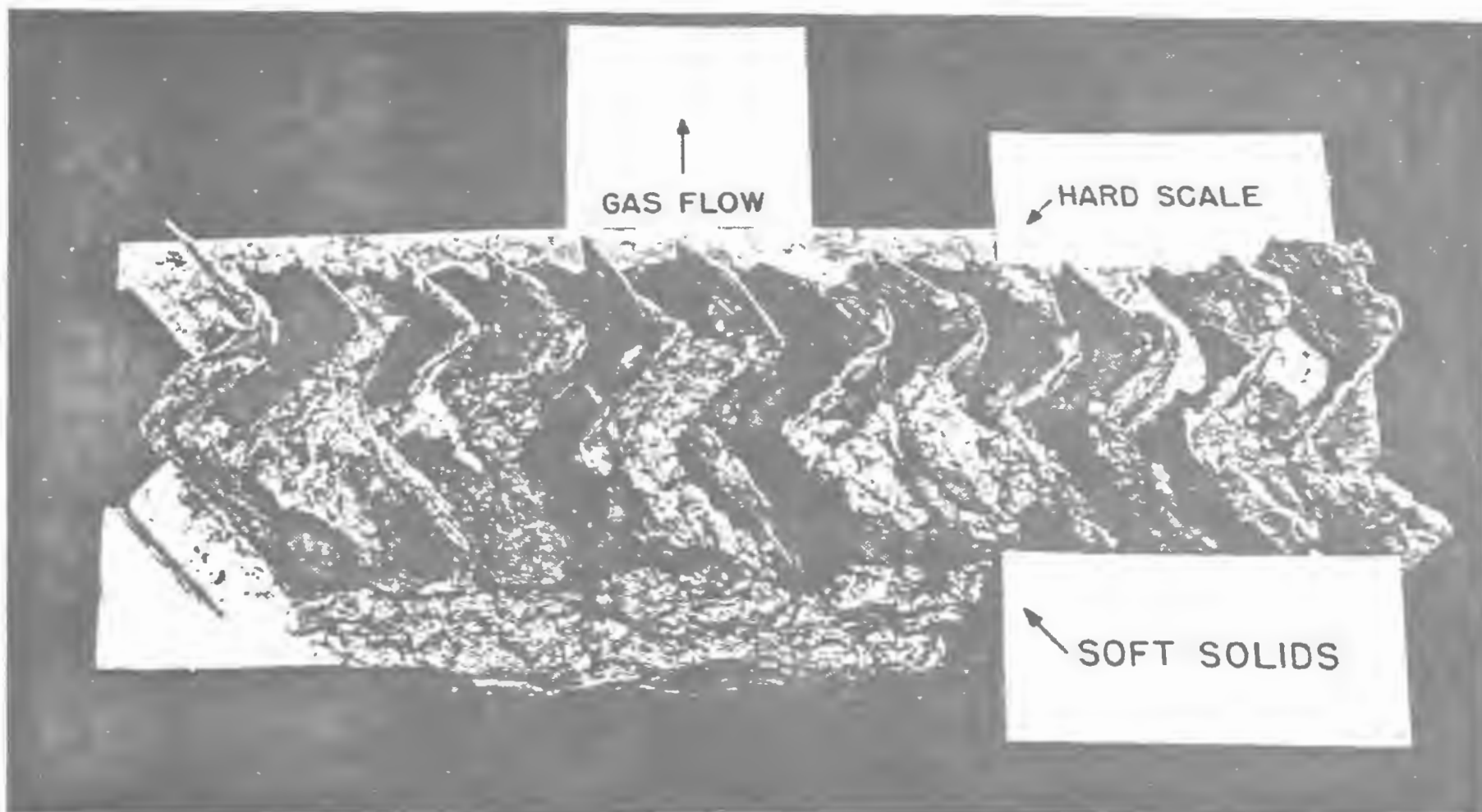


FIGURE 3

Mist Eliminator After 270 Hours of Operation

(Washed Intermittently from Both Sides with a Blend of Clarified Settling Tank Liquor and Fresh Water)

TABLE II

Composition of Effluent Water from Once-Through Mist Eliminator Wash System^aLimestone - Wet-Scrubbing Pilot Plant

Component	Composition, mg/l at the following wash rates			
	Wash rate, gpm/ft ²			
	1.0	0.50	0.25	0.25 ^b
Total dissolved solids	1000	1900	2200	1900
Aluminum	<0.2	<0.2	<0.2	0.5
Ammonia nitrogen	0.21	0.25	0.34	1.9
Arsenic	0.002	0.002	0.010	0.001
Barium	<0.1	<0.1	<0.1	<0.1
Beryllium	<0.01	<0.01	<0.01	<0.01
Cadmium	0.0042	0.0013	0.0031	0.0015
Calcium	220	440	430	370
Chloride	24	40	120	70
Chromium	<0.05	<0.05	<0.05	<0.05
Copper	0.02	0.02	0.03	0.02
Cyanide	<0.01	<0.01	<0.01	<0.01
Iron	5.8	0.07	5.5	13.0
Lead	0.033	0.011	0.016	<0.010
Magnesium	6.5	8.2	18	10
Manganese	0.16	0.14	0.37	0.22
Mercury	<0.0002	<0.0002	<0.0002	<0.0002
Nickel	<0.05	<0.05	<0.05	<0.05
Phosphate	0.11	0.03	0.03	0.10
Potassium	2.2	3.0	2.6	10
Selenium	0.012	0.024	-	0.008
Silver	<0.01	<0.01	<0.01	<0.01
Sodium	8.1	8.8	11	11
Sulfate	700	1000	1200	1200
Zinc	0.07	0.02	0.14	0.08
pH	3.1	7.2	2.7	2.5

^a Gas velocity through the multigrid scrubber (containing 5 grids) was 12 ft/s. Undissolved solids content of the scrubbing slurry was 15%. SO₂ removal efficiency averaged 70%.

^b Supernatant liquor from the fly ash pond was used for this test. All other tests were made with river water.

Grid Configuration: The SO₂ removal efficiency obtained in the multigrid scrubber is dependent upon the gas-liquid contact imparted by the grids. Tests were made to determine the effect on SO₂ removal efficiency and pressure drop caused by varying the number and open area of the grids. When the scrubber was operated with 5 wire mesh-type grids (75% open area, 1/8-inch-diameter wire with 7/8-inch-square openings) at an L/G of 50, the SO₂ removal efficiency and pressure drop averaged 70% and 1.7 inches of H₂O, respectively. Only 2 to 3 percentage points increase in SO₂ removal efficiency was obtained when the number of grids was increased to 10. The pressure drop increased only slightly (less than 0.5 inch H₂O). The relationship of the number of grids to SO₂ removal efficiency is shown in Figure 4.

Another series of tests was made to determine the effect of less grid open area and consequently more contact surface on the pressure drop and SO₂ removal efficiency. Combinations of five and six stainless steel wire mesh grids containing 40 and 60% open area were tested. The 40% open grids were made of 0.075-inch-diameter wire with 1/8-inch-square openings. The 60% open grids were made of 0.094-inch-diameter wire with 1/2- by 5/16-inch openings. The wire used in these grids was smaller and more closely spaced than that previously used to provide more surface (target) area for gas and slurry contact. In some tests, additional grid surface area was obtained (with respect to the downward flow of slurry) by installing a 40% open grid on a 65-degree angle between two horizontal grids. A summary of the grid combinations tested and operating data obtained are shown in Table III.

There was no significant improvement (compared with previous tests with 75% open area grids) in the SO₂ removal efficiency or pressure drop across the scrubber when the open area was reduced to 60%. The removal efficiency and pressure drop increased to 78% and 3.7 inches of H₂O, respectively, when the bottom four 60% open grids were replaced with 40% open area grids. The SO₂ removal efficiency was further increased to 82% by increasing the L/G from 50 to 60. The addition of a sixth grid (40% open, slanted between the bottom two grids) did not cause any significant change. Grids with 40% open area, although better for SO₂ removal, are not practical because of the tendency of the grid to collect trash that would normally pass through a grid having 60% or more open area.

On the basis of this evaluation, five grids containing approximately 65% open area will be used in the Widows Creek installation. The construction of the grids may be similar to floor grating (5/8- by 3-3/4-inch-rectangular openings) made of reinforced plastic or Type 316 stainless steel. The pressure drop and SO₂ removal efficiency obtained in the pilot plant with this type of grid construction was essentially the same as that obtained with the standard wire mesh grids.

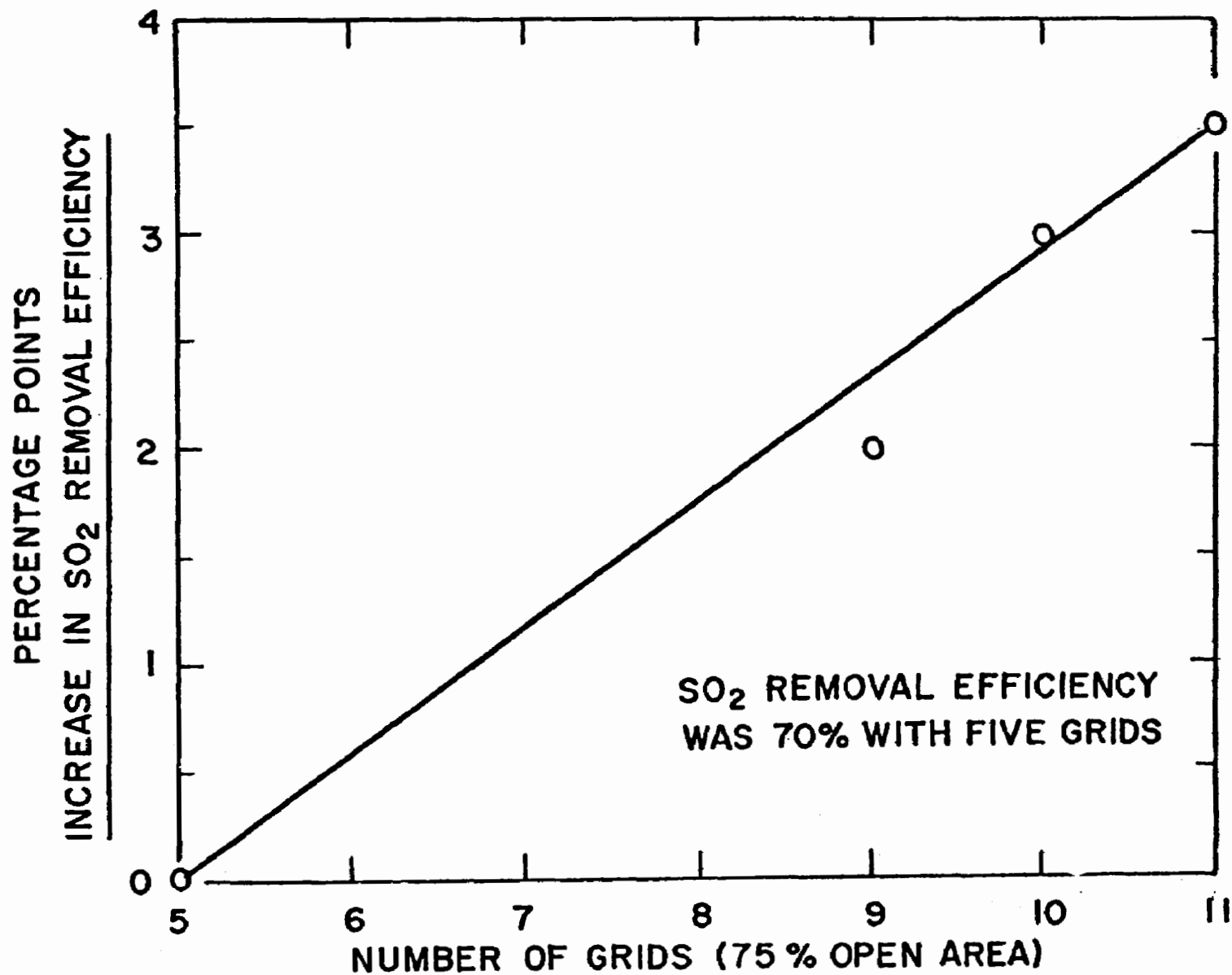


FIGURE 4

Effect of the Number of Grids on SO₂ Removal Efficiency

Limestone - Wet-Scrubbing Pilot Plant

TABLE III

Evaluation of Grids in the Multigrid Scrubber^aLimestone - Wet-Scrubbing Pilot Plant

Test No.	Total	Grids		L/G	ΔP , in H ₂ O	SO ₂ removal efficiency, %
		Distribution ^b				
		No.	Open area, %			
1	5	5	60	50	1.7	70
2	5	1 4	60 40	50	3.7	78
3	5	1 4	60 40	60	4.0	82
4	6	1 4 1	60 40 40 (Slanted)	50	4.1	77
5	6	1 4 1	60 40 40 (Slanted)	60	4.4	84

^a All tests made at 12 ft/s superficial gas velocity.^b Grid distribution listed in order starting from top of scrubber.

Slurry Temperature: During the course of a year's operation of the pilot plant, the SO_2 removal efficiency varied as much as 10% (Figure 5). This change in efficiency is largely attributed to the change in temperature of the scrubbing slurry (about 25°F , from 100°F in winter to 125°F in summer) caused by ambient temperature fluctuations. The lower vapor pressure of SO_2 over the scrubbing slurry at the lower temperatures presumably gave better SO_2 removal during cool weather.

The feasibility of removing heat from the scrubbing slurry to obtain satisfactory SO_2 removal efficiency was tested in the pilot plant. A Teflon-tube heat exchanger manufactured by DuPont was submerged in the multigrid slurry retention tank and river water (57°F) passed through the tubes at a rate of 10 gpm. The heat exchanger was effective in reducing the temperature of the slurry from the normal 120° to 125°F and maintaining it at 100°F . About 50% of the heat load for the cooling was accounted for in the cooling water discharged from the heat exchanger; the remainder was assumed to be lost by convection. An overall heat transfer coefficient (U) of 25 was obtained. This method of increasing the SO_2 removal efficiency is not practical because of the large heat transfer area and high water rate required, which would be even higher in a larger unit because a smaller percentage of the cooling would be accomplished by convection. Also, the temperature of the cooling water obtained from the river in summer would be about 80°F , reducing the ΔT significantly. An equivalent increase (L/G of about 20) in the pumping rate of uncooled slurry to the scrubber would increase the SO_2 removal efficiency about as much as cooling the slurry to 100°F .

Power Plant Simulation Tests: A series of tests was made in the pilot plant to determine whether the limestone - wet-scrubbing process could be operated and controlled over a range of simulated power plant operation conditions. The flow rate and SO_2 concentration of the gas, the recirculation rate of the scrubbing slurry, and the $\text{Ca}:\text{SO}_2$ mole ratio were varied to simulate scheduled and unscheduled changes in boiler operation. A diagram of the pilot-plant configuration used for this series of tests is shown in Figure 6.

Six tests were run consecutively, all on a closed-loop basis. The retention time and the solids content of the scrubbing slurry were 9 minutes (based on a pumping rate of 105 gpm to the multigrid scrubber) and 14%, respectively. The SO_2 removal efficiency ranged from 44% to 82%; 44% when the $\text{Ca}:\text{SO}_2$ mole ratio was reduced to 0.8, and 82% when the gas velocity through the multigrid scrubber was reduced to 8 ft/s and the $\text{Ca}:\text{SO}_2$ mole ratio and L/G were 1.5 and 77, respectively. Operation of the pilot plant was routine and no difficulty was encountered in maintaining control of the process. The SO_2 removal

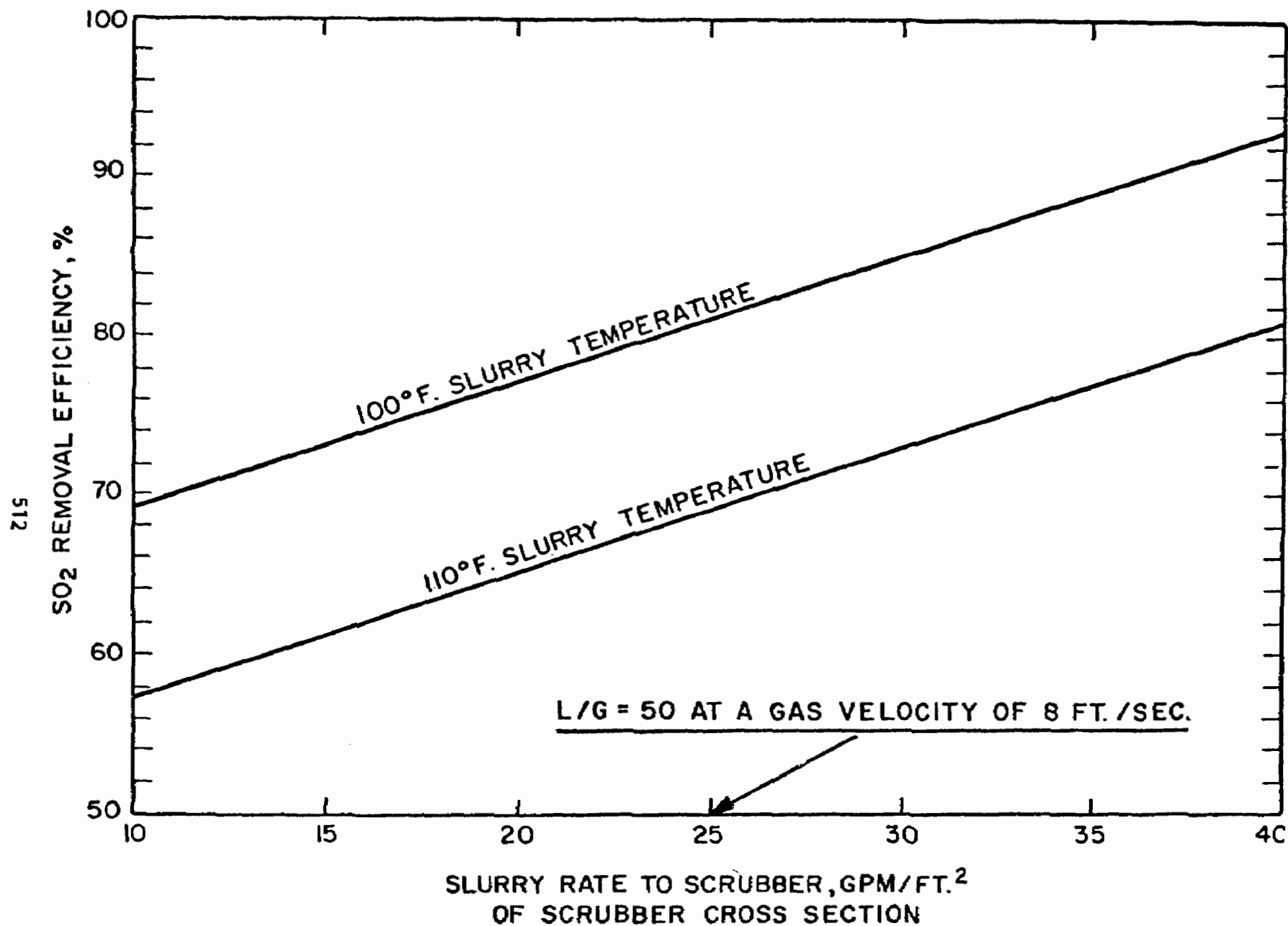


FIGURE 5

Effect of Slurry Temperature on SO₂ Removal Efficiency

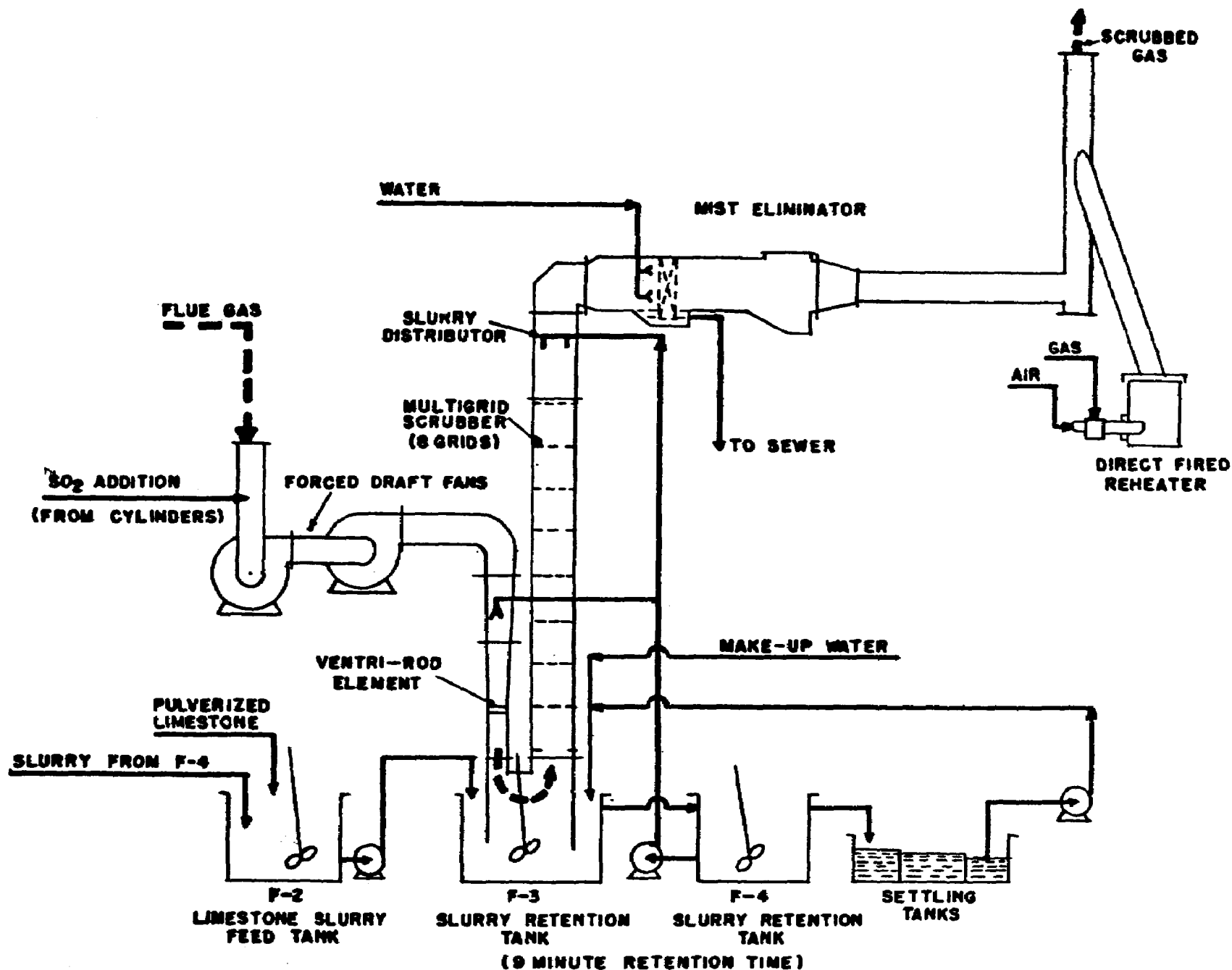


FIGURE 6

Flow Diagram: Limestone - Wet-Scrubbing Pilot-Plant Configuration Used During Power Plant Simulation Tests

efficiency fluctuated with changes in L/G and in the gas flow (simulating a 15 and 35% change in load). The pH of the scrubbing slurry and SO₂ removal efficiency declined rapidly when the flow of fresh limestone was stopped to simulate a pump failure. However, operation returned to normal within 4 hours after the flow of fresh limestone was restored. A summary of the test conditions, SO₂ removal efficiency, and pH of the scrubbing slurry for each test is shown in Figures 7 through 12.

Slurry Settling and Compaction: The slurry disposal pond planned for the Widows Creek installation represents a significant portion of the project cost. The initial size and estimated life planned for the pond depend upon the settling and compaction characteristics of the spent slurry. In the pilot-plant tests, initial settling occurred rapidly (within 24 hours) to produce a clear liquor, but little further settling took place even over extended periods of time. A summary of the long-term settling data is shown in Table IV. The poor settling and compaction are attributed to the presence of small flat calcium sulfite crystals which normally constitute about 90% of the calcium-sulfur reaction products. Only about 10% of the reacted sulfur forms gypsum, which would be a more desirable form because the crystals are large and settle well.

Attempts were made to convert (oxidize) the calcium sulfite to calcium sulfate (gypsum) by treating the spent slurry with excess oxygen (10 times stoichiometric). These tests were unsuccessful. In other tests oxidation of the slurry was promoted when the flue gas was mixed with ambient air to give a 1:1 volume ratio before the scrubber. It would not be practical to do this in a commercial-size unit because of the large volume of air required, but the method was used to determine the effect of increased oxidation on the settling and compaction characteristics of the slurry. The flue gas-air blend contained 13% oxygen and about 1100 ppm SO₂. In one short test oxidation was increased to the extent that 90% of the reacted sulfur was in the form of gypsum. No quantitative settling data were obtained during this test, but compaction of the solids appeared much improved over that of less oxidized slurry. In a longer test (9 days) only 53% of the reacted sulfur formed gypsum. There was no significant improvement in the short- and long-term settling characteristics of this slurry (53% oxidized). These data are shown in Figure 13 and Table V.

Optimum Operating Conditions: Various modes of operation and test conditions were evaluated during the pilot-plant program to determine the best combination for SO₂ removal and ease and reliability of operation. The following conditions are considered optimum and are being used for the planning and design of the Widows Creek system.

- Pressure drop across the venturi (or Ventri-Rod)
for fly ash removal 5 in H₂O
- L/G to venturi (slurry) 10 gal/1000 ft³

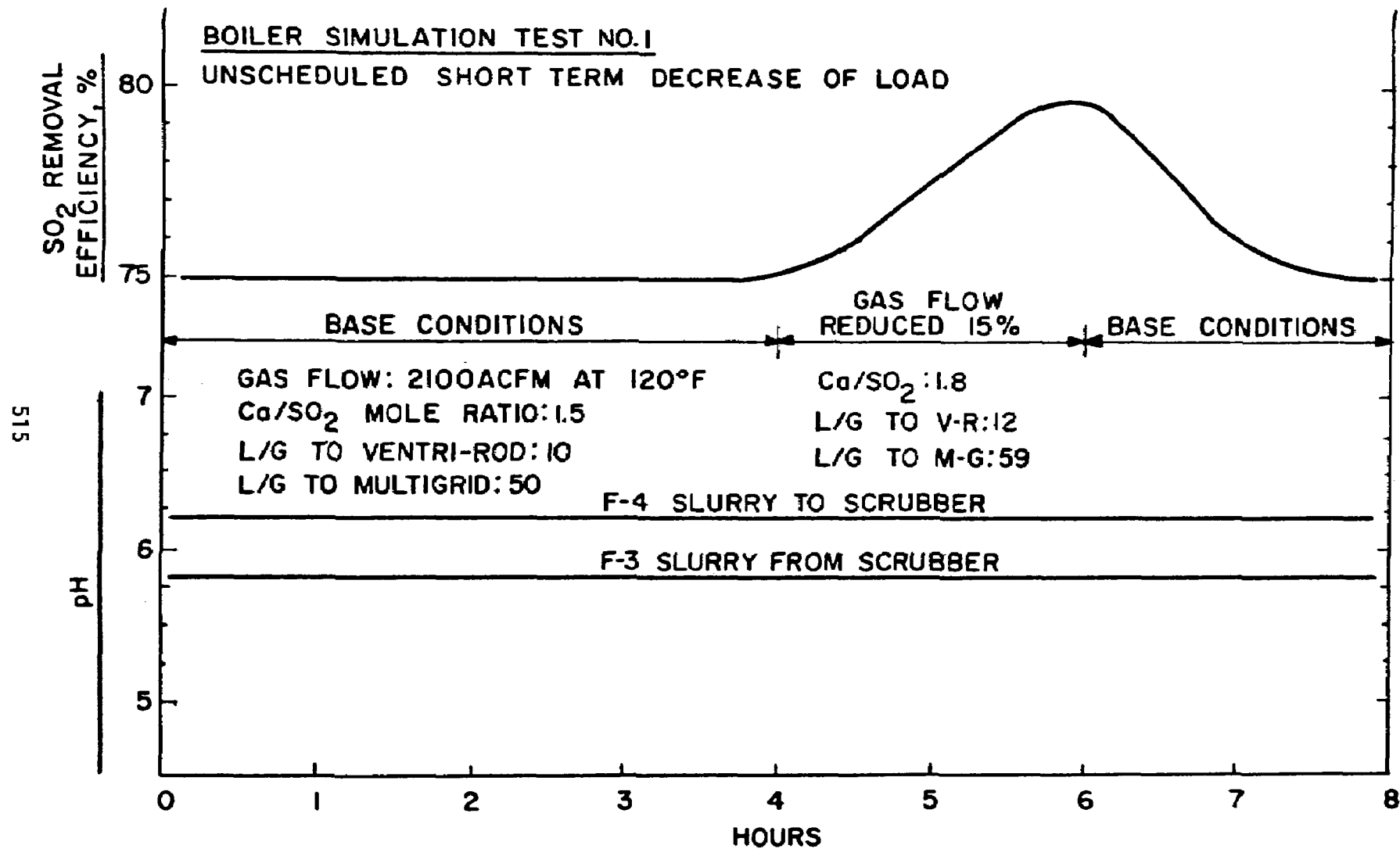


FIGURE 7

The Effect of a 15% Reduction in the Gas Flow on the SO₂

Removal Efficiency and pH of the Scrubbing Slurry

BOILER SIMULATION TEST NO.2

UNSCHEDULED SHORT TERM INCREASE IN LOAD

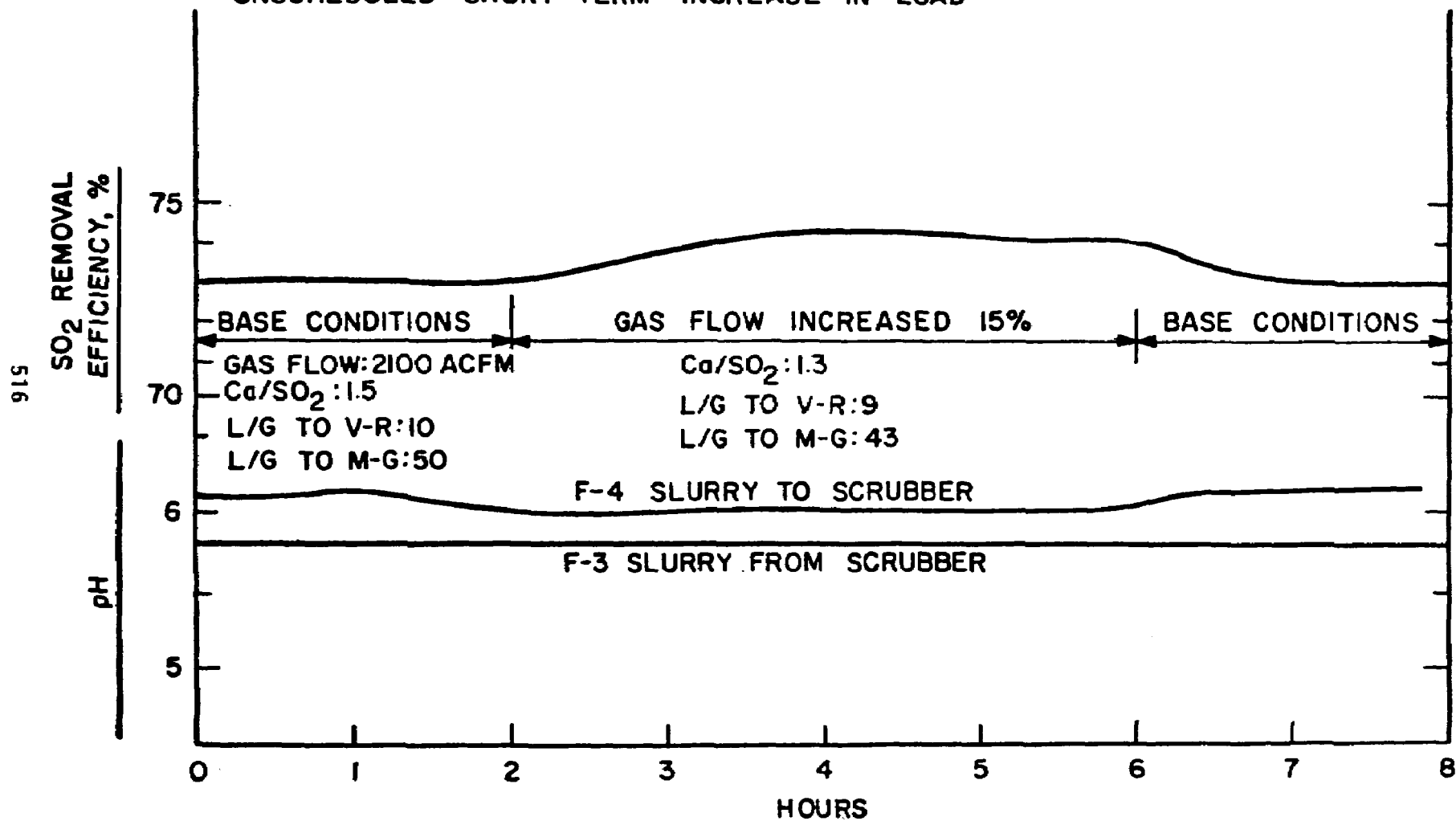


FIGURE 8

The Effect of a 15% Increase in the Gas Flow on the SO₂ Removal

Efficiency and pH of the Scrubbing Slurry

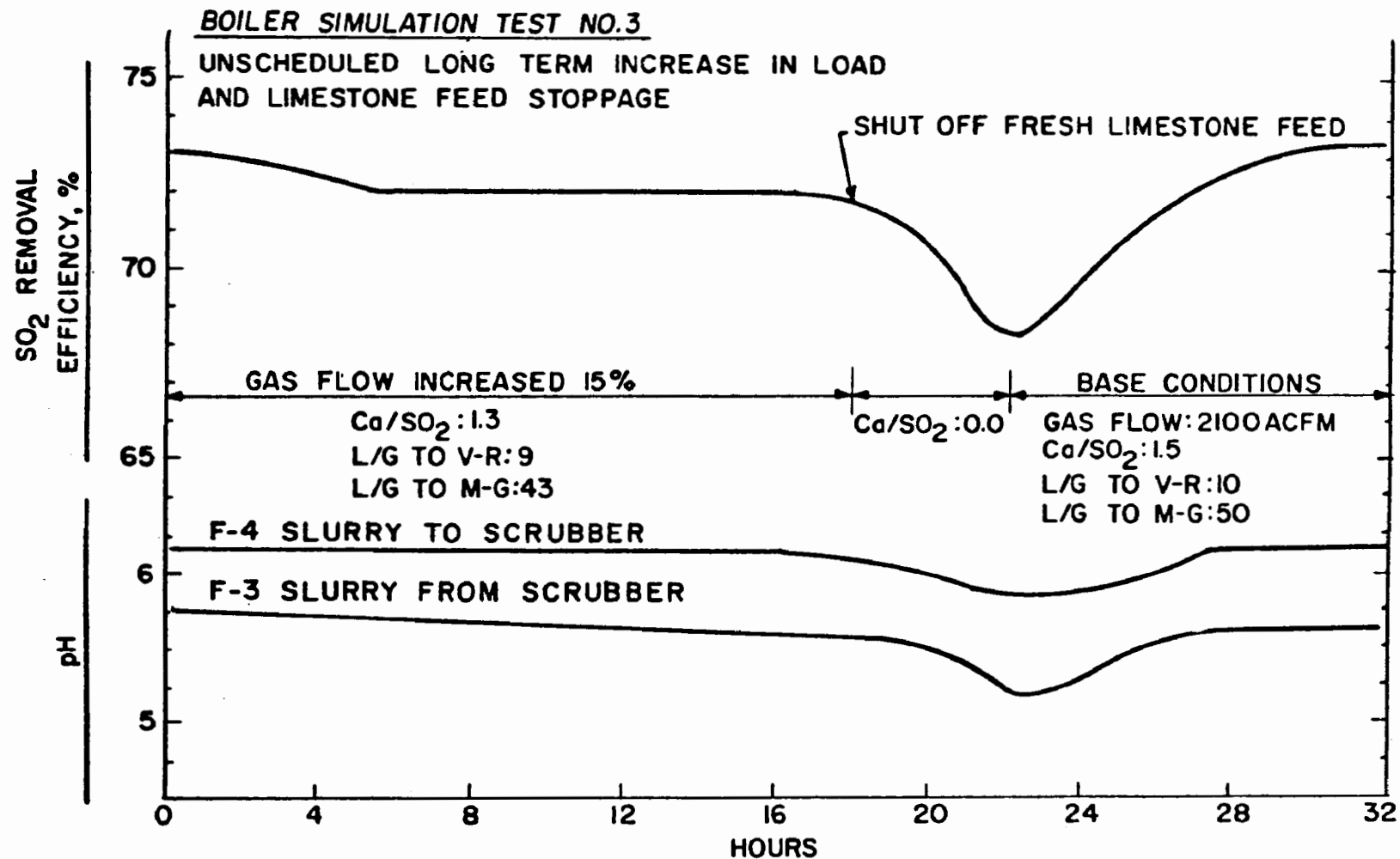


FIGURE 9

The Effect of a 15% Increase in the Gas Flow and a Stoppage of the Fresh Limestone Feed
on the SO₂ Removal Efficiency and pH of the Scrubbing Slurry

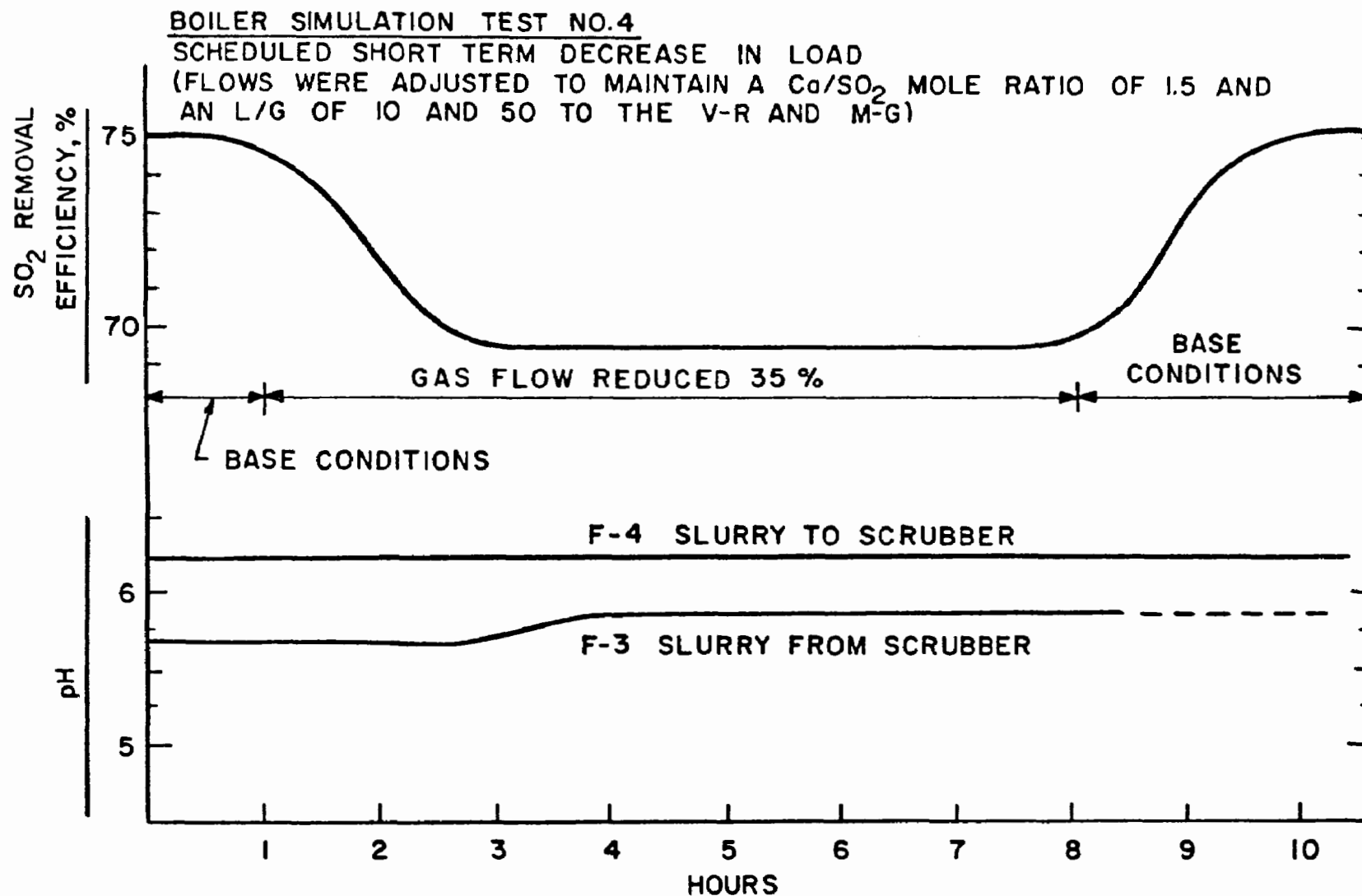


FIGURE 10

The Effect of a 35% Decrease in the Gas Flow on the SO_2
Removal Efficiency and pH of the Scrubbing Slurry

BOILER SIMULATION TEST NO.5

UNSCHEDULED AND SCHEDULED INCREASES IN SO_2 LOAD TO SCRUBBER

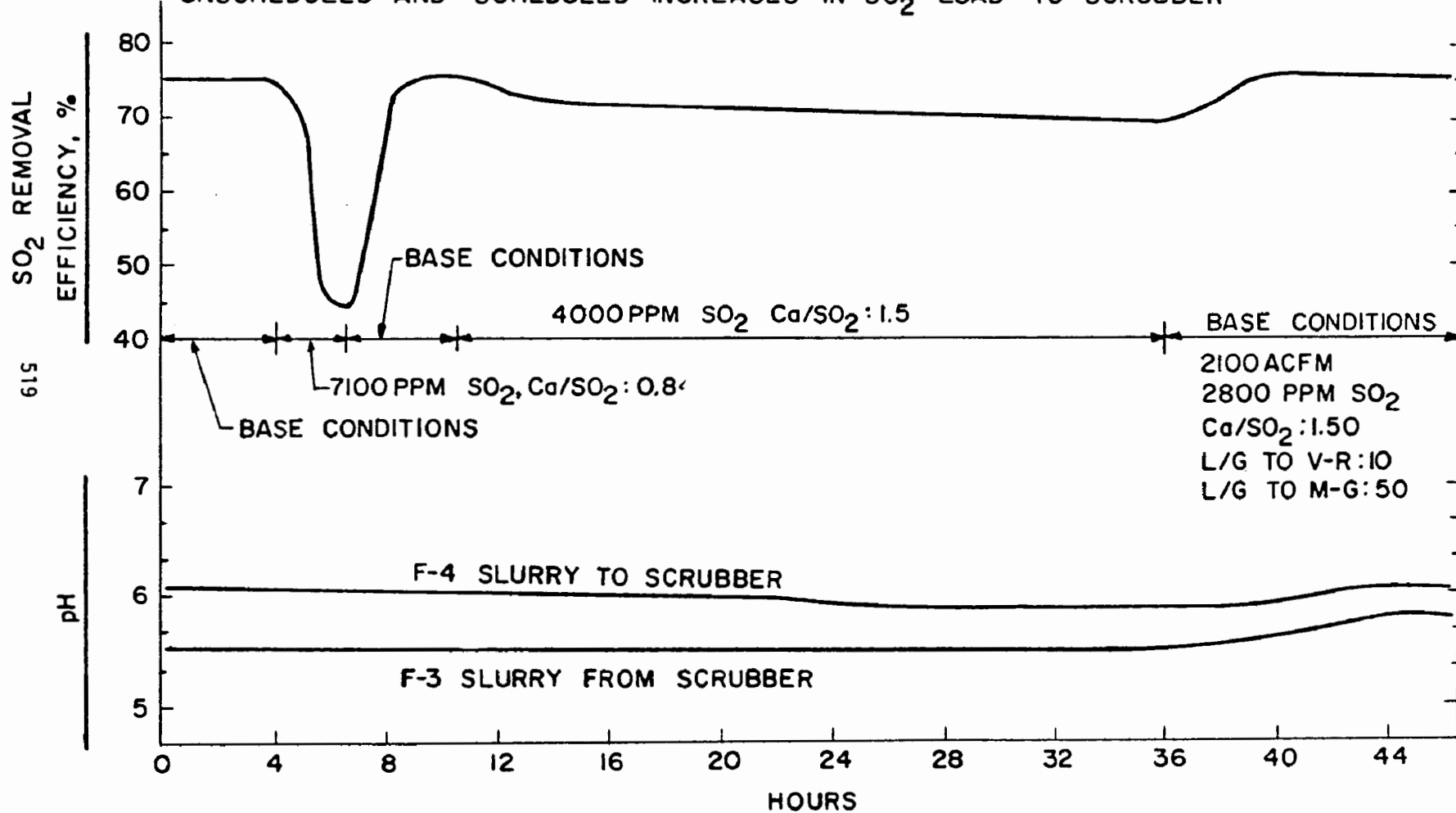


FIGURE 11

The Effect of SO₂ Concentration and Ca:SO₂ Mole Ratio on the SO₂

Removal Efficiency and pH of the Scrubbing Slurry

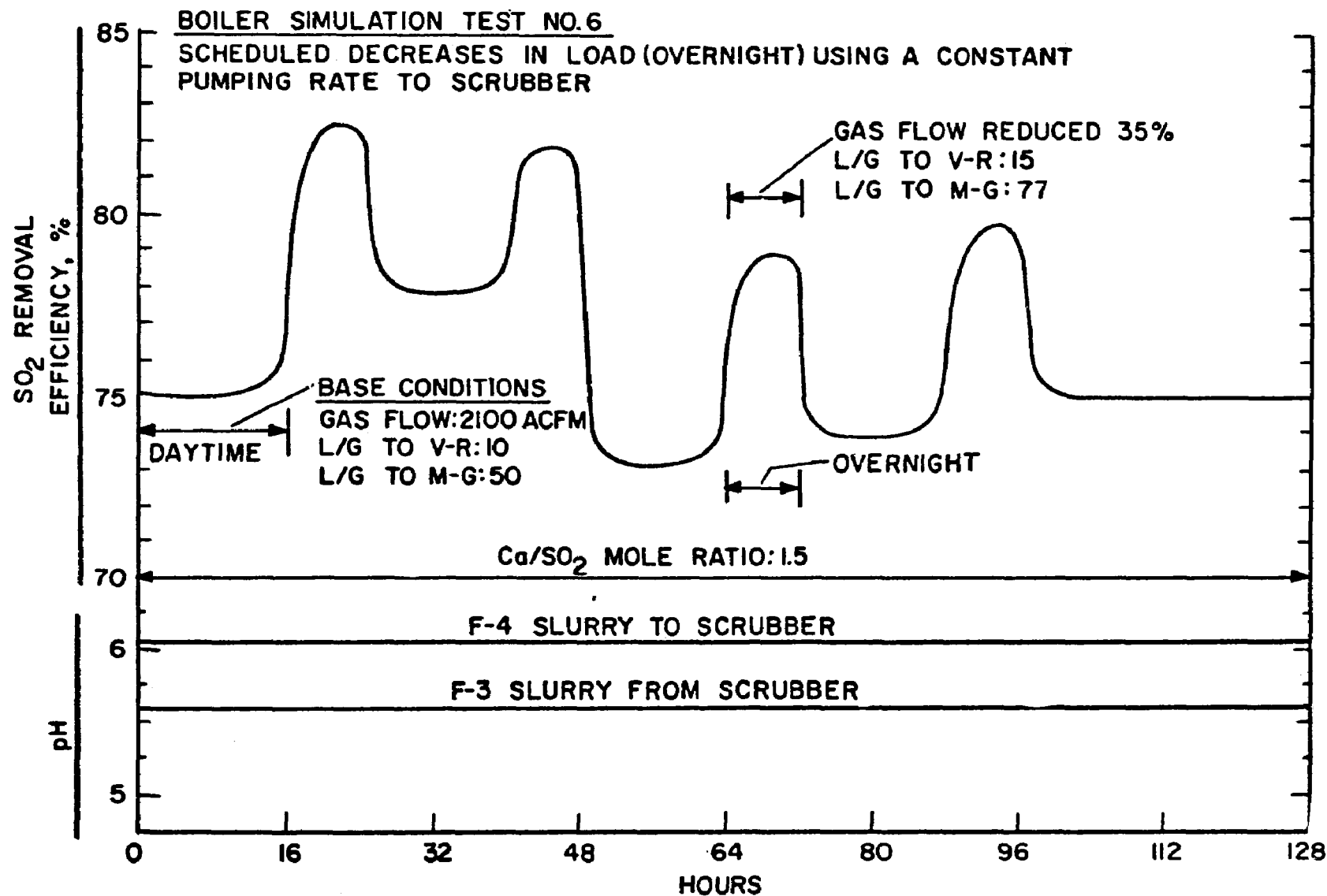


FIGURE 12

The Effect of Reducing the Gas Flow 35% and Maintaining a Constant Pumping Rate to the Scrubber on the SO₂ Removal Efficiency and pH of the Scrubbing Slurry

TABLE IV

Long-Term Settling and Compaction DataLimestone - Wet-Scrubbing Pilot Plant

Test	Limestone source and grind ^d	Percent solids in slurry at start of test ^a	Volume percent after										Percent water in settled solids after				
			30 days		60 days		180 days		240 days		300 days		Days				
			Solids	Liquid	Solids	Liquid	Solids	Liquid	Solids	Liquid	Solids	Liquid	30	60	180	240	300
1 ^b	A	13.7	33	67	32	68	-	-	32	68	32	68	67	66	-	66	66
2 ^b	B	12.9	31	69	30	70	27	73	-	-	27	73	66	66	63	-	63
3 ^c	C	14.0	-	-	24	76	23	77	-	-	23	77	-	57	57	-	57
4 ^b	D	15.0	29	71	-	-	-	-	-	-	29	71	60	60	-	-	60

^a Includes fly ash removed from the flue gas.^b Flue gas contained a fly ash loading of 2 to 5 grains per standard cubic foot.^c Flue gas contained a fly ash loading of 0.1 to 0.5 grain per standard cubic foot.^d A = The Stoneman, Inc. (Tiftonia), Chattanooga, Tennessee, 74% minus 200 mesh.

B = The Stoneman, Inc. (Tiftonia), Chattanooga, Tennessee, 88% minus 325 mesh.

C = Longview Lime Company, Birmingham, Alabama, 75% minus 200 mesh.

D = Fredonia Valley Quarries, Inc., Fredonia, Kentucky, 79% minus 200 mesh.

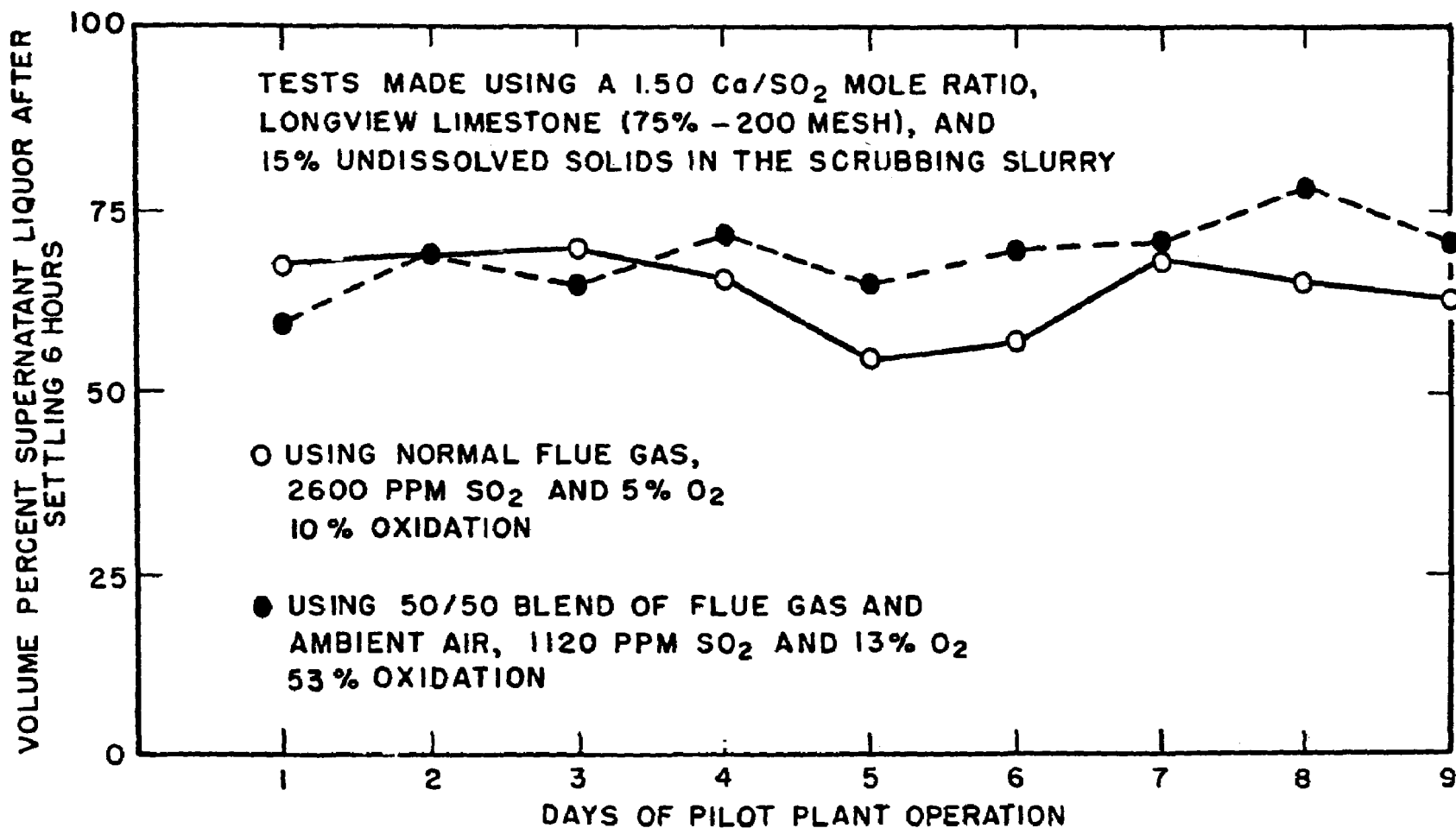


FIGURE 13

Effect of Increased Oxidation on Settling of Solids from Scrubbing Slurry

TABLE V
Effect of Oxidation on the Settling and Compaction Characteristics
of Spent Scrubbing Slurry—Limestone - Wet-Scrubbing Pilot Plant

Test	Percent solids in spent slurry at start of test	Volume percent after				Percent water in settled solids after	
		40 days		120 days		Days	
		<u>Solids</u>	<u>Liquid</u>	<u>Solids</u>	<u>Liquid</u>	<u>40</u>	<u>120</u>
1 (10% oxidation)	15.0	23.5	76.5	23.1	76.9	57	57
2 (53% oxidation)	16.7	27.0	73.0	26.0	74.0	53	53

NOTE: The percent oxidation is defined as the percent of the total reacted sulfur in the slurry existing as calcium sulfate (gypsum).

● Gas velocity through multigrid scrubber (Superficial, based on outlet conditions)	12 ft/s
● L/G to multigrid scrubber (slurry)	50-60 gal/1000 ft ³
● Number and spacing of grids in multigrid scrubber	5 on 5-ft centers
● Open area of grids	60-65%
● Solids content of scrubbing slurry (total undissolved, including fly ash)	15%
● Retention time in delay tank of slurry fed to multigrid scrubber (based on pumping rate)	7 minutes
● Retention time in delay tank of slurry fed to venturi	Not critical
● Ca:SO ₂ mole ratio (based on inlet SO ₂ concentration)	1.5
● Limestone particle size	75% -200 mesh
● Solids content of fresh limestone slurry	60%
● Mist eliminator wash rate (fresh water on a once-through basis)	1 gpm/ft ²

Operation of Prototype Scrubber

Tests were made in one of the three EPA prototype (10 mw) scrubbers (designed by Bechtel Corporation) located at TVA's Shawnee Power Plant near Paducah, Kentucky. Over a period of 2 months, tests were made which were designed to simulate previous operation in the 1-megawatt pilot plant at Colbert and to provide scale-up and design information for the Widows Creek installation. The TCA scrubber was used; the packing spheres were removed and 5 grids were installed at approximately 4-foot intervals. The slurry system was modified to closely duplicate the closed-loop mode of operation used in the pilot plant. A diagram of the prototype plant is shown in Figure 14. Initial operation was suspended after 48 hours of operation because the chevron mist eliminator, located in the vertical scrubber housing, became plugged with solids from entrained scrubbing slurry. This problem was anticipated based on pilot-plant experience.

The design of the prototype system precluded the installation of a horizontal mist eliminator housing at the outlet of the scrubber to duplicate the system developed in the pilot plant. Instead, a multiple venturi tray device (FlexiTray, manufactured by Koch Engineering Co., Inc.) was installed in the vertical scrubber tower between the slurry distributor and mist eliminator. The FlexiTray was designed to provide an interface between the closed-loop scrubbing slurry system and a once-through wash

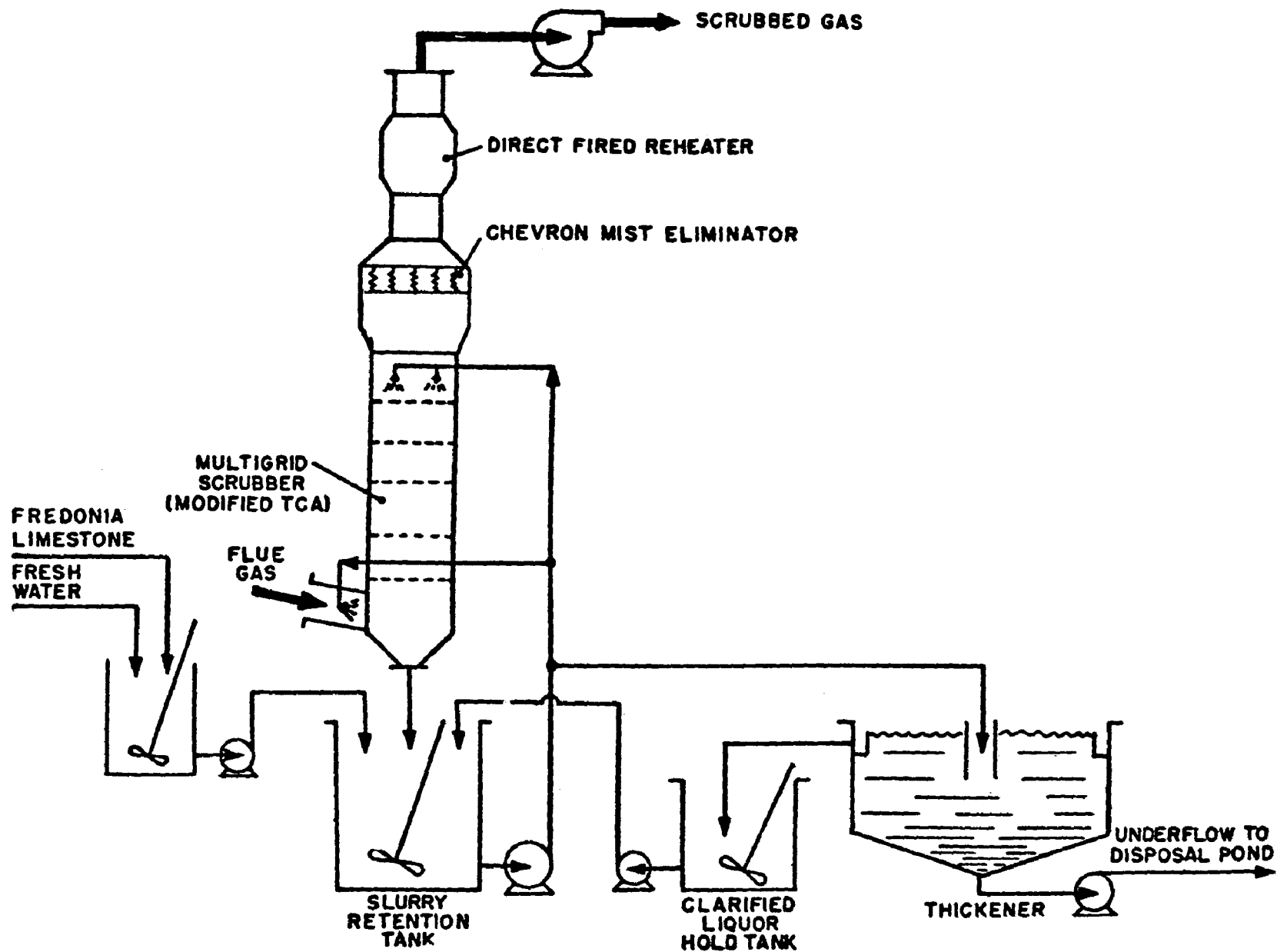


FIGURE 14

Flow Diagram - Modified TCA Prototype Scrubber at Shawnee Power Plant

system for the mist eliminator. Fresh water, fed across the top of the FlexiTray at a rate of about 60 gpm, was effective in keeping the top of the tray and the mist eliminator clean; the water was discarded. Blasting the bottom of the tray with steam (150 psig) once per shift for about 1 minute was effective in preventing accumulation of solids in this region. A diagram of the prototype scrubber and FlexiTray installation is shown in Figure 15.

When the scrubber was operated at a gas velocity of 12 ft/s (design rate for Widows Creek at full load), carryover of scrubbing slurry into the open-loop FlexiTray wash system was excessive (30 gpm). Continuous operation could not be maintained at the high gas flow rate because (1) the maximum slurry purge rate to the disposal pond during closed-loop operation is only about 1 gpm per megawatt (10 gpm total) and (2) slurry lost to the FlexiTray wash system was routed to the fly ash disposal pond and could not be returned to the closed-loop slurry system. Excessive carryover of scrubbing slurry did not occur in the pilot plant when the scrubber was operated at a gas velocity of 12 to 13 ft/s. These data are shown in Figure 16. The reason for the excessive entrainment of slurry in the prototype scrubber is not known but may be caused by the smaller ratio of scrubber wall area to gas volume as the size of the scrubber increases. The relationship between velocity and entrainment for the larger Widows Creek scrubber is not predictable.

Carryover of scrubbing slurry into the FlexiTray wash system was negligible when the gas velocity was reduced to 8 ft/s (two-thirds of Widows Creek design). This velocity was selected for a long-term test designed to compare the operating characteristics of the prototype system with the Colbert pilot plant. Scrubbing slurry containing 15% undissolved solids was fed to the multigrid scrubber at an L/G of 50. The hot flue gas was humidified with slurry fed to the inlet duct at a rate of 30 to 50 gpm. The retention time of the scrubbing slurry in the delay tank was 7 minutes based on the pumping rate to the multigrid. The top of the FlexiTray was irrigated with fresh water on a once-through basis at a rate of 45 to 60 gpm. The bottom of the tray was blasted with steam (150 psig) once per shift.

Crushed limestone (1-1/2-inch) was supplied by Fredonia Valley Quarries, Inc., Fredonia, Kentucky, and pulverized by TVA at the Shawnee site. The limestone is relatively soft and easily pulverized to produce a large fraction (95%) of minus 325-mesh material, of which about 50% is minus 8 microns. The pulverized limestone was fed as a 60% slurry into the scrubber system at a rate intended to maintain a Ca:SO₂ mole ratio of 1.5 based on the inlet SO₂ concentration; however, chemical analysis of the solids from the spent scrubbing slurry taken near the end of the test indicated a Ca:SO₂ mole ratio equivalent to 3.0. The magnetic flowmeter used to measure the fresh limestone feed rate was calibrated at the beginning and end of the test, and the indicated flow rate at the end of the test was only about one-half of the actual rate.

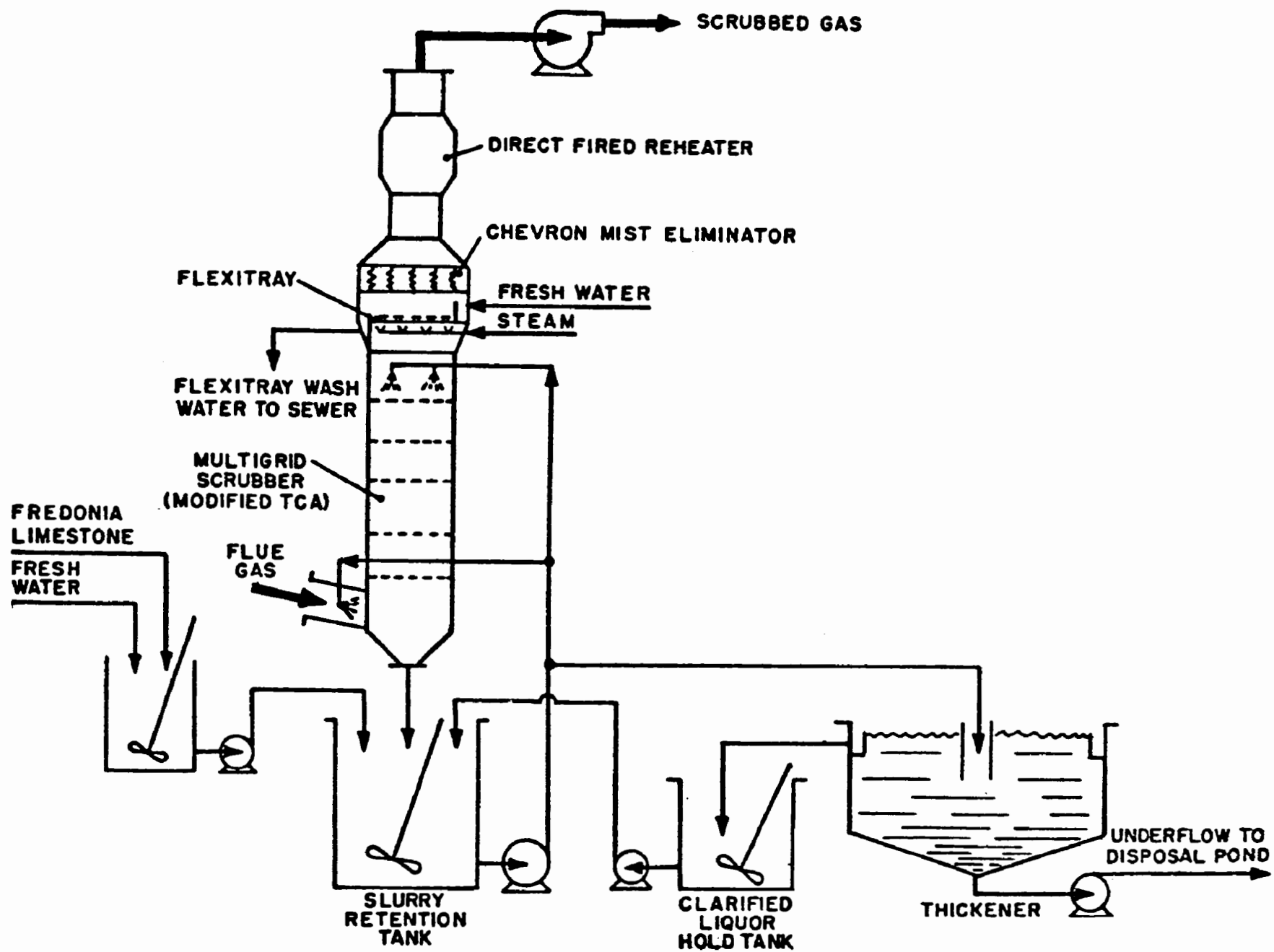


FIGURE 15

Flow Diagram - Modified TCA Prototype Scrubber with FlexiTray

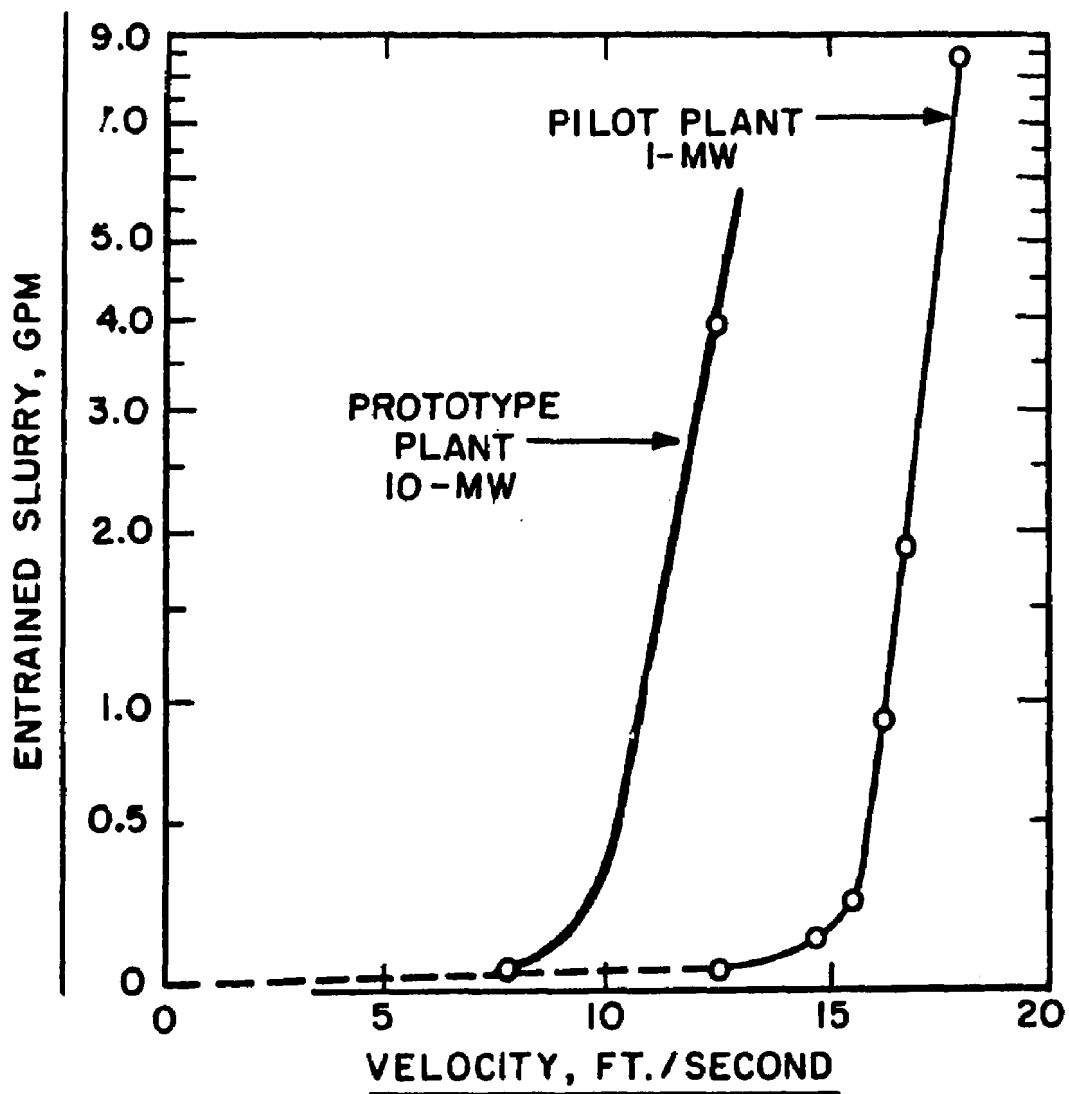


FIGURE 16

Effect of Gas Velocity on Entrainment
of Scrubbing Slurry

The SO₂ removal efficiency gradually increased from about 70% in the beginning of the test to 80% at the end. The pressure drop across the system (including the wet-dry junction, scrubber, FlexiTray, and mist eliminator) increased from 3.5 to 6.0 inches of H₂O during the course of the test (19 days). The undissolved and dissolved solids contents of the scrubbing slurry were steady at about 14 and 0.5%, respectively. The pH of the slurry fed to the scrubber ranged from 5.8 to 6.0. The trends in SO₂ removal efficiency, pH and solids content of the slurry, and pressure drop are shown in Figure 17.

From 10 to 20% (5-10 gpm) of the FlexiTray wash water fell through the tray into the multigrid scrubber. The fall-through water exceeded the closed-loop water balance based on a water content of 50% in the discarded spent slurry. The extra water (5-10 gpm) was removed from the system with the dilute thickener underflow (about 25% solids) which was discarded to the disposal pond. No clarified liquor was returned to the scrubbing system from the disposal pond.

Operation of the scrubbing system was routine and control of the system was maintained without difficulty. However, the performance of the thickener was marginal, yielding a more dilute underflow than expected. The dilute underflow provided a convenient means of purging the excess water from the system caused by leaking of the FlexiTray wash water into the slurry system.

After the long-term test was completed, and before the plant was shut down, a series of short-term screening tests was made designed to determine the effects of L/G, gas velocity, and Ca:SO₂ mole ratio on the SO₂ removal efficiency. These data are shown in Table VI. In all tests, the SO₂ removal efficiency increased with increased L/G and with increased gas velocity (over the range of 8 to 10.4 ft/s). The effect of the Ca:SO₂ mole ratio on the SO₂ removal efficiency could not be identified. This is attributed to the high mole ratio due to the error in the flowmeter. These data agree closely with data obtained in the pilot plant while operating under similar conditions (except for the high Ca:SO₂ mole ratio).

Operation of the prototype plant was discontinued after completing the screening tests. The plant had been operated continuously for 27 days. Following the shutdown the plant was inspected. Heavy deposits of scale (mostly calcium sulfite and sulfate) had accumulated on the grids and walls of the scrubber. A discussion of the inspection follows.

Wet-Dry Junction: The flue gas entered the scrubber through a 40-inch-square horizontal duct. Scrubbing slurry (about 30-50 gpm) was sprayed into the duct (90 degrees to the gas flow) 4 feet from the entrance to the scrubber. The slurry spray was effective in reducing the temperature of the flue gas from 300°F to about 125° to 150°F before entering the rubber-lined scrubber, thus affording protection to the liner. About 70% of the cross-section area of the duct was plugged with an accumulation of fly ash and solids from the scrubbing slurry. The accumulation extended about 2 feet upstream from the point of slurry

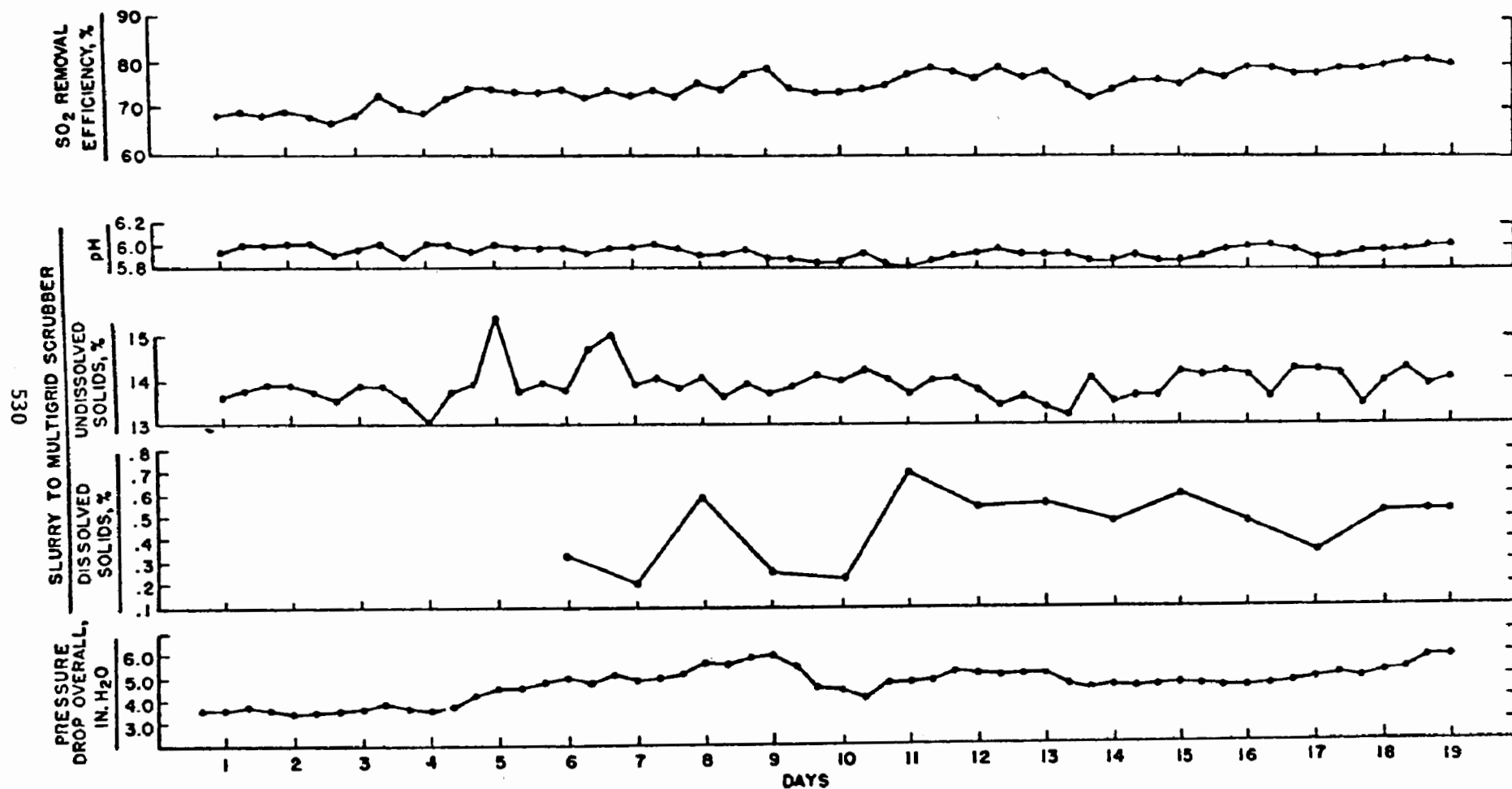


FIGURE 17

Prototype Multigrid Scrubber—Trends in SO₂ Removal, pH and Solids Content of the
Scrubbing Slurry, and Pressure Drop Across System

TABLE VI
Screening Tests, Prototype Limestone - Wet-Scrubbing Pilot Plant at Shawnee Steam Plant
(Multigrid Scrubber with Five Grids)

Test No.	Duration, hr	Flue gas		Ca:SO ₂ mole ratio Indicated Actual	Δ P across scrubber, in H ₂ O ^a	FlexiTray					Scrubbing slurry				SO ₂ removal, %	
		Flow rate, acfm at 120°F	Velocity through scrubber, ft/s			Once-through wash water				L/G	pH	Temp, °F	Solids, %			
						To tray, gpm	From tray ^b , gpm	Solids, %	Fall through, gpm					Δ P in H ₂ O ^c		
WC-4A	8	14,720	8.0	1.5	3.0	3.8	60	48	0.10	12	2.5	70	5.9	99	14	88
WC-5A	432	14,720	8.0	1.5	3.0	1.4-3.5	60	56	0.10	4	2.4	50	5.9	-	14	75
WC-6A	8	14,720	8.0	1.5	3.0	3.0	60	48	0.10	12	2.4	35	5.9	-	14	76
WC-7A	3	14,720	8.0	1.5	3.0	2.7	60	46	-	14	2.4	25	6.0	99	15	72
WC-8A	8	19,170	10.4	1.5	3.0	5.6	60	85	3.6	-	3.4	25	5.8	97	14	79
WC-9A	4	19,170	10.4	1.5	3.0	6.3	60	85	-	-	3.5	35	5.8	94	14	86
WC-10	4	19,170	10.4	1.5	3.0	6.5	60	86	-	-	3.4	50	5.9	105	14	90
WC-11	24	14,720	8.0	1.2	2.4	4.4	60	50	0.7	10	2.6	50	5.9	103	13	88
WC-12	64	14,720	8.0	1.2	2.4	3.9	60	45	1.1	15	2.6	25	5.9	110	14	75

^a Combined pressure drop across wet-dry junction and grid section of scrubber.

^b Includes entrained scrubbing slurry collected by FlexiTray wash system.

^c Combined pressure drop across FlexiTray and chevron mist eliminator.

NOTE: Slurry retention time was 7.2 minutes, based on 14,720 acfm at 120°F and an L/G of 50.

injection. The soot blower (operated once per shift with air at 90 psig) was not effective in keeping this area clean. No accumulation of solids occurred downstream from the point of slurry injection.

Grids: The scrubber contained five Type 316L stainless steel grid assemblies spaced at approximately 4-foot intervals. The open area of the wire mesh (1-1/8-inch-square openings with 0.148-inch-diameter wire) was 75%, but the effective open area of the grid assembly was only about 50% because of the grid support and retaining structures.

A coating of hard scale formed on all of the grids and about 40 to 50% of the open area was obstructed. The scale deposits were identified as predominately calcium sulfite, although small amounts of calcium sulfate and calcium carbonate were present.

The bottom grid was scaled the most. The scale was about 1/8-inch thick on the grid wires and retaining assemblies. Nodules of scale (about 3/4-inch diameter) had formed on the top and bottom sides of the grid where the wires intersected. The scale formation was most severe in the center section of the grid; an area of about 1 square foot was completely plugged.

The deposit on the intermediate grids was uniform and about 1/16-inch thick. The top grid was partially plugged with a mixture of scale and soft solids from the scrubbing slurry.

Scrubber Walls: The rubber-lined walls of the scrubber were coated with hard scale ranging from 1/8- to 1-inch thick. Petrographic examination indicated alternate layers of calcium sulfite and calcium sulfate of varying thickness. Approximately equal portions of calcium sulfite and calcium sulfate were present according to chemical analysis.

In addition to the general scaling, an accumulation of solids resembling a stalactite occurred on one wall between the top two grids. The formation, about 12 inches thick and 3 feet long, was a soft mixture of scale and solids from the scrubbing slurry.

FlexiTray and Mist Eliminator: Solids from entrained scrubbing slurry had accumulated on the bottom of the FlexiTray to a thickness of 2 to 4 inches, but the openings in the tray were not plugged.

The chevron mist eliminator was generally clean except for the portion located directly above the FlexiTray overflow and drain trough. The pressure drop across the FlexiTray and mist eliminator assembly increased from 2.3 to 2.6 inches during the period of operation (27 days).

Pilot-Plant Simulation of Prototype Operation

Scaling of the scrubber did not occur during prolonged operation (8000 hours) of the Colbert pilot plant. The reason for the heavy accumulation of scale in the prototype scrubber is unknown, but it may have been caused by the following:

- Inadequate humidification of the hot flue gas before it entered the scrubber.

- Poor distribution of the gas and scrubbing liquor in the scrubber.
- Fine particle size of the Fredonia limestone.
- High $\text{Ca}:\text{SO}_2$ mole ratio (1.5 to 3.0) caused by inaccurate metering of the fresh limestone feed.

A test was made in the pilot plant to determine if the conditions used in the prototype plant would also cause scaling in the pilot plant.

The pilot plant was arranged to closely duplicate the equipment configuration and operating conditions used in the prototype. The velocity of the gas through the scrubber was maintained at 8 ft/s. Scrubbing slurry containing 15% solids was fed to the scrubber at an L/G of 50. The retention time of the scrubbing slurry was 7 minutes based on the pumping rate to the scrubber. Finely ground Fredonia limestone was obtained from the prototype grinding and storage facility. The $\text{Ca}:\text{SO}_2$ mole ratio was maintained at 2.5 to duplicate the average limestone feed rate used during the test in the prototype system. Makeup water was added to simulate the partial open-loop operation of the prototype system caused by the dilute thickener underflow.

Operation was routine. The SO_2 removal efficiency averaged 68% compared to 75% in the prototype. A comparison of the trends in the SO_2 removal efficiency and pH and solids content of the scrubbing slurry for the prototype and pilot plants is shown in Figure 18.

The test was terminated after 13 days of continuous operation. The grids and walls of the scrubber were coated with heavy deposits of scale. The extent and composition of the scale deposits in the pilot-plant scrubber were very similar to the deposits found in the prototype. A comparison of the chemical composition of the scrubbing slurry and scale deposits from the pilot-plant and prototype operations is shown in Table VII.

Based on these tests and similar tests conducted by EPA in a small pilot plant at Research Triangle Park, North Carolina, it has been concluded that the scaling of the prototype and pilot-plant scrubbers was primarily caused by the combination of (1) high $\text{Ca}:\text{SO}_2$ mole ratio and (2) the fine particle size of the soft Fredonia limestone.

Process Equipment and Construction Materials

One of the primary objectives of the pilot-plant program was to evaluate process equipment and construction materials. This information is required for the design of the Widows Creek system.

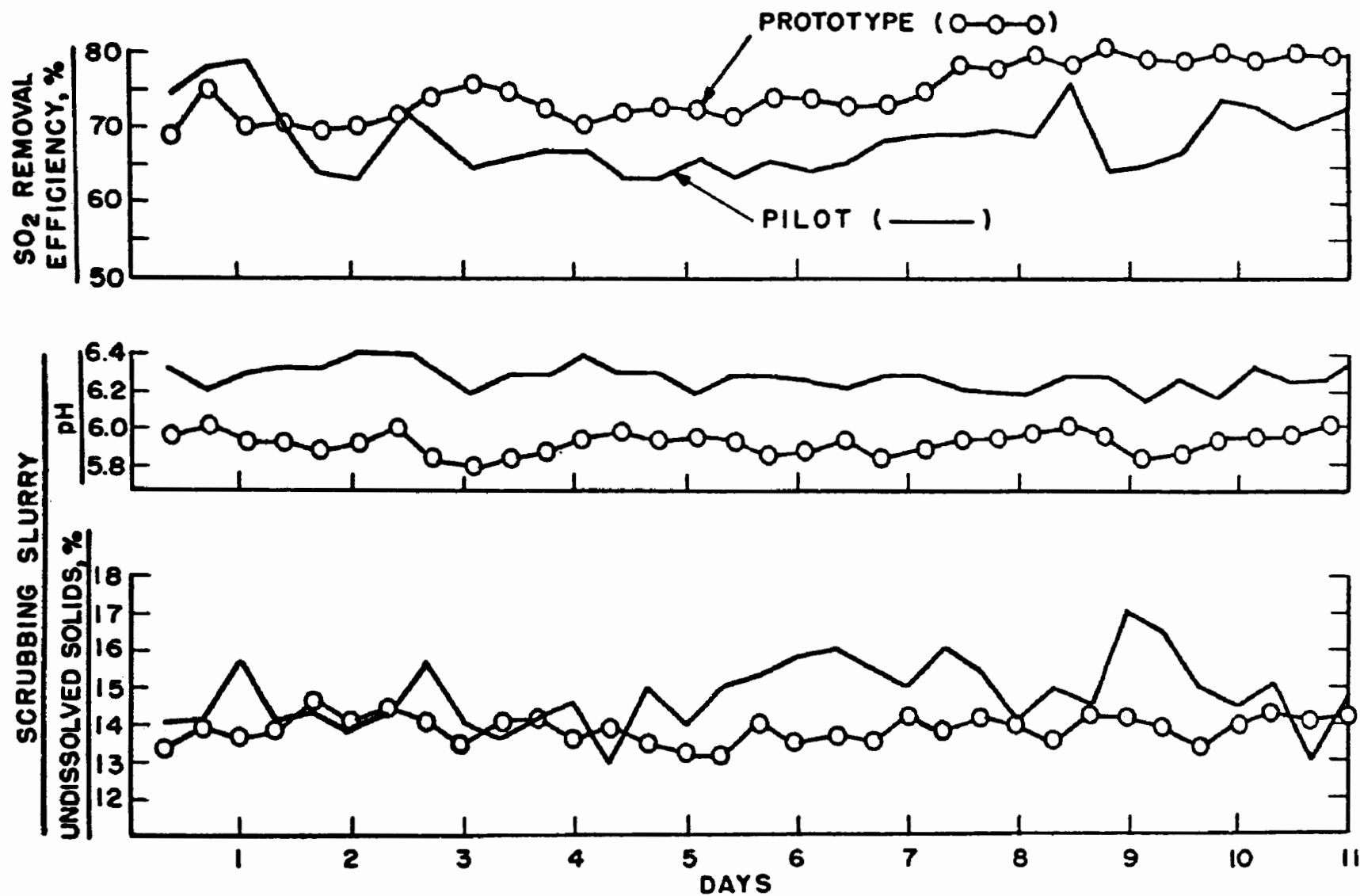


FIGURE 18

Comparison of Trends in SO₂ Removal Efficiency and pH and Solids Content
of the Scrubbing Slurry in the Prototype and Pilot Plant

TABLE VII

Comparison of Chemical Analysis of Limestone - Wet-Scrubbing Slurry
and Scale Deposits from the Prototype Multigrid Scrubber
at Shawnee Steam Plant and Pilot Plant at Colbert Steam Plant

Plant	Duration, hr	Limestone source ^a	Scrubbing slurry ^b							Chemical scale, % by wt							
			Cake, % by wt				Filtrate, gm/l			Grid				Walls			
			Ca	Mg	Sulfite S	Total S	Ca	Total S	Total dissolved solids	Ca	Mg	Sulfite S	Total S	Ca	Mg	Sulfite S	Total S
Prototype	500	Fredonia	27.4	2.0	3.8	5.5	0.8	0.4	5.4	23.2	0.4	10.4	16.4	25.5	0.1	9.3	19.2
Pilot plant	310	Fredonia	30.7	0.9	4.2	4.9	1.1	0.5	7.1	21.5	0.1	14.5	17.1	19.7	0.4	8.9	11.3

^a Limestone supplied by Fredonia Valley Quarries, Inc., Fredonia, Kentucky, and ground by TVA (50% -8 microns) in prototype dry ball mill at the Shawnee Steam Plant.

^b Scrubbing slurry contained 15% undissolved solids by weight.

NOTE: Both plants were operated using a Ca:SO₂ mole ratio of 2.5-3.0 based on the SO₂ concentration of the inlet flue gas (normally 2800 ppm). The SO₂ removal efficiency varied from 65 to 75%.

In as many cases as possible, commercially available equipment was used and observed over extended periods of time. Pumps, valves, piping, and process instrumentation were evaluated in this manner. Most of the construction materials and coatings were evaluated in a special test device designed to simultaneously expose several different materials to the same chemical and erosive environment.

A summary of the conclusions drawn from this evaluation follows.

Pumps: Soft rubber-lined (natural or neoprene) centrifugal pumps were normally used to circulate the scrubbing slurry. The rubber housing liner and impeller coating showed very little wear after 9000 hours of operation. Severe erosion of the housing and impeller occurred within 500 hours when an unlined Type 304 stainless steel pump was used.

Flow Control and Isolation Valves: Plug, pneumatic pinch, and butterfly valves were evaluated for controlling the flow of scrubbing slurry. The plug and pinch valves were lined with soft rubber. The body and disk of the butterfly valve was coated with abrasion-resistant polyethylene.

The 3/16-inch-thick rubber coating on the body and plug of the plug valve eroded through during 1200 hours of operation. The pneumatic pinch valve was not suitable because of severe vibration caused by pulsation of the rubber sleeve. The butterfly valve provided an effective means of trimming the flow of slurry, although positive shutoff was not possible. The polyethylene lining was in good condition after 1000 hours of service.

Knife-type gate valves (unlined stainless steel construction) were effective for isolation and on-off service.

Piping: Rubber hoses were used for most of the slurry piping in the pilot plant. The hoses had soft rubber (neoprene) liners and gave excellent service. The velocity of the slurry through the hoses and piping normally did not exceed 8 ft/s. In addition to the rubber-lined hose, special test sections of pipe of the following construction were tested:

- Mild steel
- Type 316L stainless steel
- Glass-reinforced polyester
- Mild steel lined with polypropylene
- Mild steel lined with urethane
- Mild steel lined and coated with polyethylene

Unlined mild steel pipe is not suitable because of severe erosion and corrosion. Some types of urethane-lined steel pipe failed because of blistering of the liner. All other materials tested gave good service. Selection of any one of the types of pipe construction tested in the pilot plant (except mild steel and some urethane linings) for a commercial unit would depend largely upon cost.

Instrumentation: Several instruments were used for process control. A discussion of the performance of the instruments follows.

- SO₂ Determination—An ultraviolet analyzer (DuPont photometric) was used to monitor the concentration of SO₂ in the flue gas before and after the scrubber. This unit has given good service and required only a minimum of maintenance. Leaky valves in the automatic sample selection system caused the initial installation to be unreliable. Replacement of the automatic sample selection valves with manual valves cured the problem.
- pH Measurement—The pH of the slurry in the multigrid retention tank was measured continuously with a system manufactured by Universal Interloc, Inc., consisting of a waterproof sensor and amplifier assembly submerged directly in the slurry retention tank. The pH measurement is indicated and recorded by an instrument located in the control room. This system has worked very well and agrees closely with laboratory pH measurements. The unit has required no maintenance. There has been no indication of electrode scaling or erosion over 6 months of continuous exposure to the scrubbing slurry.
- Slurry Density—The solids content (density) of the slurry was monitored continuously with a differential pressure (bubble tube) device. Two tubes (1-inch pipe) are submerged directly in the slurry retention tank at a fixed pressure differential. A constant air purge is supplied to each tube. The differential in pressure of the air purge is proportional to the density of the slurry. This device has been very reliable and useful as a trend indicator. The absolute solids content of the slurry is determined gravimetrically in the pilot-plant laboratory.
- Measurement of Slurry Flow—The flow rates of the fresh limestone slurry (60% solids) and the scrubbing slurry (15% solids) are measured with magnetic flowmeters manufactured by the Foxboro Company. The meters are lined with an abrasion-resistant material (Adiprene-L) similar to soft rubber. The readout system is all electronic, consisting of a field-mounted signal converter and a recorder located in the control room. The performance of these meters has been very good and only a minimum of maintenance has been required over a period of 18 months.

Metals and Coatings: Several metals and coatings were evaluated for possible use in the Widows Creek installation. Types 316 and 316L stainless steel showed good resistance to corrosion and erosion in the scrubber (grids) and piping system. Severe pitting and general corrosion occurred when stainless steel was used as a tube material for an indirect reheater in the scrubber exhaust gas duct. Reheat tubes made of other materials (Inconel 625, Incoloy 825, Carpenter 20 Cb-3, and Hastelloy C-276) are currently being evaluated. Mild steel, Cor-Ten and Type 304 stainless steel are generally not suitable for use in the slurry or gas systems because of severe pitting and general corrosion.

Soft rubber (natural or neoprene) showed good resistance to erosion; however, blistering and separation from the base metal (mild steel) occurred frequently. Excellent bonding and resistance to erosion was obtained with a urethane elastomer (Urecal 2003) manufactured by the Urecal Corporation.

Summary

Limestone wet scrubbing provides an effective method for removing SO₂ from boiler flue gases. An SO₂ removal efficiency of 70% can be expected with a multigrid type of scrubber at an L/G of 50 to 60. The efficiency can be increased to about 90% if a two-stage mobile-bed (TCA) scrubber is used.

Long-term operating reliability is largely determined by proper design and selection of suitable construction materials to cope with the erosive and plugging characteristics inherent in slurry scrubbing.

STATUS OF C-E's AIR QUALITY
CONTROL SYSTEMS

by

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STATUS OF C-E's AIR QUALITY CONTROL SYSTEMS

INTRODUCTION

The need for removing SO₂ from stack gases of oil and coal-fired combustion equipment has been and is being emphasized by the stringent emission limitations established by the Environmental Protection Agency and other government agencies. The EPA standards are 1.2 lb/10⁶ Btu for coal and 0.8 lb/10⁶ Btu for oil. More stringent requirements in certain districts have been passed. An example is Clark County, Nevada which limits SO₂ emissions for a 1,500,000 kw steam generating station to 0.15 lb/10⁶ Btu or 1/8th of the EPA requirement. In order to meet these requirements, a very high percentage of SO₂ produced by the combustion of most oil and coal fuels must be removed from stack gases.

There are several ways to classify processes for the removal of SO₂ from stack gases: wet or dry, recovery or non-recovery, and absorption, adsorption, or catalytic oxidation.⁽¹⁾ In reviewing these processes and many others, Combustion Engineering decided that wet lime/limestone scrubbing without recovery of sulfur was most worthy of development.

The development of C-E's air quality control system started in 1964 with the construction of a small pilot facility in our laboratories. A second pilot application on a Detroit Edison Co. unit in 1966 and 1967 followed. Table I lists the full-scale installations⁽²⁾ that have been sold to date by C-E. In a move to further accelerate development, a large prototype unit of 12,500-cfm capacity was constructed in our laboratory and began operations in early 1970.⁽³⁾

This paper describes the C-E AQCS for the removal of particulate matter and SO₂ from stack gases of steam generators emphasizing C-E's experience with the full-size field units.

SYSTEM DESCRIPTION

In the tail-end C-E Air Quality Control System (Fig. 1), a slurry of pulverized limestone or slaked lime enters directly into the reaction tank (located at the bottom of the scrubber). Recirculation pumps convey the scrubbing slurry from the reaction tank to underbed spray nozzles. The incoming gas, laden with dust and SO₂, contacts the sprayed slurry and continues to the bed. The removal of SO₂ and particulate matter occurs in the bed. The scrubbing cycle continues with the reacted materials draining to the reaction tank which is designed to provide for completion of chemical reactions and precipitation of solids. From the reaction tank, pumps recirculate the scrubbing solution.

A bleed line provides the necessary solids removal to a clarifier or pond. Here, solids settle and clarified water is available for recirculation. The cleansed flue gas passes through a mist eliminator for removal of the remaining water and is then reheated for induced-draft fan protection and plume control.

The furnace injection process (Fig. 2) involves the injection of an additive which contains a high percentage of calcium, such as limestone, into the furnace of a steam generating unit. The pulverized additive calcines in the furnace and reacts with the combustion gases, removing 20 to 30% of the sulfur oxides, including all the SO₃. The flue gas enters the scrubber and the process proceeds as described above. Due to additive distribution and boiler deposit problems, the furnace injection system is not now being offered.

The basic design variations of tail-end systems result from additive selection — limestone or lime — and are additive preparation and system control. Although both additives enter the system as a slurry, the limestone (usually received in the -1/2 to -2-inch size range) re-

TABLE I
C-E CONTRACTS FOR AIR QUALITY CONTROL SYSTEMS

Utility	Unit	Size, Mw	Fuel	System
Union Electric	Meramec 2	140	Coal	Furnace Injection, Limestone
Kansas Power & Light	Lawrence 4	125	Coal/Gas	Furnace Injection, Limestone
Kansas Power & Light	Lawrence 5	430	Coal/Oil/Gas	Furnace Injection, Limestone
Kansas City Power & Light	Hawthorn 3	100	Coal/Gas	Furnace Injection, Limestone
Kansas City Power & Light	Hawthorn 4	100	Coal/Gas	Converted Tail-End, Limestone
Northern States Power	Sherburne 1	690	Coal, Low Sulfur	Tail-End, Limestone
Northern States Power	Sherburne 2	690	Coal, Low Sulfur	Tail-End, Limestone
Northern States Power	Black Dog	Prototype 15000 cfm	Coal, Low Sulfur	Tail-End, Limestone
Louisville Gas & Electric	Paddy's Run 6	65	Coal/Gas	Tail-End, Lime (Ca(OH) ₂ Sludge)
Southwest Public Service	Nichols Station B	350	Coal/Gas	Tail-End, Lime

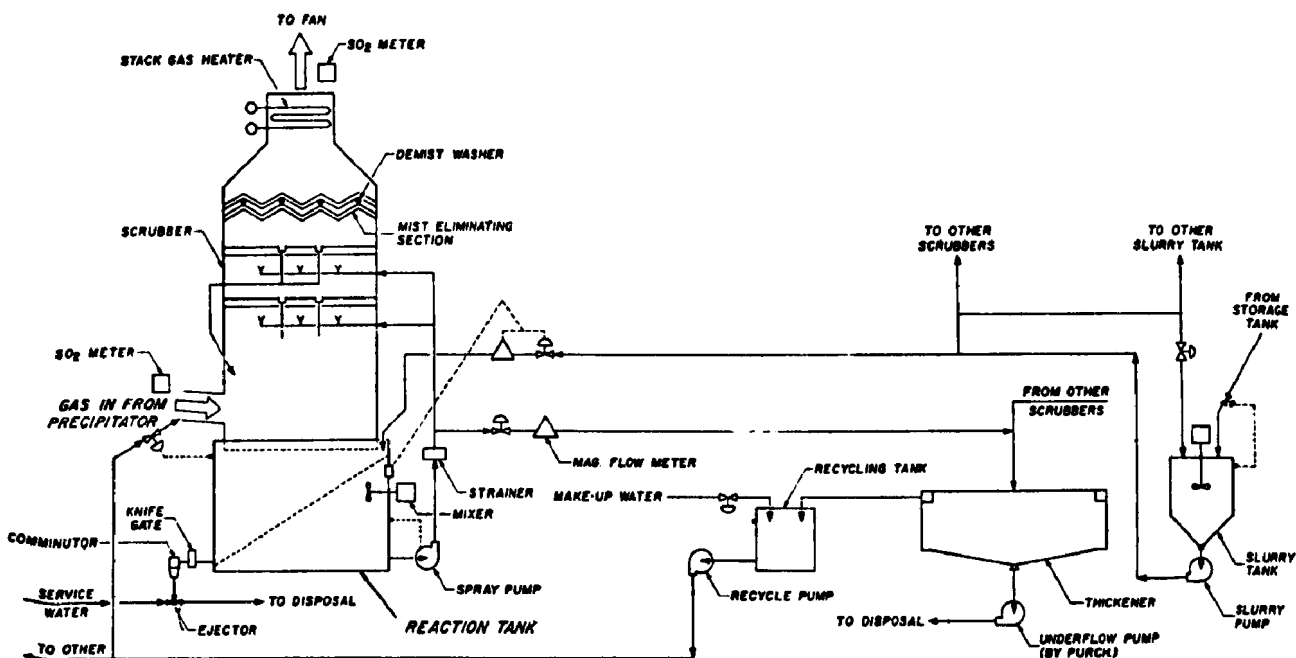


Fig. 1: C-E tail-end AQCS

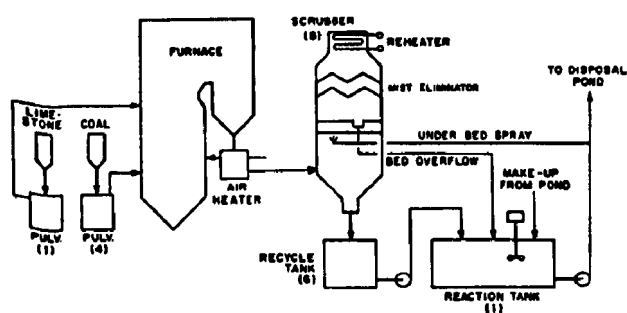


Fig. 2: C-E furnace injection AQCS

quires size reduction and water addition. A wet milling system is used for this. Lime requires a slaking operation to form a calcium hydroxide ($\text{Ca}(\text{OH})_2$) slurry. A direct supply of solid $\text{Ca}(\text{OH})_2$ is slurried to facilitate intra-system transport and control.

For a $\text{CaO}/\text{Ca}(\text{OH})_2$ system, the additive enters the reaction tank as required to maintain the spray slurry pH at a level high enough to maintain SO_2 removal efficiency, yet low enough to avoid CaSO_3 scaling. For a calcium carbonate system, fuel sulfur content determines additive feed rate.

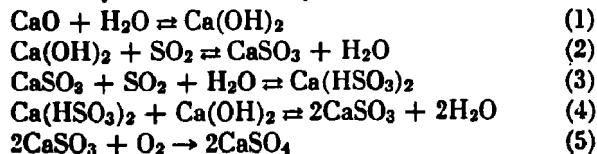
SYSTEM DESIGN⁽⁴⁾

System Chemistry

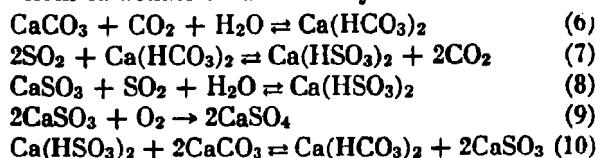
The possible reactions taking place in the wet lime/limestone SO_2 removal system have been studied. Our conclusions relative to the controlling reactions are based on consideration of theoretical equations in light of operating experience in both field and laboratory

systems. Because there are considerable differences in the operating conditions required to provide adequate SO_2 removal in the absence of scale or deposit formation when utilizing lime or limestone as additives, the chemistry of the systems are treated separately. The essential reactions governing these systems are:

Calcium hydroxide or lime system reactions



Calcium carbonate or limestone system reactions



Following the initial steps of hydration (Eq. 1) and formation of calcium sulfite (Eq. 2), removal of SO_2 in the lime or calcium hydroxide system depends upon the formation of calcium bisulfite by reaction of suspended calcium sulfite with sulfur dioxide and water (Eq. 3).

The control of sulfite scaling requires that a minimum amount of free hydroxide ion be recirculated to the scrubber, therefore, fresh additive (lime or slaked lime) is added in a reaction tank external to the scrubber where calcium sulfite is formed (Eq. 4). An amount of calcium sulfite equivalent to the SO_2 removed (or the

fresh $\text{Ca}(\text{OH})_2$ added) is conveyed from the system to a pond or vacuum filter and the remainder recycled to continue the removal process.

The principal absorption reactions for the calcium carbonate system are shown in Eqs. 6, 7 and 8. Sulfur dioxide reacts with the relatively soluble bicarbonate to form calcium bisulfite. In addition, solid calcium sulfite recycled from the reaction tank reacts with SO_2 to form bisulfite.

The reactions in which sulfite is oxidized to sulfate (Eqs. 5 and 9) and soluble bisulfite is converted to insoluble calcium sulfite (Eq. 10) account for the waste products as well as the regeneration of the solid calcium sulfite reactant that is recirculated to the scrubber. The ratio of calcium sulfite to calcium sulfate found in the air quality control system solid waste depends upon the extent to which these reactions go to completion.

Scrubber Design

The primary function of the scrubber is to transfer SO_2 from the flue gas into the liquid. The SO_2 remains in the liquid or is converted partially to solid sulfur compounds in the scrubber. Hence, knowledge of vapor-liquid mass transfer rates is important in scrubber design. The marble bed scrubber, which has a turbulent layer, acts like an absorption tray.

The vapor-liquid equilibrium line and efficiency are needed for tray design. Typical operating and equilibrium lines are shown in Fig. 3. The operating line is the material balance line and has a negative slope of L/G (liquid to gas ratio).

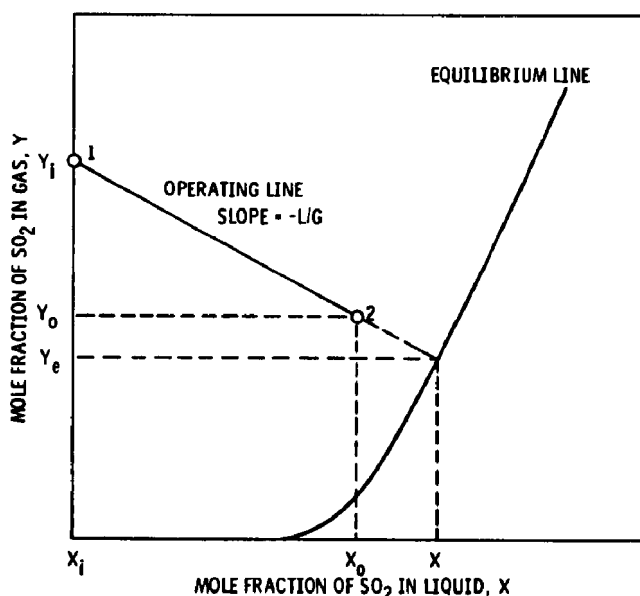


Fig. 3: Vapor-liquid mass transfer

The inlet gas composition Y_1 is known, and the SO_2 concentration in the incoming liquid X_1 , which is usually zero, is also known. Hence, point 1, which

represents the inlet condition is known. The operating line can be drawn through X_1, Y_1 with a negative slope of L/G .

The intersection of the operating and equilibrium lines (X, Y_e) represents the scrubber outlet gas and liquid conditions for a theoretical stage which represents 100% overall tray efficiency. The overall tray efficiency E is defined as:

$$E = \frac{Y_1 - Y_o}{Y_1 - Y_e} \quad (11)$$

and is usually less than 100%. It can be seen both from Fig. 3 and Eq. 11 that the actual outlet liquid and gas compositions (X_o, Y_o) can be predicted using the tray efficiency and the point of intersection of the operating and the equilibrium lines.

Laboratory tests show that the tray efficiency of the marble bed scrubber is 90 to 95%. This indicates that the marble bed scrubber is a good liquid-gas contactor.

Once the tray efficiency is known the number of marble beds needed to obtain a required SO_2 removal can be determined from the operating and the equilibrium lines.

Knowing the total alkalinity of the liquid available in the scrubber, which is a function of the additive dissolution rate for slurry systems, the equilibrium line is plotted using a computer program.⁽⁵⁾ For a specific L/G , the equilibrium line shown in Fig. 3 moves to the left or right depending on the alkalinity of liquid available in the scrubber and, hence, affects the SO_2 removal efficiency. The SO_2 removal efficiency is defined as:

$$\eta = \frac{Y_1 - Y_o}{Y_1} \quad (12)$$

If the additive dissolution rate is high enough to maximize the available alkalinity in the liquid in the scrubber, the equilibrium line will move to the far right to a point where Y_e can become zero. This represents the most favorable condition for SO_2 transfer from gas to liquid. Comparison of Eqs. 11 and 12 shows that the SO_2 removal efficiency will approach the tray efficiency as Y_e approaches zero.

Reaction Tanks

The function of the reaction tanks is to provide:

- Dissolution of the additive in order to convert the highly soluble bisulfite present in the liquid leaving the scrubber to relatively insoluble sulfite.
- Precipitation of calcium sulfate which is formed in the system (scrubber and/or reaction tanks) due to the oxidation of sulfite.
- Precipitation of calcium sulfite.

Additive dissolution rates vary considerably with the type, origin, preparation, and concentration of the additive. At C-E, a prototype scrubber system, pilot

plant scrubber system, continuous flow stirred tank reactors, and batch reactors have been used to determine the dissolution rates for individual additives used.

The following rate expression for the precipitation of calcium sulfate has been developed:⁽⁶⁾

$$R = -KZ(C - C_e)^2 \quad (13)$$

The rate of desupersaturation, R , is proportional to the gypsum seed crystal concentration, Z . The difference between the actual concentration, C , and the equilibrium concentration, C_e , of SO_4^{2-} or Ca^{++} is the driving force term. Although it is more accurate to express the driving force in terms of the activity and the solubility products, the driving force in Eq. 13 is given in concentrations for convenience, by including the factor for converting activities into concentrations in the rate constant K . Using the rate constants determined by experimentation,⁽⁷⁾ the rate expression given by Eq. 13 is employed in the design of reaction tanks to ensure that calcium sulfate supersaturation is eliminated.

Laboratory studies are in progress to determine the calcium sulfite precipitation kinetics and the oxidation kinetics of sulfite to sulfate.

DEPOSIT AND SCALE FORMATION

Calcium sulfite and calcium sulfate scaling can be a problem for lime/limestone wet scrubber systems. Scaling occurs when the solutions are supersaturated to a point where heterogeneous crystallization takes place resulting from nucleation. The ratios of the products of the activities (A) of Ca^{++} and SO_4^{2-} or SO_3^{2-} to their solubility product constants (K_{SP}) as a measure of the degree of supersaturation are:

$$\left[\frac{A_{\text{Ca}^{++}} A_{\text{SO}_4^{2-}}}{K_{SP}(\text{CaSO}_4)} \right], \left[\frac{A_{\text{Ca}^{++}} A_{\text{SO}_3^{2-}}}{K_{SP}(\text{CaSO}_3)} \right] \begin{matrix} < 1 \text{ Subsaturation} \\ = 1 \text{ Saturation} \\ > 1 \text{ Supersaturation} \end{matrix}$$

Laboratory experiments have shown that heterogeneous crystallization is not significant until the ratio of the activity product to the solubility product constant reaches about 1.5 for calcium sulfate and about 7 for calcium sulfite.

Heterogeneous crystallization is minimized by providing seed crystals for homogeneous crystallization and by designing the reaction tanks so that the liquid leaving them is close to saturation and not highly supersaturated. This requires knowledge of precipitation kinetics of calcium sulfate and sulfite.

Calcium Sulfite Deposition

Calcium sulfite ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) is formed in the scrubber under those conditions that favor sulfite formation. These conditions are apparent when one considers the sulfite-bisulfite equilibrium and compares the relative solubilities of the corresponding calcium salts. As seen in Fig. 4, extremely soluble bisulfite in

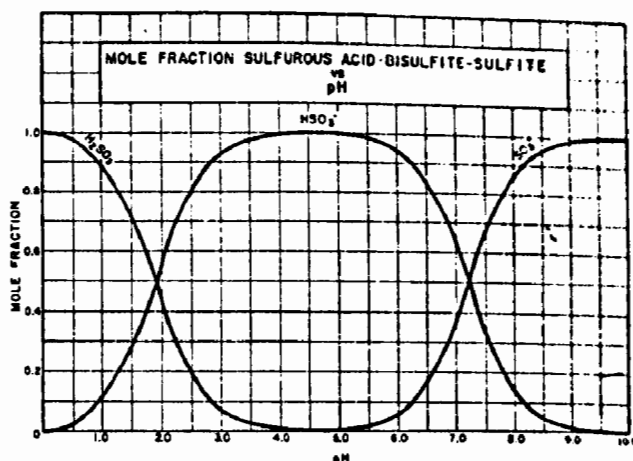


Fig. 4: Mole fraction sulfurous acid-bisulfite-sulfite vs. pH

solution changes to relatively insoluble sulfite when the solution pH shifts from 4 to 10. When SO_2 is absorbed, the scrubber solution is usually between pH 4 and 6 and, therefore, the predominant species is bisulfite. If the pH of the scrubber solution containing bisulfite is suddenly raised either in localized areas or in a reaction tank, crystallization of calcium sulfite will occur.

Experimental work with lime scrubbing has shown that sulfite scaling occurs in the scrubber bed when free hydroxide is introduced according to the above explanation. By proper control of the pH of the spray slurry (less than 10) entering the scrubber, calcium sulfite scaling will not occur in the scrubber.⁽⁸⁾

In the calcium carbonate system, the buffering action of the carbonate-bicarbonate couple (Eq. 6) maintains a system pH between 5 and 7, thus sulfite scaling is not encountered.

Calcium Sulfate Deposition

The solubility of calcium sulfate is only slightly increased with increasing pH, and calcium sulfate scaling is related to the tendency of this material to form extensively stable supersaturated solutions. While chemical theory predicts that a given ionizable species will not remain in solution when the solubility product of its component ions has been exceeded, calcium sulfate may be held in solution to an extent twice that predicted before crystallization of calcium sulfate will occur (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The significance of this phenomena to scrubber operation is that SO_2 removal can be accomplished while scrubbing with solutions containing more than the theoretical calcium and sulfate ion concentrations, but less than some experimentally determined level at which precipitation will occur within the scrubber proper.

Crystallization from supersaturated solutions can occur by two processes, formation of new crystals or nucleation and growth of existing crystals.

The internal surfaces of the scrubber can provide nucleation sites, thus resulting in scale formation. For many crystal systems, growth will occur without significant nucleation if sufficient seed crystals are provided. Work by other investigators⁽⁶⁾ has shown that supersaturated calcium sulfate solutions can be effectively desupersaturated by circulation of 1 to 5% gypsum seed crystals.

By employing this technique, operation free of calcium sulfate scaling has been demonstrated in both laboratory and field installations. This seeding technique is the key to "closed loop" operation in which the only liquid leaving the system is by evaporation or combined with the solid by-product of the scrubbing system.

The potential for sulfate scaling is generally more prevalent in the calcium carbonate system than in the calcium hydroxide system. The calcium hydroxide system reaches steady state below the value of calcium sulfate saturation.

Control Techniques⁽⁸⁾

The controls for the C-E AQCS depend upon the additive type. The limestone tail-end system can be controlled by the limestone feed to the system. The limestone feed is determined by the SO₂ in the flue gas or sulfur in the fuel. The solids concentration in the slurry is maintained to prevent calcium sulfate scaling.

The tail-end lime system is controlled by the pH of the spray slurry and the total solids in the system.

Slurry Circulation

Slurries containing 2 to 10 wt. % solids are circulated in the lime/limestone wet scrubber systems in order to control scaling in the system and to improve SO₂ removal and additive utilization. The circulation of the high solids slurries in the system could cause serious erosion problems in pumps, piping, nozzles, etc.

AQCS solids are different from other solids. Little technology is available to design pumps, piping, and nozzles that can handle AQCS solids, therefore, C-E undertook extensive testing of these components.

Several pumps of different materials have been installed on C-E systems both in the field and in the laboratory. The information obtained from the evaluation of these pumps is being used in current system designs.

Several different materials have been evaluated to determine piping material that can withstand erosion and corrosion. The piping is designed so that slurry velocities in the pipes are high enough to prevent settling.

Severe nozzle plugging problems have occurred when commercially available nozzles were used. Therefore, C-E has developed a nozzle that does not plug, erode, or corrode in the scrubber environment.

Solid-Liquid Separation

Solid-liquid separators such as clarifier-thickeners and vacuum filters separate the solids from the liquid. The solids are disposed of and the liquid is returned to the system. This equipment is presently being designed by vendors to C-E's specifications.

Gas-Liquid Separation

The gas leaving the bed carries water droplets which contain solid particles and dissolved solids. Mist eliminators are used to remove water droplets from the gas. Proper design of these sections is essential to prevent both plugging with solids and re-entrainment of the liquid collected on the surfaces.

Gas velocity and the distance between the bed and the mist eliminators are important operational and design variables. Extensive test work has been conducted in the laboratory and in the field to evaluate these variables. Results of these studies are being used in the design of mist eliminators for C-E systems.

Reheating

The purpose of reheating the gas leaving the scrubber bed is to protect the I.D. fan and to reduce plume formation. The amount of reheat required depends upon several factors such as atmospheric conditions and stack height.

Additive Preparation and Feeding

The limestone is ground to a small size (about 80% thru 200 mesh). The slurry from the limestone mill scalpers (about 60 to 70% by weight) is stored in the limestone slurry storage tanks. The slurry is then transferred to tanks, where it is diluted with make-up water to reduce the solids content to 10 to 15% by weight. This dilute slurry is added to the reaction tanks for use with the slurry spray to the scrubber bed.

For a lime system, slaking, storage, dilution, and transport steps are involved. Use of Ca(OH)₂ rather than CaO eliminates the slaking operation.

The additive handling system is designed so that the solids do not settle in pipes and tanks.

EPA CONTRACT

C-E has recently completed a research contract for the Environmental Protection Agency (EPA) to optimize lime/limestone wet scrubbing processes for SO₂ and particulate removal in a marble bed scrubber.

Three types of tests were conducted on the 12,000-CFM C-E marble bed scrubber. Soluble system tests using once-through sodium carbonate scrubbing solutions were conducted using a single marble bed to determine the vapor-liquid mass transfer characteristics. Limestone furnace injection tests were conducted using boiler calcined limestone and flyash mixture to determine the system performance and the solid-liquid mass transfer rates. Limestone tail-end system tests

were conducted using limestone slurry to determine whether single marble bed results can be extrapolated to predict the performance of a two-bed scrubber and to determine the solid-liquid mass transfer rates.

The results of the once-through soluble system tests using a Na_2CO_3 scrubbing solution show that:

1. The marble bed scrubber is a good liquid-gas contacting device with an overall tray efficiency of 90 to 95%.
2. The SO_2 removal in the marble bed scrubber is limited by the vapor-liquid equilibrium.
3. Liquid to gas (L/G) ratio and the scrubber liquor alkali composition strongly influence SO_2 removal.

The C-E scrubber at EPA's Shawnee test facility was originally supplied with one marble bed. The current commercial systems offered by C-E for high sulfur fuel applications have scrubbers with two marble beds. Therefore, C-E recommended that a second marble bed be installed in the scrubber so that a meaningful evaluation of C-E's current commercial offering could be accomplished. Due to the lack of available funds and the scheduling problems, EPA decided against installing the second bed. As a reasonable alternative, both C-E and EPA agreed that tests would be run on the C-E AQCS prototype to determine

whether the performance of a two-bed scrubber could be predicted from the single marble bed performance of the EPA test facility at Shawnee.

A series of tests were run on the C-E AQCS prototype using limestone slurry with one and two marble beds. Test results show that the performance (SO_2 removal efficiency and elimination of scaling) of the scrubber with two marble beds can be predicted by extrapolating the single bed test results. The SO_2 removal efficiencies of the lower and the upper beds appear to be the same based on the SO_2 concentrations entering the respective bed.

Kansas Power and Light — Lawrence 4

This 125-Mw coal and gas fired C-E boiler was retrofitted with a furnace injection AQCS in 1968. The AQCS consisted of two wet scrubbers and related equipment (Fig. 5). During 1971, it was recognized that this system could not continue to operate as an open system (i.e., liquid blowdown). While liquid was never discharged to a natural body of water, the sludge disposal pond constructed at the plant site in 1968 never reached saturation because of the small quantity of scrubber effluent flow into this pond during the three years of operation and because of intermittent operation of the AQCS on Unit 4.

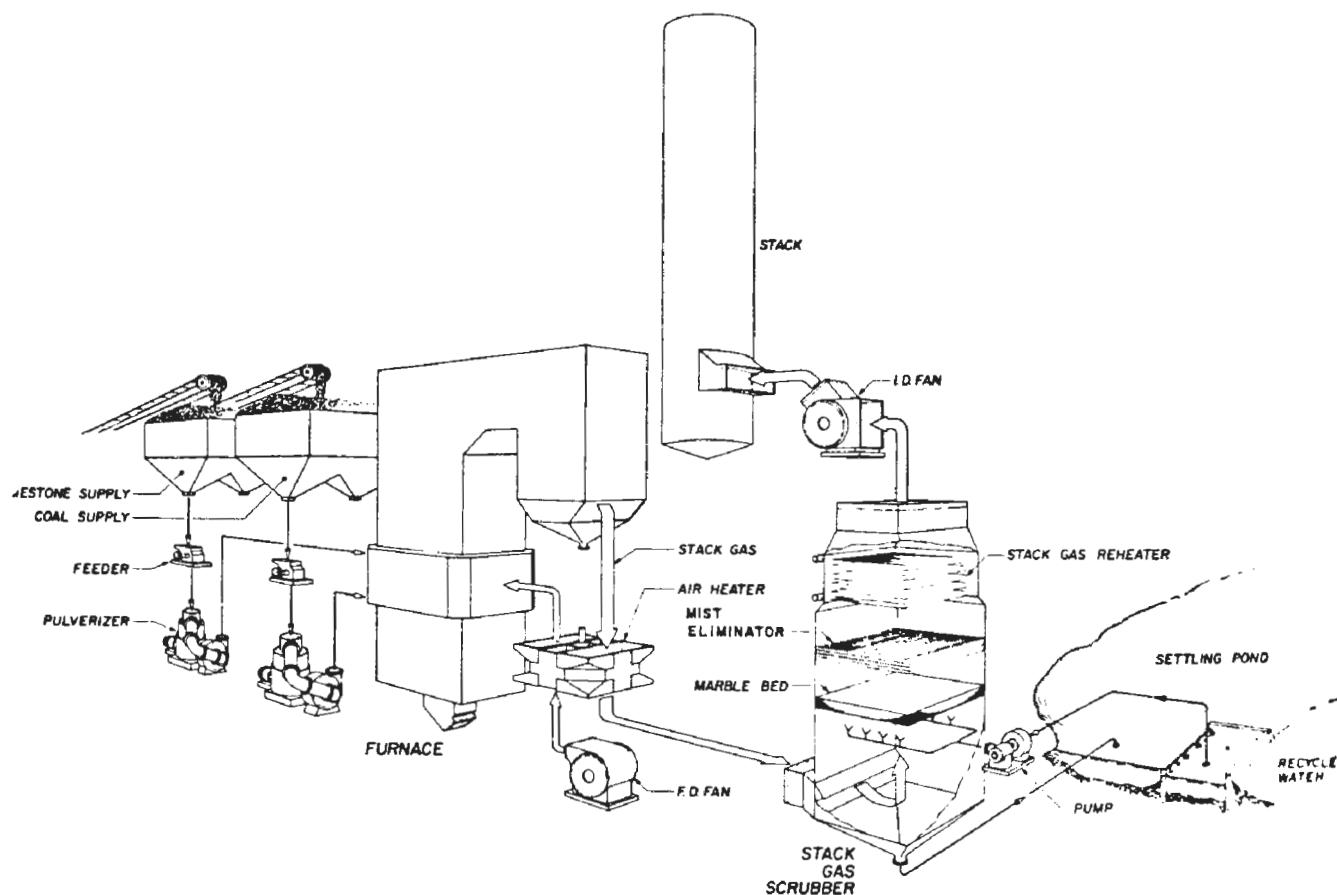


Fig. 5: Flow diagram of AQCS for Unit 4 at KP&L

Utilizing the results of tests conducted at our Kreisinger Development Laboratory during 1971, it was decided that the system could be modified to ensure scale-free closed-loop operation. In order to verify the design modifications, a series of tests were conducted in February and March of 1972 which demonstrated scale-free operation for periods extending to two weeks.

During these tests, all process streams were measured for chemical constituents in both the solid and liquid phases. In addition, the flue gas entering and leaving the AQCS was measured for both gaseous and solid constituents using EPA approved methods. Table II gives a typical set of data obtained in this test series.

TABLE II
TYPICAL OPERATING DATA
KANSAS POWER & LIGHT 4
February, 1972

Inlet dust	5.0 gr/DSCF	
Outlet dust	0.06 gr/DSCF	
Inlet SO ₂	1800 ppm	
Outlet SO ₂	550 ppm	
pH	9.2	
	Underbed Slurry	Pot Effluent
% Solids	7.3	7.3
CaO	960 ppm	1,250
SO ₃	250 ppm	1,300
SO ₄	2,150 ppm	2,450
Solid analysis		
CaSO ₄ · 2H ₂ O	20%	
CaSO ₃ · ½H ₂ O	15%	
Flyash	60%	
CaO	5%	

Since these results agreed with the data obtained in our laboratory with respect to seed crystal concentration required to prevent CaSO₄ scaling, and SO₂ removal was maintained at 70 percent for the single marble bed scrubber, it was decided to complete the modification in order to operate the system at the 7 to 10% solids level at full load.

The modifications to Unit 4 were made during the spring and summer of last year. Subsequent operation of the system in the fall of last year revealed a problem with maintaining mist eliminator performance while operating with high solids (7 to 10%). An extensive test program has been undertaken to solve this problem.

Kansas Power and Light — Lawrence 5

Unit 5 at the Lawrence Station of Kansas Power and Light, a 430-Mw C-E coal, gas, or oil fired unit was first placed in service in the spring of 1971. The AQCS supplied for this unit was based on the same design as Unit 4. The system consisted of six scrubbers, each handling approximately 165,000 CFM of flue gas at

125 F. The additive, calcium carbonate, was pulverized and injected into the boiler, calcined, and then conveyed to the scrubber for use in the SO₂ absorption process.

The AQCS was not placed in service until November 1971 since the unit was operated on gas until that time. The system was operated for three weeks without any serious problems until the sludge pond became saturated with calcium sulfate, at which time scaling in the scrubber was observed. Since tests were already in progress on Unit 4 to enable operation of the AQCS as a closed system without scale formation, the AQCS on Unit 5 was operated on an intermittent basis during the winter season when the unit fired coal.

After the successful completion of the closed loop modifications on Unit 4, plans were made to "update" Unit 5. Figure 2 shows the modifications that were made. These modifications included installation of a reaction tank where crystallization, dissolution, and precipitation reactions take place; mixing devices for the reaction tank; fiberglass and/or rubber lined piping for the high solids recycle system; new underbed slurry pumps; improved controls that can withstand the wet scrubbing environment; redesigned slurry nozzles to decrease chemical and mechanical wear problems; and a new demist system. Further, it was decided from test data obtained during the winter of 1971-72 that we should reduce the gas throughput of the marble bed scrubbers in order to minimize carryover from the bed due to localized high velocities, and incorporate the concept of spare scrubbing capacity by adding two additional scrubbers to this unit.

The modifications were completed late last fall and the AQCS was returned to service for the winter period of coal operation.

The unit has operated approximately 1800 hours (since January). The results duplicate closely the tests run last year on Unit 4.

Presently, an extensive series of performance tests are being conducted on this unit by C-E to determine full-load capability of the system.

Kansas City Power and Light — Hawthorn 4

At the Hawthorn Station of the Kansas City Power and Light, a furnace injection system was retrofitted on a 100-Mw low-load-factor unit. The system consists of two scrubber units and related equipment, and includes a water seal by-pass (Fig. 6). The system was started up in September 1972.

Preliminary operation of the system indicated that a serious maldistribution of additive existed between the two scrubbers. After several weeks of testing, it was also determined that the back-pass of this boiler was not capable of handling the additional dust loading created by the furnace injection of limestone.

Therefore, in late 1972, it was decided to modify the system to a tail-end limestone, single marble bed

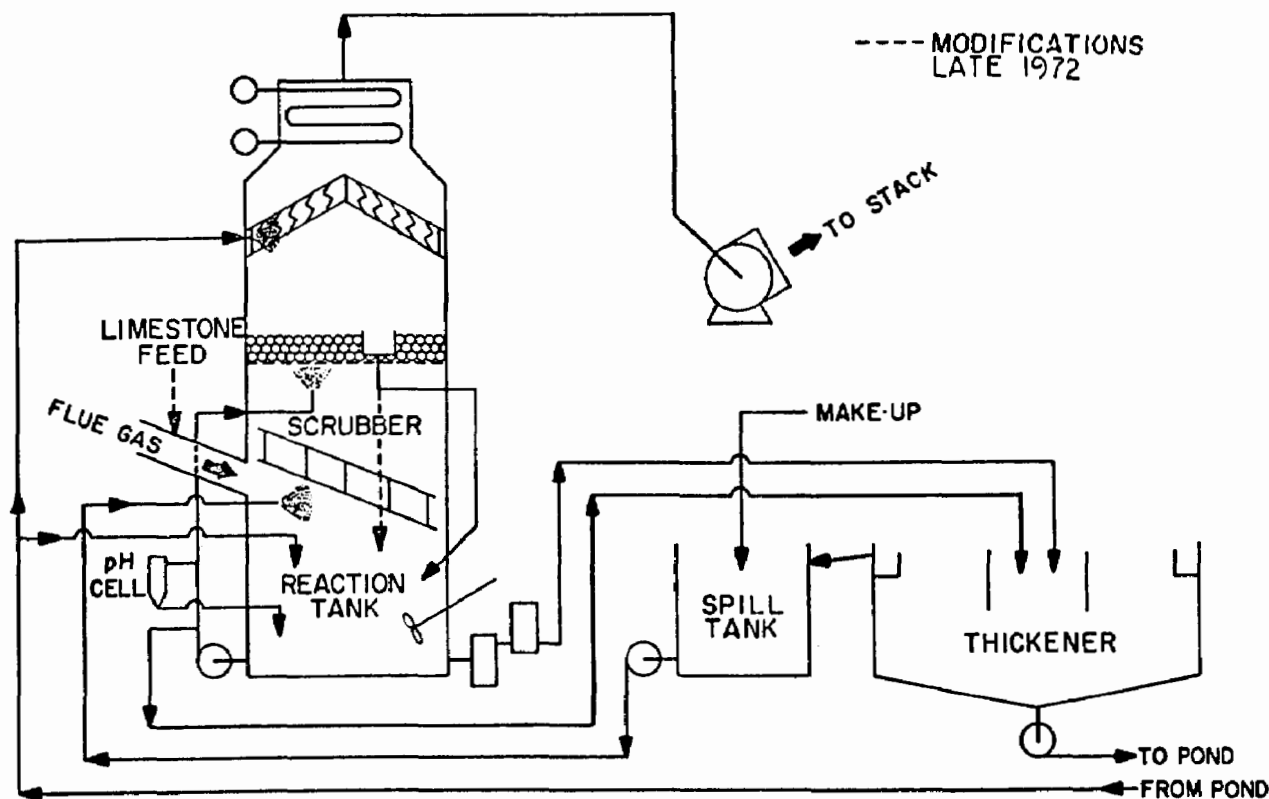


Fig. 6: Process flow schematic KP&L Hawthorn Station Units 3 and 4

system with the pulverized limestone being blown into the scrubber inlet duct (Fig. 6). Modifications have been completed, but the system has not been tested to date.

A test series was run during March to determine the performance of this system on low sulfur, high alkali Wyoming coal. The limestone feed was maintained at zero for these tests because there was significant amount of alkali in the coal. Some coal samples indicate as much as 200% stoichiometry of alkali (if all were available for reaction with the sulfur in the coal). The results shown in Table III were obtained during this

TABLE III	
OPERATING DATA	
KANSAS CITY POWER & LIGHT	
HAWTHORN 4, WYOMING COAL TEST	
Inlet SO ₂ :	700 - 300 ppm
Outlet SO ₂ :	300 - 40 ppm
% Solids	3.0 - 6.0
Underbed slurry pH	5.7 - 7.1

UNDERBED SLURRY LIQUID	
CHEMICAL ANALYSIS	
CaO	850 ppm
SO ₂	150 ppm
SO ₄	220 - 2500 ppm

test program. The SO₂ removal varied from 60 to 90% depending on the inlet SO₂ concentration (as the inlet concentration went down, the removal efficiency went

up). Further, it was determined that no calcium sulfate scaling occurred during this test period.

Kansas City Power and Light — Hawthorn 3

This unit is a duplicate of the Hawthorn Unit 4 AQCS and has been operating intermittently for the last four months as originally designed. Problems with quality control during slurry nozzle fabrication have caused some failures; but a modification in materials of construction of the nozzle and additional checks during manufacture have eliminated this problem.

Also, a problem was encountered with the scrubber drain lines plugging with mud because of low velocities and a horizontal run of gravity flow piping. This plugging was eliminated by removing the horizontal run of pipe and allowing the scrubber drains to flow directly into the reaction tank.

At the present time, consideration is being given to converting Unit 3 to a tail-end limestone pending the performance results of Unit 4.

Louisville Gas & Electric — Paddy's Run 6

C-E's first tail-end system was installed on an existing 65-Mw unit at the Paddy's Run Station of Louisville Gas & Electric. The system is comprised of two scrubbers, each having two marble beds in series; a reaction tank; a thickener; two full-size vacuum filters; and a fully automated control system. Figure 7 is a schematic of the system. The AQCS follows a precipitator which has an efficiency of approximately 90%.

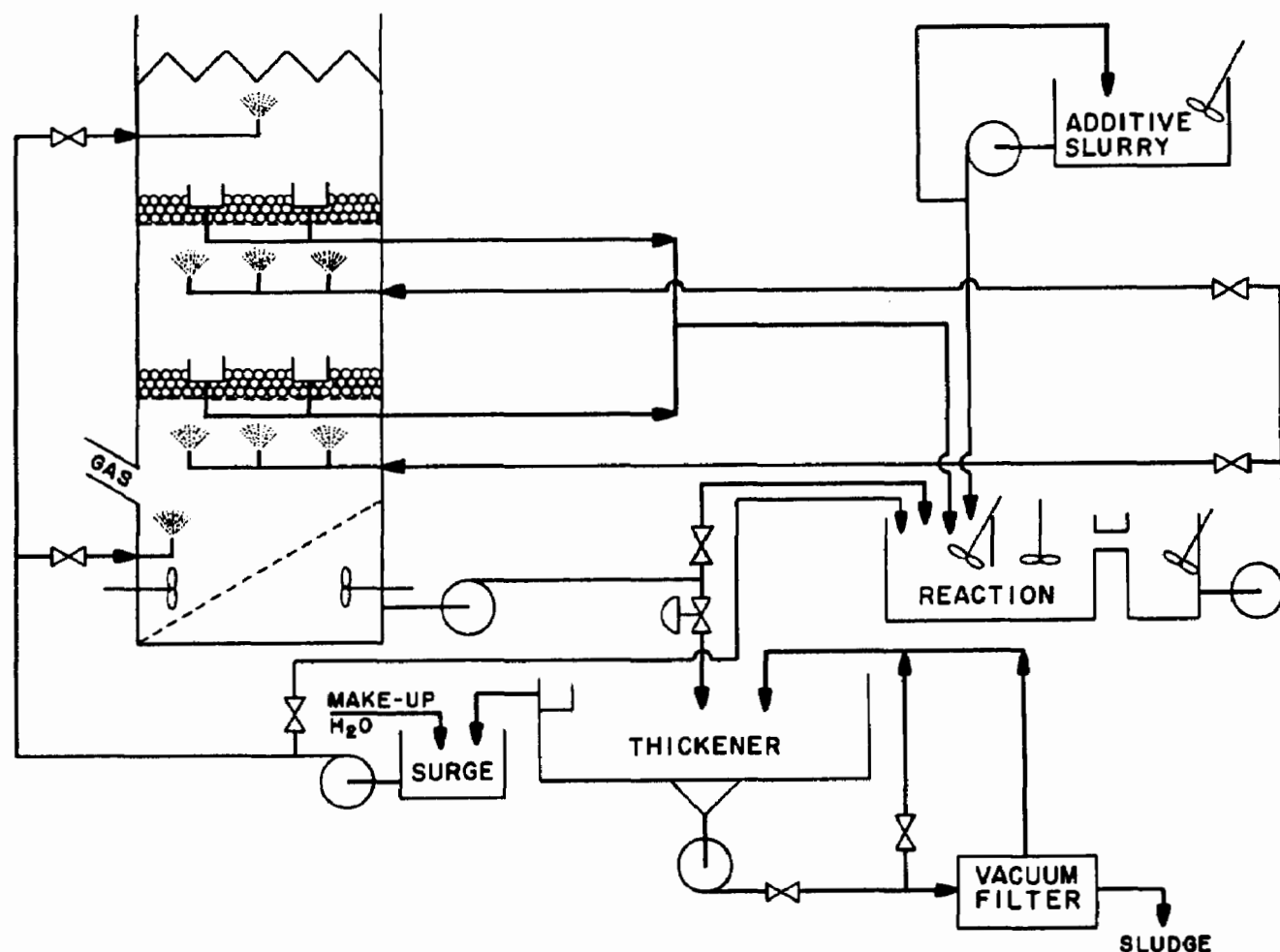


Fig. 7: Process flow schematic LG&E Paddy's Run No. 6

This system represents the culmination of a three-year effort initiated in 1970. Pilot plant tests were conducted at C-E's Kreisinger Development Laboratory in 1971 to determine if an AQCS could be designed that would operate with the $\text{Ca}(\text{OH})_2$ sludge that Louisville Gas & Electric had available. The $\text{Ca}(\text{OH})_2$ sludge is a waste product from the manufacture of acetylene.

In June 1971, a 100-hour continuous test on the 12,000-CFM prototype scrubber system at KDL was completed and, as a result, the system design was finalized and fabrication of the system began. Later in 1971, it became apparent because of more stringent water pollution regulations that the system would have to be operated as a closed system. Therefore, additional testing in the laboratory was done in February 1972. The findings of these tests showed that the closed system was accomplished by obtaining essentially zero oxidation and providing sufficient seed crystals to precipitate the calcium sulfite without forming scale.

This system is presently in the process of starting up. At this time, there has been approximately 300 hours of operation with one scrubber. The chemistry of the

system has undergone preliminary checkout and confirms the findings of our laboratory work.

The scrubbers have been operating exceptionally well. SO_2 removal has been 85% or higher depending on the L/G ratio and additive feed rate being maintained. It appears that the guarantee level of 80% sulfur dioxide removal can be obtained with a total L/G of 40.

The $\text{Ca}(\text{OH})_2$ sludge feed rate is controlled automatically by the reaction tank pH. This control system has been in service continuously since start-up without a problem.

The vacuum filter system has also operated without problems. The filter cake has varied from 30 to 50% solids, the lower solids being quite muddy and the high solids being handled easily.

The data in Table IV are for a 150-hour run conducted during the last week in April.

Northern States Power — Sherburne County 1

The systems for Northern States Power, Sherburne County Station have been designed to clean the flue gas from two 690-Mw C-E coal-fired units. These units

TABLE IV
LOUISVILLE GAS & ELECTRIC
OPERATING DATA

Inlet SO ₂	2400 - 2800 ppm	
Outlet SO ₂	300 - 450 ppm	
Underbed Slurry		Pot Effluent
pH	9.2	5.2
CaO	850 ppm	1,100 ppm
SO ₃ ⁼	200 ppm	1,300 ppm
SO ₄ ⁼	800 ppm	850 ppm
% Solids	9.5	9
Solids		
CaSO ₄ · 2H ₂ O	1-2%	
CaSO ₃ · ½H ₂ O	78%	
Flyash	20%	

will fire a low sulfur Western coal. Typical analysis of this coal is given in Table V. The addition of limestone to the system will be varied to maintain the sulfur dioxide removal to satisfy air quality requirements and balance the chemistry in the scrubbers. Since significant quantities of alkali exist in the flyash of this Western coal, the limestone addition will serve as a supplement. Tests run at our facilities indicate that for certain

TABLE V
NORTHERN STATES POWER
TYPICAL COAL ANALYSIS

COAL		
Btu/lb		8,130
Moisture		23.5%
Sulfur		0.8%
Ash		9.0%
ASH		
MgO		5.9%
CaO		21.9%
SO ₄		1.4%

sulfur concentrations in the coal, all the alkali required can be supplied by the flyash.

Another interesting aspect of the design of these systems is related to the appreciable quantity of magnesium in the flyash of the coal to be fired. The sulfur salts of magnesium are extremely soluble, therefore, the rate of dissolution of magnesium must be determined in order to predict the total dissolved solids in the systems at steady state. The prediction of total dissolved solids was required to determine possible effects on the system chemistry (i.e., ionic strength of

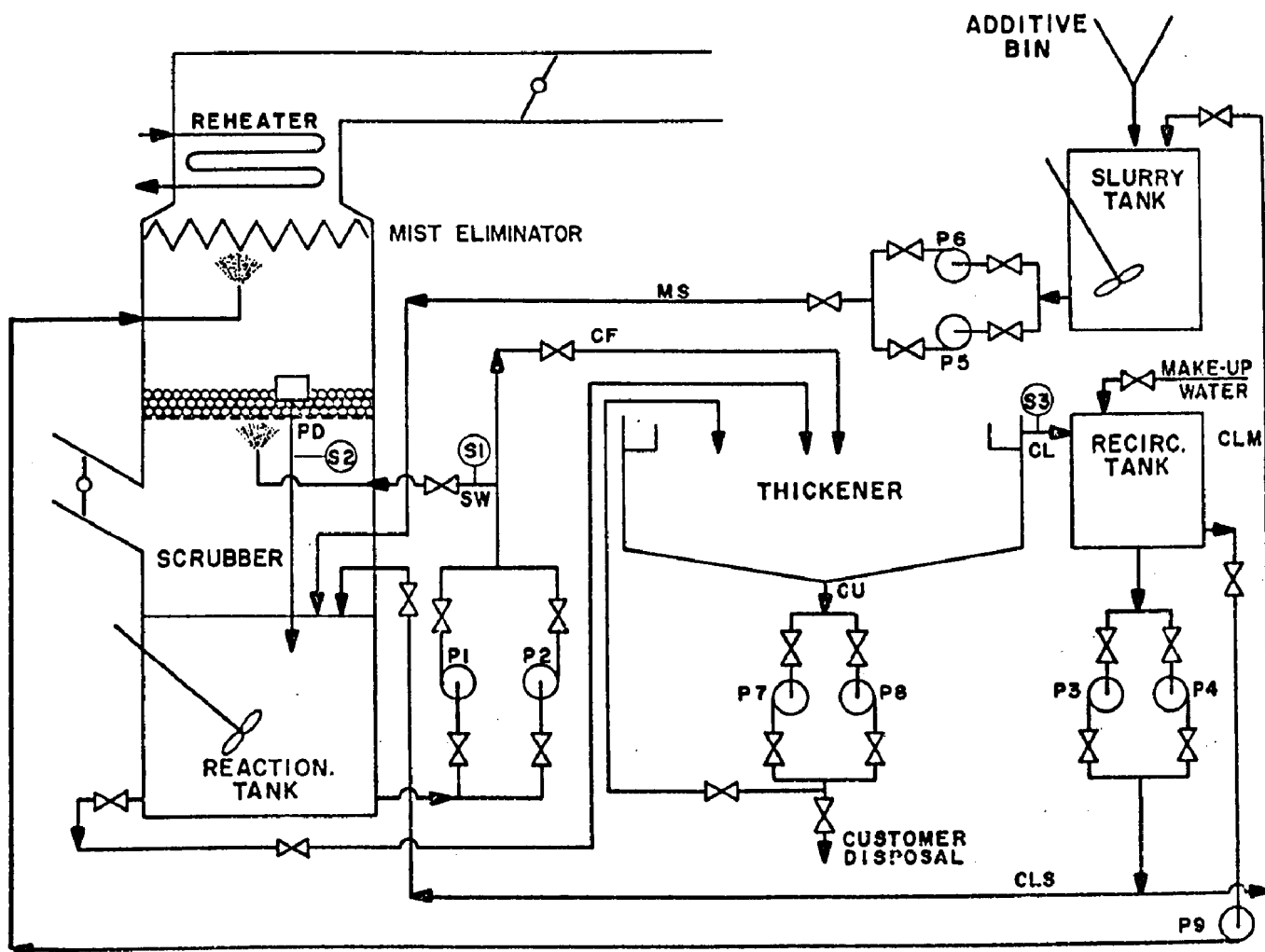


Fig. 8: Proposed process flow schematic NSP Black Dog Unit

the process solutions) and to provide information to the Water Resources Commission of Minnesota. A development program conducted at our laboratory predicted a total dissolved solids level of 15,000 ppm, dictating closed loop operation. Closed loop system operation has been incorporated by providing adequate seed crystals and a reaction tank external to the scrubber beds to carry out crystallization and precipitation.

Northern States Power — Black Dog Prototype

As part of the project to develop the tail-end limestone scrubbing systems for the Sherburne County Station of Northern States Power, a prototype facility has been constructed at NSP's Black Dog Station. The purpose of this facility is to verify the design for Sherburne County, test various system components, and provide a training facility for NSP operating personnel.

This facility is a scaled down duplicate of the Sherburne County design except that no additive grinding equipment was incorporated. The scrubber module has a capacity of 12,000 ACFM at 130 F. All other related equipment is included in the facility as shown in Fig. 8.

The Black Dog system began air/water testing during the first two weeks of March 1973. On March 11, it was placed in service with a stream of flue gas being diverted from the Black Dog unit precipitator inlet

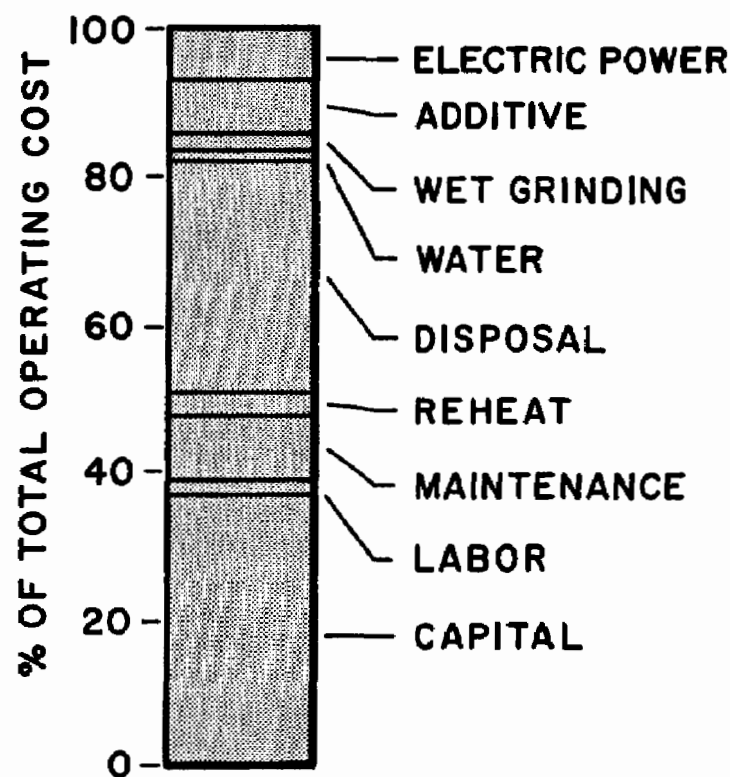
duct. Since that date, approximately 1,000 hours of operation have been logged.

The test series at the Black Dog facility includes the evaluation of the following parameters: (a) gas velocity, (b) additive feed rate, (c) percent solids being circulated, and (d) L/G ratio variation. The steady-state concentration of soluble cations (i.e., magnesium) is being studied because of their relatively high concentration in Western coal.

The initial tests at Black Dog agree with our laboratory pilot plant data as shown in Table VI. Current plans are to complete operation of this facility by late August of this year.

TABLE VI
OPERATING DATA FROM
LABORATORY PILOT PLANT TEST
FOR NORTHERN STATES POWER

Inlet SO ₂	800 ppm
Outlet SO ₂	200 ppm
L/G	20
Underbed slurry pH	6.5 - 7.1
Pot effluent pH	5.8 - 6.3
Underbed slurry	
Liquid analysis	Ca ⁺⁺ 600 ppm
	Mg ⁺⁺ 900 ppm
	SO ₄ ⁻ 150 ppm
	SO ₄ ⁻ 4,000 ppm



	MILLS PER KWHR			
%	\$/HR	¢/10 ⁶ BTU		
6.6	105	.175	1.8	
8.0	128	.215	2.3	
2.3	36	.061	0.6	
.5	8	.014	0.1	
31.3	502	.837	8.8	
3.6	57	.095	1.0	
8.9	143	.239	2.5	
2.4	39	.065	0.7	
36.4	582	.971	10.3	
100.0	1600	2.672	28.1	

Fig. 9: Operating costs for a 600-Mw AQCS

ECONOMICS

Table VII shows the assumptions for a 600-Mw unit and Fig. 9 shows the estimated operating costs.

TABLE VII
ASSUMPTIONS FOR DETERMINING
COSTS FOR A TYPICAL 600-Mw UNIT

Heat rate	9500 Btu/Kwhr
Load factor	70%
Fuel ash	12%
Sulfur	3½%
HHV	11,700 Btu/lb
Ash drop out	15%
To precipitator	85%
Electrostatic precipitator	90% effective
AQCS tail end	SO ₂ Emission Rate 1.2 lb/10 ⁶ Btu
Additive limestone	95% pure - 130% stoich. \$3.50/ton delivered \$1.00/ton wet grinding
Electric power	2.5% of 600 Mw \$.007/Kwhr
Water	1.75 gpm/Mw \$.13/1000 gal.
Disposal	\$4/ton 50% dry solids
Maintenance	4.3% of capital cost
Labor	4 men/shift - 4 shifts - \$15,000/yr/man
Capital	17.5% of \$34/Kw

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MAGNESIA SCRUBBING

by

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MAGNESIA SCRUBBING 1/

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Under the sponsorship of the Environmental Protection Agency (EPA), the Division of Chemical Development of the Tennessee Valley Authority (TVA) has just completed an intensive design and cost study of magnesia scrubbing-regeneration processes for sulfur oxides removal from power plant stack gas. This investigation, which has been carried out over the past two years, covers scrubbing systems using both aqueous slurries and solutions.

When published shortly, the study report will be the fourth in a series of conceptual design and cost studies which TVA has prepared for EPA since 1967. The first two studies were concerned with the use of lime or limestone as absorbents, which convert the gaseous sulfur oxides to solid compounds (calcium sulfite and calcium sulfate) that are discarded. These were called "throw-away" processes. The third study included processes using aqueous ammonia solutions as the scrubbing medium and recovering the sulfur oxides as ammonium sulfites which were converted to sulfate and used as an intermediate in the production of fertilizer products. This was the first recovery system examined in which materials could be produced for sale to offset, at least partially, the cost of operation.

1/ Paper presented at EPA Flue Gas Desulfurization Symposium, New Orleans, Louisiana, May 14-17, 1973.

Processes recovering the sulfur oxides in a useful form are potentially superior to the throwaway type because they do not generate solid waste disposal problems and also offer the possibility that sales revenue will reduce the cost of sulfur oxide removal. It should be kept in mind, however, that recovery processes are generally more complex, may be more expensive to install, and require a definite commitment to sell the products produced.

In recent years, numerous processes have been proposed for sulfur oxide recovery and some of these are currently undergoing demonstration on large scale (100 MW or larger). The purpose of the EPA-TVA conceptual design series is to subject the more promising of these to a detailed study in which the best design is developed from available data; capital and operating costs are estimated on a uniform basis; a market survey is made to estimate sales revenue; total cash flow is related to economic promise; and needed research and development are identified.

Scrubbing with magnesium oxide slurry to form magnesium sulfite, followed by decomposition to produce concentrated SO_2 (MgO is recycled) is one of the more promising processes for sulfur dioxide removal. Slurries of magnesia are good absorbents; however, the most outstanding assets of the concept are (1) the ease of separation of the sulfite salts formed from the scrubber liquor, (2) the ability to regenerate and recycle the absorbent, magnesium oxide, (3) the avoidance of a solids disposal problem, and (4) the capability of separating, both financially and operationally, the power unit scrubbing system from the chemical manufacturing and marketing function. At the same time, the process does require extra expense for (1) drying and calcining the intermediate MgSO_3 and MgSO_4 formed, and (2) the apparent need

for two scrubbing stages on coal-fired units to avoid mixing fly ash with the undissolved absorbent. As with all aqueous scrubbing processes, stack gas reheating, if required, would also add expense. The potential of the process, however, is outstanding enough to merit demonstration on a 155-MW, oil-fired power unit of Boston Edison. This system, jointly funded by EPA and a large group of chemical companies and utilities, started up in early 1972.

In the regeneration of the absorbent, sulfur dioxide is released at concentrations practical for conversion to sulfuric acid, liquified sulfur dioxide, or elemental sulfur. With the limited market for liquified sulfur dioxide and the higher cost of conversion to sulfur, the product receiving primary attention in the report is sulfuric acid. Commercial grades of acid including 98% concentration and oleum are easily produced in the process.

Around the world, development work on magnesia scrubbing for power plant stack gas has followed at least three major technological routes. The Russians, Japanese, and Americans have concentrated on the use of magnesium sulfite-magnesium oxide slurries having a basic pH; whereas a German company, Grillo, has researched the use of an absorbent activator, manganese dioxide, with the scrubbing slurry. In addition, using technology associated with sulfite pulping practice, at least one American company has also investigated the use of magnesium sulfites in acidic solution so that simultaneous particulate and SO₂ removal can be accomplished with a single scrubber in coal-fired unit applications.

Each of these three scrubbing schemes are given detailed review in the present study and are described as follows:

Scheme A - magnesia slurry variation--Wet scrubbing with magnesium oxide-magnesium sulfite-water slurry to absorb SO_2 and form undissolved $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ plus some $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. The $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ is thermally converted to trihydrate and dried to form anhydrous MgSO_3 . This material along with any sulfate formed by oxidation is calcined with coke to generate MgO for recycle and SO_2 for production of H_2SO_4 by the contact process. A flow diagram of Scheme A is shown in Figure 1.

Scheme B - MgO-MnO_2 slurry variation--Wet scrubbing with magnesium oxide-magnesium sulfite slurry containing a scrubbing reaction activator, manganese dioxide. The sulfites, sulfates, and unreacted manganese dioxide are dried and calcined to regenerate the absorbent and activator with the SO_2 rich gas being processed to H_2SO_4 .

Scheme C - clear liquor variation--Wet scrubbing of stack gas to remove particulates and absorb SO_2 simultaneously with an acidic solution of magnesium sulfites, followed by separation of insoluble fly ash and liquor and addition of MgO to the liquor to precipitate $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. The crystals of sulfite are then converted to trihydrate, dried, and calcined. MgO is recycled and SO_2 processed to acid.

The above variations can be applied to multiple power units more economically than with individual power plants by taking advantage of a concept called "central processing". By processing (calcining and acid production) the dried sulfite material from several scrubbing operations in a single, large plant, a more efficient operation (higher annual operating time) can be derived and economy of scale can be achieved. This concept is not a technological variation, but deserves separate consideration (Scheme D) to evaluate the economic merit of the idea which of course, can be used in some other type absorbent processes as well.

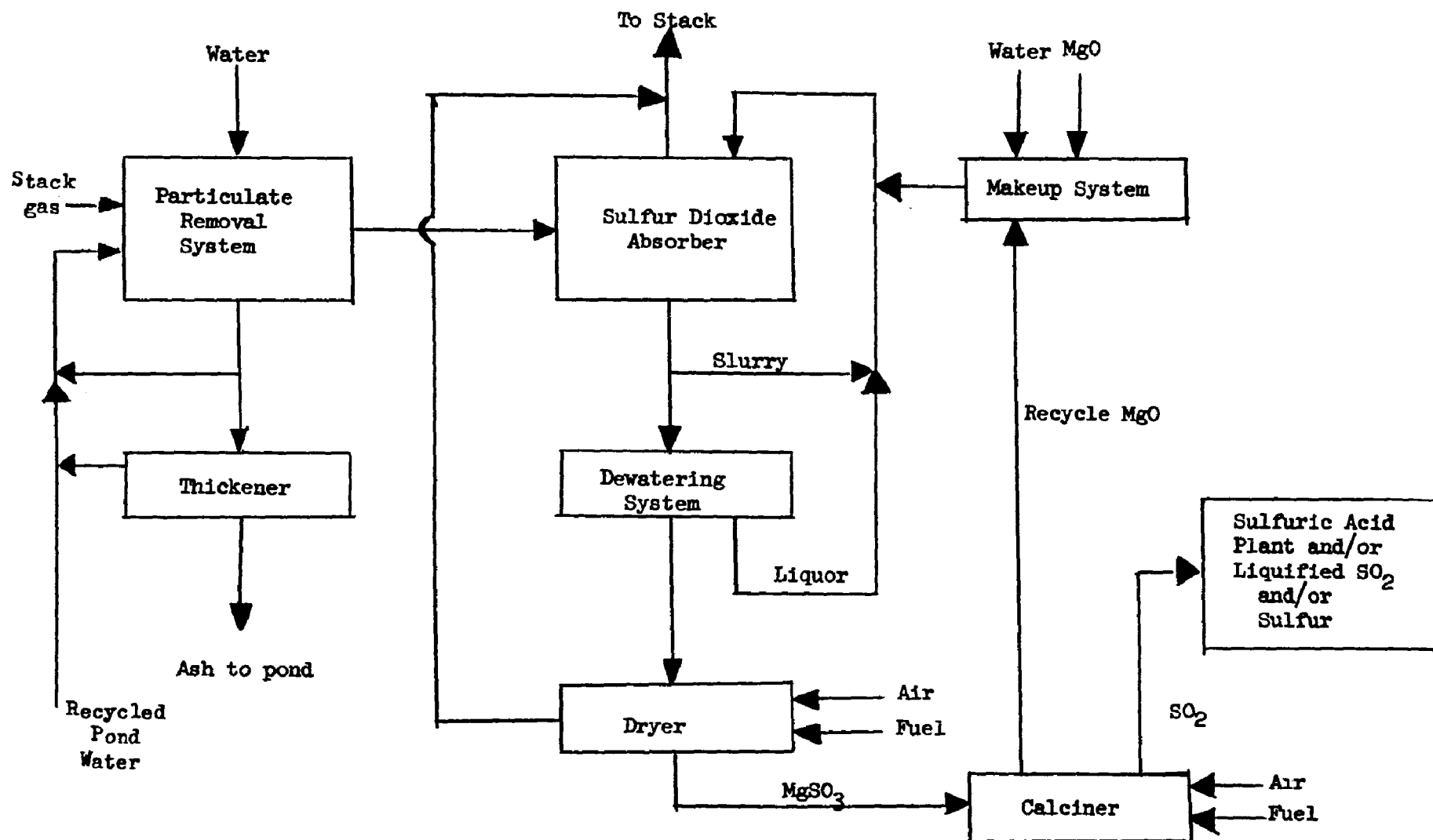


Figure 1 Flow Diagram - Magnesia Slurry Scrubbing-Regeneration

Some earlier preliminary investigations (1970) indicated the possible use of a variation in magnesia scrubbing for NO_x control. Recent work (1972), however, indicates that no more than 10% removal can be expected; therefore, magnesia scrubbing should not be counted as a means of meeting new Federal NO_x emission standards.

Study Assumptions

Recovery process economics depend on several factors including power plant size, type of fuel burned, sulfur content of fuel, operating factor, plant location, unit efficiency, and unit status (new vs. existing). For detailed design and cost estimating purposes, it was necessary to assume a combination of conditions as a base case for both oil- and coal-fired units. In the economic evaluation, the effect of variation in the major parameters was determined. The basic conditions assumed are as follows:

Power unit size, MW	500
Sulfur content of coal, %	3.5
Sulfur content of oil, %	2.5
Ash content of coal, %	12
Heating value of coal, Btu/lb	12,000
Heating value of oil, Btu/lb	18,500
Boiler excess air and leakage, %	
coal-fired unit	33
oil-fired unit	15
Degree of dust removal, %	99
Degree of SO_2 removal, %	
slurry Schemes A,B,D	90
solution Scheme C	77
Boiler type	Horizontal, frontal-fired
Plant location	Midwest
Capacity factor, % of nameplate rating	
first to 10th year	80
11th to 15th year	57
16th to 20th year	40
21st to 30th year	17
Avg over life of unit	48.5
Air preheater exhaust temp, °F	310°F
Stack gas reheat temp, °F	175°F
Unit heat rate, Btu/kWh	9,000
Product storage, days	30

Process Equipment

The scrubbers, ductwork, and fans are the most expensive items in a magnesia scrubbing process because they must handle the full flow of gas (over 1,000,000 tons/day for a 1000-MW boiler). The slurry or solution processing, drying, calcining, and sulfuric acid units handle a lower throughput of material depending on S content of fuel. Stagewise scrubbing (see Figure 2) will be necessary when using slurry scrubbing on coal-fired units to keep the majority of the fly ash from entering the drying and calcining operations. For particulate removal, a venturi type device using clarified, circulated water is chosen although electrostatic precipitators and bag filters could be used. Electrostatic precipitators have shown variations in outlet loadings due to operating characteristics and time, and bag filters are more expensive.

In scrubbing sulfur oxides, slurry systems can utilize venturi, mobile bed (plastic sphere type) or spray units. For solution scrubbing service (Scheme C), plate and packed scrubbers might be added to the list of acceptable devices, but consideration must be given to residual fly ash carryover causing plugging. In any case, corrosion and erosion protection should be provided by linings such as rubber or polyester-fiberglass resins.

At this time, mist elimination performance in slurry scrubbing service is of concern with a variety of designs and materials of construction currently in use or under study. In this design, the chevron vane type device constructed of a corrosion-erosion resistant material or coated is used.

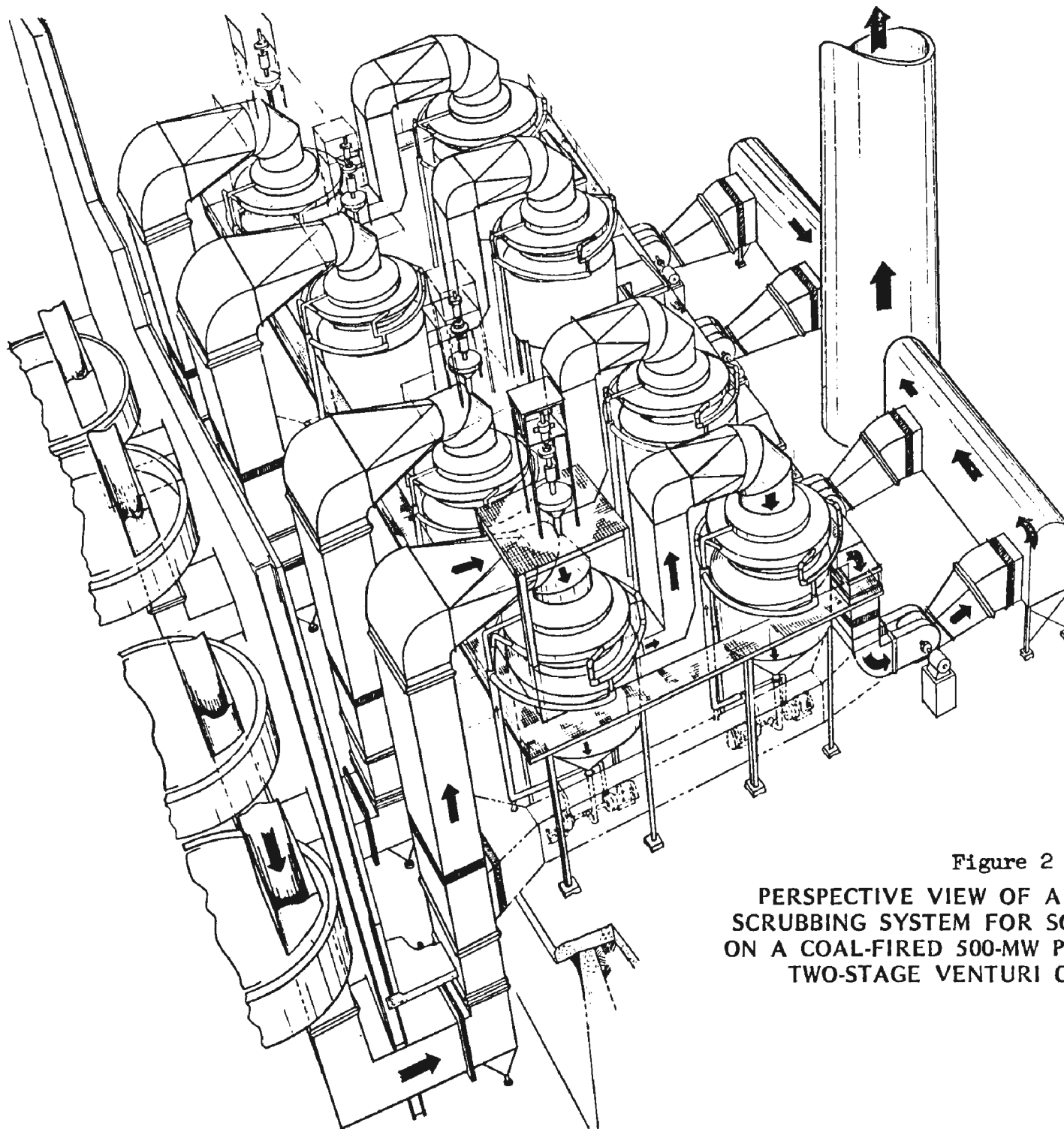


Figure 2
PERSPECTIVE VIEW OF A MAGNESIA
SCRUBBING SYSTEM FOR SO_2 REMOVAL
ON A COAL-FIRED 500-MW POWER UNIT—
TWO-STAGE VENTURI CONCEPT

Reheating can be accomplished by indirect steam heat exchange on new units for which design provisions have been made in the steam cycle; however, existing units are not likely to have excess steam available; therefore, direct fuel oil reheat is preferred. Neither of these methods is the most economical choice available, but the reliability of the indirect liquid-gas heat exchange method considered in previous studies has become suspect.

Solids separation in the magnesia slurry processing area probably can be accomplished best by first thickening the 10% solids slurry to 40% and then centrifuging to a cake containing less than 15% free water. Since good test data are not available, separation by filtration cannot be ruled out; however, cakes containing less than 15% water may be more difficult to obtain.

Although rotary type devices are being utilized for drying and calcining in the Boston Edison demonstration project, discussions with vendors have indicated that possible greater efficiency and lower cost could be obtained with fluid bed units. In the absence of test data, some doubt remains; however, fluid bed systems appear to be the better choice.

The "dry" gas cleanup system for calciner off-gas and the sulfuric acid plant utilize relatively well established technology; therefore, few unforeseen problems should arise in these areas. If desirable, the magnesia process could easily be added to existing acid units which currently burn elemental sulfur.

Investment Requirements

Summarized investment under various combinations of conditions are given for Scheme A and limestone-wet scrubbing in Table 1. Depending on sulfur in the fuel, fuel type, plant size, and status, the magnesia Scheme A investment varies from 4-27% higher than limestone-wet scrubbing; however, salable product is produced rather than a waste material. Scheme C has the lowest investment requirement (\$36.2/kW for base case) for coal-fired power unit scrubbing systems; however, SO₂ removal for Scheme C may not be sufficient in all cases to meet Federal emission standards for new units. In addition, the data supporting clear liquor scrubbing are limited; therefore, the scheme should not be considered as the leading process.

A detailed, direct investment breakdown of the 500-MW base case covering Scheme A is shown in Table 2.

Operating Costs

A summary of average annual and unit operating costs at 7000 hrs/yr operation under regulated economics are given in Table 3 for both magnesia Scheme A and limestone scrubbing (low and high cost). A detailed operating cost breakdown for the Scheme A base case (500-MW, 3.5% S in coal, new unit) is shown in Table 4.

Evaluation Considerations

Evaluation of recovery processes brings in factors such as product marketability and price, return on investment and taxes, and project financial promise, all of which make the analysis more difficult than for throwaway processes. It would be desirable, of course, that recovery methods show promise of a net profit, but this is not essential because recovery should be preferable to throwaway, even at a net loss, as long as the loss is lower than for throwaway systems. The cost of limestone-wet scrubbing was used as the criterion for

Table 1

Capital Requirements for Magnesia Scheme A
And Limestone-Wet Scrubbing

<u>Conditions</u>	<u>Capital, \$/kW of power generating capacity</u>	
	<u>Magnesia Scheme A wet scrubbing</u>	<u>Limestone-Wet scrubbing</u>
Base case - coal-fired units		
(500-MW, new power unit, 3.5% S in coal, reheat to 175°F)	43.5	35.2
Exceptions to base case (coal-fired units)		
Existing power unit	49.3	39.9
2% sulfur	37.6	32.3
5% sulfur	48.5	37.8
200-MW	58.4	46.0
1000-MW	33.1	27.4
Base case - oil-fired units		
(500-MW, new power unit, 2.5% S in oil, reheat to 175°F)	24.9	21.4
Exceptions to base case (oil-fired units)		
Existing unit	27.8	24.8
1% sulfur	19.8	19.0
4% sulfur	29.1	23.4
200-MW	33.4	28.5
1000-MW	18.8	16.6

**Table 2 Process Equipment and Installation
Analysis-Direct Cost for Scheme A^a (Thousands of Dollars)**

	<u>Particulate scrubbing</u>	<u>SO₂ scrubbing</u>	<u>Slurry processing</u>	<u>Drying</u>	<u>Calcining</u>	<u>MgO slurrying</u>	<u>New H₂SO₄ production</u>	<u>H₂SO₄ storage</u>	<u>Optional by- pass duct</u>	<u>Fuel oil storage</u>	<u>Total</u>
Equipment											
Material	828	997	424 ^b	490 ^b	665 ^b	115	925	163	-	122	4729
Labor	240	256	75	176	215	27	Inc.	Inc.	-	22	1011
Piping & Insulation											
Material	327	236	52	2	2	15	410	-	-	Inc.	1044
Labor	177	101	20	3	3	4	Inc.	-	-	Inc.	308
Ductwork, dampers, & Insulation											
Material	752	878	-	20	44	-	741	-	454	Inc.	2889
Labor	Inc.	Inc.	-	Inc.	Inc.	-	Inc.	-	Inc.	Inc.	Inc.
Concrete-foundations											
Material	105	115	30	38	46	10	188	18	-	21	571
Labor	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	-	Inc.	Inc.
Structural											
Material	135	145	26	8	14	3	99	3	-	2	435
Labor	180	190	34	11	18	4	Inc.	4	-	Inc.	441
Electrical											
Material	216	340	73	43	39	32	207	14	-	10	974
Labor	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	Inc.	-	Inc.	Inc.
Instruments			(Additional Instruments)								
Material	111	135	29	11	32	39	185	Inc.	-	1	543
Labor	57	75	10	4	11	13	Inc.	Inc.	-	Inc.	170
Paint											
Material	66	60	12	4	5	2	66	1	-	Inc.	216
Labor	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>Inc.</u>	<u>-</u>	<u>Inc.</u>	<u>Inc.</u>
Sub-total											
Direct costs	3194	3528	785	810	1094	264	2821	203	454	178	13,331

^a New plant, coal-fired, 500-MW, 3.5% sulfur in coal, 1,040,000 scfm stack gas, 378 tpd H₂SO₄. Inc. = included.

^b Includes most instrumentation.

Table 3 Average Annual and Unit Operating Cost^a
For Magnesia Scheme A and Limestone-Wet Scrubbing Under Regulated Economics

<u>Conditions</u>	<u>Magnesia Scheme A</u>		<u>Limestone-Wet Scrubbing</u>			
	<u>Average Annual Cost \$</u>	<u>Unit Operating Cost \$/ton coal</u>	<u>Low Limestone Cost,^b On-Site Solids Disposal</u>		<u>High Limestone Cost,^c Off-Site Solids Disposal</u>	
			<u>Average Annual Cost \$</u>	<u>Unit Operating Cost \$/ton Coal</u>	<u>Average Annual Cost \$</u>	<u>Unit Operating Cost \$/ton Coal</u>
Base case - Coal-fired units						
(500-MW, new power unit, 3.5% S in coal, reheat to 175°F)	7,048,900	5.37	5,376,300	4.10	7,621,500	5.81
Exceptions to base case (coal-fired units)						
Existing Power unit	7,762,500	5.79	5,927,900	4.42	8,253,700	6.15
5.0% Sulfur	8,066,600	6.15	5,894,000	4.49	8,861,700	6.75
200 MW	3,870,700	7.21	2,869,200	5.35	3,633,400	6.77
1000 MW	10,635,400	4.19	8,230,900	3.24	12,883,100	5.08
	<u>\$</u>	<u>\$/bbl oil</u>	<u>\$</u>	<u>\$/bbl oil</u>	<u>\$</u>	<u>\$/bbl oil</u>
Base case - Oil-fired units						
(500-MW, new power unit, 2.5% S in oil, reheat to 175°F)	4,159,800	0.83	3,343,600	0.66	4,112,500	0.82
Exceptions to base case (oil-fired units)						
Existing Power Unit	4,548,800	0.88	3,755,100	0.73	4,566,000	0.89
4.0% Sulfur	4,973,500	0.99	3,747,300	0.74	5,046,700	1.00
200 MW	2,305,600	1.12	1,836,700	0.89	2,046,900	0.99
1000 MW	6,317,100	0.65	5,160,400	0.53	6,848,000	0.70

^a 7000 hrs/year operation

^b Limestone at \$2.05/ton and variable on-site disposal costs for calcium solids, ranges from \$2.85/ton to \$1.33/ton

^c Limestone at \$6.00/ton and \$6.00/ton for disposal of calcium solids

**Table 4 , Regulated Company Economics—Total Venture Average Annual
Manufacturing Costs for 98% H₂SO₄ from Scrubbed Power Plant Stack Gas^a
Scheme A—Magnesia Slurry Scrubbing-Regeneration**

(500-mw new coal-fired power unit, 3.5% S in fuel; 110,400 tons/yr 100% H₂SO₄)

	Annual quantity	Unit cost, \$	Total annual cost, \$	Cost/ton of acid, \$
<i>Direct Costs</i>				
Delivered raw material				
Lime	134.1 tons	16.00/ton	2,100	.019
Magnesium oxide (98%)	1,086 tons	102.40/ton	111,200	1.007
Coke	763 tons	23.50/ton	17,900	.162
Catalyst	1,800 liters	1.51/liter	2,700	.024
Subtotal raw material			133,900	1.212
Conversion costs				
Operating labor and supervision	39,200 man-hr	6.00/man-hr	235,200	2.130
Utilities				
Fuel oil	5,356,000 gal	0.09/gal	482,000	4.366
Steam	440,000 M lb	0.55/M lb ^b	242,000	2.192
Heat credit	20,300 MM Btu	-0.40/MM Btu	(8,100)	(.073)
Process water	2,207,500 M gal	0.03/M gal ^b	66,200	.600
Electricity	66,760,000 kwh	0.006/kwh ^b	400,600	3.629
Maintenance				
Labor and material, .06 x 21,732,000			1,303,900	11.811
Analyses			85,000	.770
Subtotal conversion costs			2,806,800	25.425
Subtotal direct costs			2,940,700	26.637
<i>Indirect Costs</i>				
Average capital charges at 14.9% of initial fixed investment			3,238,100	29.331
Overhead				
Plant, 20% of conversion costs			561,400	5.085
Administrative, research, and service, 11% of conversion costs			308,700	2.797
Subtotal indirect costs			4,108,200	37.213
			Cost/ton of coal burned, \$	Cost/ton of acid, \$
Total annual manufacturing costs for H ₂ SO ₄			5.371	63.850

^aBasis:

Remaining life of power plant, 30 yr.

Coal burned, 1,312,500 tons/yr—9,000 Btu/kwh.

Stack gas reheat to 175° F.

Power unit on-stream time, 7,000 hr/yr; acid plant on-stream time, 7,000 hr/yr.

Midwest plant location—1972 costs.

Capital investment, \$21,732,000; working capital, \$505,600.

^bCost of utility supplied from power plant at full value.

comparison. Both high cost (\$6/ton limestone, \$6/ton solids disposal cost) and low cost (\$2.05/ton limestone, variable cost on-site solids disposal) limestone systems were estimated using the same basis as used for the magnesia schemes.

The basis on which the recovery process is financed is a major consideration in evaluating economic promise and acceptability. If a power company finances the entire project, it can be assumed that the investment would become part of the rate base on which the company is allowed to earn what the regulatory authority regards as a reasonable return on investment. If sulfur oxide removal, either by throwaway or recovery method, were to increase operating cost, then the price of power to consumers presumably could be raised to offset the extra cost. Under such basis, sulfur oxide removal (even by recovery) could be considered as necessary for production of power just as is the boiler operation, dust removal, or cooling water system, and the costs, therefore, passed on to the consumer. It is true that rate increases are often strongly contested and delayed, and that the full adjustment may not always be allowed, so that the power company has the incentive to avoid extra investment and expense. In general, however, the power company has a more or less assured profit. For this reason, there is little risk and capital can be attracted at regulated rates of return.

Since power companies generally are not familiar with chemical production and marketing, there would be some advantage if a chemical company built and operated the recovery process for a fee and marketed the products. For a private, nonregulated company to enter into such an activity, however, the project would have to be promising enough to attract the necessary capital from investors. It is difficult to say how much promise is needed because this varies with the situation. Generally, it is considered that the projected cash flow (depreciation plus profit after taxes) should pay out

the original investment in less than five years or on another basis which takes into account the time value of money, the interest rate of return after income taxes should be about 15%. For the relatively high investment required by sulfur oxide recovery processes, this is a major hurdle.

A characteristic of the central process concept is that features of both regulated and nonregulated economics can be utilized to advantage. If by cooperative arrangement, magnesia scrubbing and drying operations are placed under power industry (regulated) economics, and regeneration and acid manufacture are covered under nonregulated economics, the power company can avoid any responsibility for acid production and marketing, and the chemical company can reduce its capital responsibility to levels more likely to achieve successful profitability. By charging the power company for regenerated MgO and also by selling sulfuric acid, enough revenue might be obtained for a chemical company to justify manufacturing acid from magnesium sulfite rather than by the more conventional purchase of elemental sulfur. The revenue obtained for regenerated MgO would, of course, depend on the resultant cost to the power company for magnesia scrubbing as opposed to limestone-wet scrubbing or other feasible alternatives.

Comparison and Profitability

An important consideration for comparison under regulated economics, and in profitability analysis under nonregulated economics, is net sales revenue for the sulfuric acid. A market review for the acid resulted in the following conclusions:

1. The growth rate of sulfuric acid production is about 4-6% per year generally paralleling that of the phosphate fertilizer industry.

Capacity from magnesia scrubbing-regeneration will most likely enter

the market at a moderate to slow pace.

2. The best end-use market appears to be the phosphate fertilizer industry as an acidulant for phosphate rock. The product is used in many other applications, however, any of which merit consideration.
3. The most promising locations for magnesia scrubbing-regeneration systems appear to be on waterways serving the areas where sulfuric acid is now heavily marketed. Areas on the Ohio and Mississippi Rivers, and along the Gulf and East Coasts are prime spots.
4. Sales price will be based on competition in each individual area plus flexibility of demand. In those areas where by-product acid or low cost sulfur are available, competition will be greatest.
5. Expected net sales revenue after shipping and sales expense are deducted could average about \$8.00/ton of 100% acid for single-site systems and \$12.00/ton for large central processing units. In the better locations, these net backs and maybe more should be attainable through the 1970's.
6. Long term marketing contracts appear to be practical since the likelihood of escalating sales revenue due to prolonged product shortages is not expected.

Comparison under regulated economics--A comparison of Scheme A with both high and low cost limestone scrubbing is given in Table 5. The values shown are the cumulative net annual costs over the life of the power unit; thus, the values represent the total bill including return on investment and income taxes for particulate and SO₂ control over the power plant life.

Table 5. Cost of Magnesia Scheme A vs. Limestone-Wet Scrubbing under Regulated Economics

<u>Conditions</u>	<u>Cumulative net annual costs, \$ millions</u>		
	<u>Scheme A^a</u>	<u>Limestone-Wet Scrubbing</u>	
		<u>Low limestone process cost^b</u>	<u>High limestone process cost^c</u>
Base Case - coal-fired units (500-MW, new unit, 3.5% S in coal, 48.5% avg. capacity factor over 30 yrs, reheat to 175°F)	162.1	136.2	170.6
Exceptions to base case (coal-fired units)			
Existing unit (27 yr life)	160.2	133.4	162.3
5% sulfur	180.5	148.5	194.3
200-MW	91.1	72.7	82.6
1000-MW	237.9	208.3	283.2
Base Case - oil-fired units (500-MW, new unit, 2.5% S in oil, 48.5% avg. capacity factor over 30 yrs, reheat to 175°F)	95.9	84.2	94.2
Exceptions to base case (oil-fired units)			
Existing unit (27 yr life)	93.7	84.1	92.3
4% sulfur	111.0	93.8	112.1
200-MW	54.4	46.3	47.7
1000-MW	141.6	129.5	154.3

^a Net sales revenue assumed at \$8.00/ton of acid.

^b Limestone cost - \$2.05/ton; on-site pond disposal of solids.

^c Limestone cost - \$6.00/ton; off-site solids disposal cost, \$6.00/ton.

The only magnesia case with costs lower than the low cost limestone system is a 1000-MW, coal-fired unit using Scheme C, the least developed variation. Units smaller than 300-MW would most likely use limestone scrubbing if funding were under regulated economics. Because the incremental cost of producing additional acid exceeds \$8.00/ton (net sales revenue for acid), increasing on-stream time and higher sulfur content of fuel do not improve the magnesia process economics.

Profitability under non-regulated economics--Based on projected revenue from acid sales alone, all magnesia cases examined have negative interest rates of return and no payout. If additional revenue in the form of a fee equivalent to the cost of limestone-wet scrubbing or other competitive SO₂ control method is charged by the chemical company for sulfur oxide abatement, profitability can be derived. Shown in Table 6 are payout periods in years and interest rates of return in % for Scheme A assuming revenue from both a fee and acid sales.

As would be expected, the results depend on the size of the fee charged; for a fee equivalent to a high cost limestone scrubbing process, desirable profitability could be achieved in some cases and for a smaller fee equivalent to a low cost limestone process, low profitability would result in all cases. Funding under this concept will probably be limited.

Profitability of cooperative central process ventures--With the separation of investment and operating responsibility and the advantage of economy of scale for large central acid complexes, cooperative ventures (Scheme D) between power companies and chemical companies are the best route to financial funding of magnesia systems. Given in Table 7 are the

**Table 6. Profitability of Scheme A with Supplementary Income as Payment
for Pollution Abatement**

<u>Conditions^a</u>	<u>Low equivalent payment^b</u>		<u>High equivalent payment^c</u>	
	<u>Payout, yrs</u>	<u>Interest rate of return, %</u>	<u>Payout, yrs</u>	<u>Interest rate of return, %</u>
Base Case - coal-fired units (500-MW, new unit, 3.5% S in coal 48.5% avg. capacity factor over 30 yrs, reheat to 175°F)	7.6	8.8	5.6	14.9
Exceptions to base case (coal fired)				
Existing unit (27 yr life)	7.7	8.4	5.7	13.6
5% sulfur	7.7	8.5	5.4	15.7
200-MW	8.3	7.4	6.7	11.0
1000-MW	7.1	10.0	4.8	18.1
573 Base Case - oil-fired units (500-MW, new unit, 2.5% in oil, 48.5% avg. capacity factor over 30 yrs, reheat to 175°F)	7.2	9.8	6.1	13.0
Exceptions to base case (oil fired)				
Existing unit (27 yr life)	7.0	10.0	6.0	12.7
4% sulfur	7.5	9.0	5.8	14.0
200-MW	7.6	8.8	7.1	9.9
1000-MW	6.8	10.9	5.3	15.8

^a Net sales revenue assumed at \$8.00/ton of acid.

^b Equivalent to limestone-wet scrubbing cost assuming low limestone price, on-site pond disposal of solids.

^c Equivalent to limestone-wet scrubbing cost assuming high limestone price, off-site disposal of solids.

Table 7.

Profitability of Central Regeneration-Acid Manufacturing Unit Under Cooperative Economics.^a Magnesium Sulfite Supplied from Combinations of New 200, 500, or 1000-MW Units Burning Coal with 3.5% Sulfur. Regulated Magnesia Scrubbing Costs Equalized to High and Low Projected Limestone-Wet Scrubbing Process Costs.

Case Units and size	Payout, years		Interest rate of return, %	
	Recycle MgO ^b at \$25/ton	Recycle MgO ^c at \$55/ton	Recycle MgO ^b at \$25/ton	Recycle MgO ^c at \$55/ton
200-MW equiv.	None	8.4	Neg.	3.3
5 x 200-MW equiv.	6.6	3.4	8.2	26.6
10 x 200-MW equiv.	5.2	2.7	14.0	35.5
15 x 200-MW equiv.	4.6	2.4	17.2	40.6
	Recycle MgO ^b at \$15/ton		Recycle MgO ^b at \$55/ton	
	Recycle MgO ^b at \$15/ton	Recycle MgO ^c at \$55/ton	Recycle MgO ^b at \$15/ton	Recycle MgO ^c at \$55/ton
500-MW equiv.	None	5.1	Neg.	14.4
2 x 500-MW equiv.	9.9	3.5	0.3	25.3
4 x 500-MW equiv.	7.7	2.8	5.1	34.1
6 x 500-MW equiv.	6.5	2.4	8.7	39.7
	Recycle MgO ^b at \$10/ton		Recycle MgO ^b at \$55/ton	
	Recycle MgO ^b at \$10/ton	Recycle MgO ^c at \$55/ton	Recycle MgO ^b at \$10/ton	Recycle MgO ^c at \$55/ton
1000-MW equiv.	None	3.6	Neg.	24.4
2 x 1000-MW equiv.	9.9	2.9	0.1	33.0
3 x 1000-MW equiv.	8.3	2.5	3.5	38.5

^a Nonregulated portion of system with 10 yr life; acid revenue - \$12/ton.

^b Equivalent to limestone-wet scrubbing costs assuming low limestone price, on-site pond disposal of solids.

^c Equivalent to limestone-wet scrubbing costs assuming high limestone price, off-site disposal of solids.

payouts and interest rates of return for Scheme D systems assuming revenue from both acid and recycle MgO sales. The price of recycle MgO must be such that magnesia scrubbing cost does not exceed that of competitive limestone scrubbing for the same power unit. For a 500-MW, coal-fired unit, only about \$15-\$20/ton could be paid for recycle MgO before exceeding the low cost limestone system; however, approximately \$55/ton could be paid if competition came from a high cost limestone system.

The results in Table 7 indicate that the smaller the power unit supplying MgSO_3 and the larger the acid complex, the better the profitability which could be achieved. A 3000-MW equivalent acid plant supplied by fifteen 200-MW units would show excellent profit making potential - 17.2% interest rate of return with \$25/ton for recycle MgO and \$12/ton for sulfuric acid or 40.6% return for \$55/ton recycle MgO and \$12/ton acid.

Conclusions

The more important conclusions derived from this study can be summarized as follows:

1. Sulfur dioxide absorption by magnesia slurry scrubbing is effective and the major portions of the process as conceptualized utilize proven technology.
2. Magnesia scrubbing, like limestone scrubbing, is not an effective means of NO_x removal from power plant stack gas.
3. Magnesia slurry scrubbing-regeneration has been tested in laboratory and pilot plant stages and at least one large scale demonstration is underway.
4. Although limited experience is available to guarantee performance, equipment for commercial systems can be obtained at this time from vendors and fabricators.

5. For most U. S. fossil -fueled power plants, achievable net sales revenue for recovered 98% sulfuric acid will probably average only \$8-12/ton over the next decade or so; however, there will be applications where better netbacks are obtainable. Competition will continue from other sources of by-product sulfuric acid and virgin acid made from low cost sulfur.
6. Primary economic factors are investment, product volume (depending on power unit size and sulfur content of fuel), net sales revenue (from all sources), competitive cost of alternatives and basis of financing. Raw material, labor, shipping costs, on-stream time, and plant age are significant, but not nearly as important as the primary factors.
7. Under total regulated financing, magnesia systems can compete with limestone scrubbing on larger (400-MW or greater) power units. The limestone process would be favored in rural areas (low cost limestone and space for solids disposal) whereas the magnesia scrubbing-regeneration process would appear more desirable in crowded metropolitan areas.
8. Total nonregulated industry financing and operation appear unlikely; however, with a large fee for pollution abatement and large size units, such funding can be considered.
9. A cooperative venture between several power companies and a chemical company with each supplying capital for and operating their portion of the process, appears to be a good way to fund a magnesia system. It will be necessary for the regeneration-acid plant to charge a service fee for MgO processed from MgSO_3 in order to obtain sufficient revenue for desirable profitability.

10. Thus far, interest in the magnesia scrubbing-regeneration process has centered more on replacement of sulfur as raw material in existing sulfuric acid plants with existing markets rather than for added capacity to meet increasing acid markets.
11. There are a limited number of locations that can support a central process installation. The Midwest, along the Ohio and Mississippi Rivers, and the Gulf and East Coasts are prime targets.
12. For short range shipping distances (0-50-miles), the cost of shipping MgSO_3 and MgO between sites is a small part of the total process cost and will not greatly influence process application; however, as distances exceed 100 miles, shipping cost becomes much more significant.

Additional research and development of the process should be performed primarily on the demonstration level to determine effect of process factors such as contamination build-up over long periods of MgO recycle, corrosion-erosion of construction materials, scaling difficulties, and adaptability to power plant operation. Some work on oxidation, crystal growth, effectiveness of additives such as manganese dioxide and the manufacture of sulfur in the calciner should be performed on the bench or pilot levels.

OPERATIONAL PERFORMANCE OF THE
CHEMICO BASIC MAGNESIUM OXIDE SYSTEM
AT THE BOSTON EDISON COMPANY
PART I

by

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This paper is Part I of a two part paper and supplements Part II of this paper being presented by Mr. C. P. Quigley of Boston Edison Company.

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OPERATIONAL PERFORMANCE OF THE
CHEMICO/BASIC MAGNESIUM OXIDE SYSTEM
AT THE BOSTON EDISON COMPANY

PART I

G. R. Koehler

INTRODUCTION

The necessity for control of sulfur oxides emissions to the atmosphere has become increasingly apparent. The deleterious effect of this compound on human health and the environment has been documented. The growing demand for energy compounds the problem. Total SO₂ emissions in 1965 were 25 million tons per year. It is anticipated that within the next decade, if no control is imposed, these emissions will rise to 75 million tons per year in the United States. Of this amount, two-thirds will originate from the products of combustion of fossil fuel fired power generating stations. Of the available technology, one of the most promising seems to be flue gas scrubbing at the generating facility itself.

In its search for suitable technology to control sulfur oxides emissions CHEMICO developed a process scheme which uses the well established technology of acid gas absorption by alkaline scrubbing media with precipitation of the sulfite formed as a solid product. Further process steps include dewatering of the solid product and eventual reclamation of the alkali with recovery of the SO₂.

In June 1970, the United States Environmental Protection Agency and the Boston Edison Company agreed to provide the funds for a large prototype Sulfur Dioxide Recovery Plant using the Chemico/Basic MgO Sulfur Recovery Process. These integrated facilities were comprised of an SO₂ absorption plant at Boston Edison's Mystic Station and a regeneration facility at Essex Chemical's Rumford, R.I. Sulfuric Acid Plant. Construction at both plants was completed by April, 1972.

Capital funds for the absorption system were provided by the Boston Edison Company while E.P.A. furnished funds for installation of the magnesium oxide regeneration system and appropriate acid plant modifications as well as operating funds for the absorption/regeneration systems.

The SO₂ absorption plant is designed to remove 90% of the sulfur dioxide formed when burning fuel oil containing two and one half percent sulfur. The regeneration facility is designed to recover the alkali in a form suitable for recycling to the absorption facility and send the recovered SO₂ to a sulfuric acid plant for the production of 98% sulfuric acid.

Operations to date have demonstrated each of the process steps. SO₂ removal efficiencies of 90% or better have been consistently obtained despite the use of a lower sulfur fuel oil than originally expected. Several hundred tons of commercial grade sulfuric acid have been produced and marketed in the conventional manner. Operations have, however, been intermittent due to the necessity to make numerous relatively minor changes and adjustments to the system. Yet to be demonstrated is the long term operability of the process and the ability to use Magnesia which has been recycled many times. Present efforts are being concentrated on entering into long term operations in order to ascertain system availability and reliability.

Problems associated with process consideration are addressed in this Part I. Mr. C. P. Quigley of Boston Edison will describe mechanical problems encountered, corrosion--erosion experience and related equipment malfunctions in the second part of this paper.

GENERAL PROCESS DESCRIPTION

Chemico/Basic's Magnesium Oxide System for the recovery of sulfur dioxide from power plant flue gases is shown schematically in Figure 1.

This process, which utilizes the sulfur dioxide absorption characteristics of an aqueous slurry containing magnesium oxide, magnesium sulfite and magnesium sulfate is comprised of five primary operations:

- Absorption System
- Centrifuge System
- Dryer System
- Magnesium Oxide System
- Calcination System

Absorption System

The flue gas containing sulfur oxides enters a venturi absorber (Figure 2) and contacts the absorbing media which is an aqueous slurry magnesium oxide, magnesium sulfite and magnesium sulfate. The process of SO_2 removal is explained by conventional mass transfer principles. The venturi absorber can be shown by analogy to correspond to a co-current packed vessel.

In the scrubber, the liquid slurry is injected and flows on surfaces over which passes an accelerating gas stream. The high velocity gas passing over the liquid causes wave motion on those surfaces. The waves increase in amplitude finally dispersing as fine droplets in the gas stream. Thus, the whole mass of liquid is dispersed in the form of atomized droplets.

In the process described in this paper, the dispersed droplets have a median size of 400 micron and the surface area available for mass transfer averages 13 ft^2 per ft^3 of gas. This absorption surface is dispersed thru and flows with the gas stream eliminating the problems of plugging associated with conventional packed towers (the surface area per unit volume is approximately equivalent to dumped 3 inch rachig rings). Due to system dynamics this surface area relation is relatively invarient over wide turn-down ratios in the venturi scrubber and can be used as an approximation over the power plant boiler's operating range of 40 to 155 MW.

Similarly, system efficiency can be predicted with a fair degree of accuracy by substituting a Sherwood Number of 2 ($\text{SH} = 2$) in conventional mass transfer relations. Using this estimate a maximum efficiency of 96% can be predicted for the system, deviations from that removal efficiency being caused by equilibrium partial pressures of SO_2 over the droplet surfaces greater than zero in the dynamic system.

To date, the absorption system has operated satisfactorily. Sulfur dioxide removal efficiencies of 90% or greater have been consistently obtained with SO_2 concentrations in the outlet flue gas being generally 90 ppm or less measured by both a DuPont 460 process analyzer and wet chemical methods. No scaling or pluggage in the venturi absorber has been encountered despite almost conti-

nual operation of this equipment in a recycle mode during the duration of the operations at the Mystic Station.

Centrifuge System

A bleed from the absorption system (Figure 3) enters the centrifuge where the solids in the slurry are separated and the centrate is returned to the absorption system. This bleed stream is controlled to maintain a constant solids content in the recycle slurry and to remove product magnesium sulfite and any unreacted magnesium oxide and precipitated magnesium sulfate. The system is operated so that the absorbed SO_2 is removed as an equivalent amount of magnesium sulfur compounds. A Bird solid bowl centrifuge is used to dewater the solids preparatory to drying. Except for a few isolated incidents of shear pin breakage, this item of equipment has operated satisfactorily, yielding 50% or greater removal of the solids in the slurry bleed stream.

Dryer System

The wet centrifuge cake containing magnesium sulfite, magnesium oxide and magnesium sulfate plus carbon and other solids removed in the venturi absorber-centrifuge system is passed to a rotary counter-current dryer to remove both unbound water and water of crystallization.

The dryer with its associated feed conveyor and product conveying system has been the most frequent cause of the operational difficulties which have caused shut-down of the complete system. The problems encountered have ranged from an initial complete carry-over of dryer product into the off-gas due to excessive dryer gas velocity to an inability to convey the dryer product resulting from auxiliary equipment breakdown. In order of occurrence these problems and their subsequent solutions have been:

1. Total carryover of dryer material in the exit gas stream.

The dryer was designed to process a material of much greater crystal size than encountered in actual operation. High draft resulted in a gas velocity which exceeded the pneumatic transport velocity of the dried material. Dryer action placed all of the dryer inventory in the air stream. All lifter flights were modified or removed in order to reduce internal dusting in the dryer. Normal operating draft

was reduced from a design of 1" to a range of 0.1" to 0.01" (this caused subsequent problems in draft control).

2. Adherence of centrifuge cake to dryer walls causing plugging of the dryer. This was caused by a change in the consistency of the centrifuge cake from a dry, fine sand-like material to a wet, fluid mud-like material. Increasing exit gas temperatures to increase feed end surface temperatures resulted in granulation of the feed (this problem of adherence was a recurring one and was associated with other properties of the centrifuge cake as described in later sections).
3. Granulation of the dried material resulted in a nonuniform product. Many of the granules were several inches in diameter and jammed product materials handling equipment. The cross screw conveyor and weigh belt at the top of the product silo were bypassed and a lump crusher was installed at the boot of the bucket elevator to reduce the size of any large granules to 1" or less.
4. Disintegration of the hydrated crystal during drying caused excessive production of "fines" (Figure 4). Heavy loading of fines in the dryer off gas caused excessive carryover of particulate matter from the cyclone emission control equipment installed with the dryer. Dryer off-gas was ducted to introduce it to the venturi absorber after initial clean up in the cyclones. The venturi absorber, operating at a five inch pressure drop across its throat provides satisfactory particulate emission control of the dust carryover from the dryer. Further complications were anticipated as the dryer off-gas was expected to furnish 15⁰F of reheat to the saturated flue gas after sulfur oxide removal. With the dryer gas now diverted to the inlet of the absorber during normal operations, it now enters the stack at saturation temperature. To date no raining or pre-

cipitation from the stack has been noted despite exit gas velocities of nearly 80 ft. per second. A careful watch is being kept over this part of the operation and initial design of a reheat system has been completed should it be needed.

5. Dust accumulation on a baffle installed over the spill back bin of the dryer built up to restrict the flow of gas from the dryer. Initially, this material was manually pushed from the shelf. Recently the feed screw conveyor has been lengthened to introduce the centrifuge cake further into the dryer and a dust collection system was installed to transport dust accumulated in the spill back bin to the product silo, allowing removal of the baffle.
6. Addition of cyclone underflow to the centrifuge cake fed to the dryer caused setting of the centrifuge cake accompanied by fouling of the screw and overloading of the dryer feed conveyor motor. Cyclone underflow was diverted from the feed screw conveyor; recently a dust collection system was installed to remove cyclone underflow to the product silo.
7. Operation with recycled MgO caused a reoccurrence of dryer feed sticking on the dryer walls which eventually plugged the dryer. It is felt that this was caused in part by a higher percentage of unreacted MgO in the centrifuge cake due to inadequate slaking of the recycled MgO produced in the early reclamation attempts. Continued efforts to improve the quality of the recycled MgO in the calcination facility, installation of "knockers" on the dryer feed end, provision for heating the MgO slurry tank to improve the slaking of the recycled MgO (Table 1) appears to have eliminated this problem.

Magnesium Oxide System

The anhydrous magnesium sulfite and magnesium sulfate produced in the dryer is conveyed to a storage silo before transportation by truck to the recovery acid plant. The same transportation facilities are used to return regenerated magnesia to the magnesium oxide silo at the power plant. No problems of pluggage of these silos has been encountered to date. The measured rate of rehydration of the magnesium sulfite on standing in the atmosphere is relatively low, Figure 5. The "lump" crusher installed upstream of the silo allowed the passage of very large pieces (1-1/2" x 2"). These pieces proved difficult to handle in the pneumatic trucks and Rumford's conveying system. A scalping screen was installed in the truck loading chute and oversize material is conveyed to the load-out belt by additional conveying equipment.

Recycled alkali absorbent and make up magnesium oxide are fed with water to an agitated tank where a slurry is prepared for introduction to the recycle system manually on pH control. Numerous pluggage problems were traced to tramp material entering at this point including granules of magnesium sulfite not completely removed from the truck in the transport operation. Initially, system protection was provided by interposing a vibratory screen at the discharge of the weigh belt feed. Eventually the necessity to slake the recycled MgO at higher temperatures in order to increase its reactivity required the addition of an MgO tank equipped with seal legs to prevent steaming in the weigh house. This device now serves as a "tramp" materials trap.

Calcination System

The dry product transported from the power plant is received, weighed and pneumatically conveyed to a storage silo. It is fed to a direct fired rotary calciner at a metered rate, and calcined to generate sulfur dioxide gas while regenerating magnesium oxide. Coke can be added to provide a reducing atmosphere to reduce the residual magnesium sulfate to MgO and sulfur dioxide. The hot flue gas containing sulfur dioxide and MgO dust enters a hot cyclone where essentially all the MgO dust is returned to the calciner. The flue gas then enters a venturi scrubber for final MgO dust cleaning. At the same time the gas is cooled and adiabatically saturated.

At the Essex Chemicals installation, the resultant product from the recovery of the sulfur dioxide is 98% sulfuric acid. The saturated flue gas is cooled in a direct contact cooler to meet the requirements of the acid plant water balance. The cleaned, cooled flue gas then directly enters the drying tower of an existing 50T/D acid plant.

The regenerated magnesia is cooled, conveyed to the magnesia storage silo and recycled back to the power plant site for reuse.

As would be expected in a plant of this complexity numerous operating problems occurred. These problems and their solutions were:

1. Excessive leakage at the seals of the rotary calciner preventing the attainment of the required neutral or reducing atmosphere. All seals had to be remachined to provide minimum clearances. Careful attention was required to see that all view and instrument ports are closed during operation. Finally a new seal was designed and installed to completely correct the problem.
2. Granular nature of dryer product caused material handling problems which required the installation of heavy duty belts on weigh feeders to prevent ripping of the belts.
3. Balancing the draft requirements of the calcination facility and acid plant caused "puffing" at feed hood and weigh house. Modification of the gas exit transition of the calciner to provide smooth gas flow was one of the steps taken to reduce pressure loss.
4. Gritty nature of calciner product caused unreactivity in reuse at Boston Edison. Installation of pulverizing equipment to provide a grind of 100% thru 100 mesh and 70% thru 325 mesh proved satisfactory.

5. Tramp materials in calciner product caused breakage of pulverizer. Installation of magnetic separator and vibrator screen at screw conveyor discharge eliminated this.
6. Severe dusting in calciner obscured flame, tripping flame safety controls and interrupting operations. Installation of secondary "flame scanner" and extension tubes partly alleviated problem. Eventual employment of full time operator on the firing platform during operation reduced the number of shutdowns.
7. Inability to use coke. Initial charge of coke received was off specification, and contained 47% ash. Fear of contamination of the calcined product and the acid plant precluded its use. For several months the calcining facility was operated without the introduction of additional carbon and attempts were made to adjust the fuel ratio to compensate; this resulted in a harder "burn" of the product magnesium oxide. Finally a coke of less than 10% ash was substituted and coupled with the improved operations detailed above produced dramatic results. A comparison of the two cases is given in Table 2.

DESCRIPTION OF INSTALLED FACILITIES

Boston Edison's Mystic Station located in Everett, Mass. is presently comprised of six oil-fired power generating units having a total rate capacity of 619 MW. All units are equipped with electrostatic precipitators which are presently de-energized as the station burns fuel oil exclusively instead of coal. An additional unit which will be nominally rated at 600 MW is now under construction.

The Chemico/Basic Magnesium Oxide System is operated on Unit No. 6 of this installation. This unit has a rated capacity of 150 MW and was placed in commercial operation in May 1961. The boiler is a Combustion Engineering controlled circulation unit with a rating of 935,000 pounds per hour continuous

capacity at 2,150 psi max. The unit burns 9700 gallons per hour of No. 6 fuel oil at full rated capacity. Design criteria for the scrubber installation are given in Table 3.

PROCESS CHEMISTRY

Magnesium oxide is introduced into a mixing tank with water where conversion to the hydroxide commences. This mixture is added to the recycle stream of the venturi absorber where it is contacted with the entering flue gas containing sulfur oxides. The reaction between these two components produces principally magnesium sulfite, some of which is oxidized to magnesium sulfate. Conventional representation of the chemical reactions is shown in Figure 6.

A better representation of the postulated reaction mechanism shown in Figure 7 which indicates that the formation of the magnesium sulfite proceeds thru the reaction of magnesium ion in solution and sulfite ion in solution. The product of this reaction is a salt of low solubility (MgSO_3 solubility 15 gm/liter versus MgSO_4 solubility of nearly 1800 gm/liter). As mentioned in the previous section a bleed stream is sent to a centrifuge where the crystalline magnesium sulfite is removed in a quantity sufficient to balance the incoming sulfur oxides, while the centrate (a slurry containing magnesium sulfite nuclei) is returned to the absorption unit.

Upon initiation of operations from a cold start, a major change in the consistency of the centrifuge cake takes place after a period varying from 8 to 16 hours. The cake changes from a dry, fine sand-like consistency to a thin mud. Quantitatively, during the initial period the centrifuge cake may contain as much as 65% crystals of size 40 to 80 micron while in operations after the first several hours the particle size of the centrifuge cake is less than 15 micron.

It was also determined that the state of hydration of the crystalline magnesium sulfite varied between these two conditions. The larger particle size material was associated with a higher percentage of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ while the centrifuge cake containing more of the finer crystals contained approximately equal amounts of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. The distribution of this latter case is shown in Table 4.

Initially, the slurry had been held at 120°F for several days with no flue gas scrubbing. The complete absence of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in the slurry confirms that at temperatures above 110°F only $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ is stable, and the hexahydrate formed has a metastable existence.

The proposed mechanism for this phenonema is shown in Figure 7. The existence of the $(\text{Mg} \cdot 6\text{H}_2\text{O})^{++}$ coordinate ion is known and has been identified by infrared spectroscopy. Apparently this material dehydrates in solution at elevated temperatures to form the trihydrate. A proposed alternate path shows the formation of the coordinate ion $(\text{Mg} \cdot 3\text{H}_2\text{O})^{++}$ which may combine directly to form $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$.

In the system as currently operated, the compounds crystallize as distinct entities. The magnesium sulfite hexahydrate as a rhombic crystal and the trihydrate of the same salt crystallizes as a trigonal pyramid.

Operating difficulties have been associated with this transition of the centrifuge cake. However, adherence of dryer feed to the dryer walls has also occurred while drying a centrifuge cake containing 40 to 80 micron size crystals. Dryer heat load is not adversely affected by the transition during start-up as the $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ contains half as much water of crystallization as the hexahydrate and therefore an equivalent amount of unbound moisture can be removed in the dryer without affecting process economics.

A comparison between the average stream analysis obtained during operations with virgin magnesia and recycled regenerated MgO produced prior to sustained coke introduction is given in Table 5. Recent operations incorporating all the improvements outlined thus far have shown a return to a stream analysis similar to that for virgin MgO; most importantly, a reduction in unreacted MgO in the centrifuge cake to 1.4% instead of the higher average value indicative of hard burned magnesia.

FUTURE INSTALLATIONS

With limited operation of the plant and lack of data on the effect of repeated recycle of the absorbing alkali it is difficult to determine what other modifications might be incorporated in a new plant. Based on the initial operating experience at Boston Edison's Mystic unit it appears that future installations should have additional "lump breakers" and screening equipment located at

at strategic points in the plant. These should be installed at the MgO tank in the absorber recycle stream at the dryer product discharge and the magnesium sulfite storage silo discharge.

The type of centrifuge cake encountered up to the present time could be handled readily in a dryer of different design. A dryer incorporating internal chains, external rappers, lowered gas velocity and provisions to reduce the internal dust recycle would be suitable.

The calcining facility should incorporate pulverizing equipment of more robust design in order to ensure more continuous operation with a grind suitable for reuse in the absorption system.

POTOMAC ELECTRIC POWER CO. - DICKERSON #3

The previously mentioned provisions have been incorporated into the pollution control facility currently being constructed for Potomac Electric Power Co. This plant is a coal fired unit and the venturi absorption system has been designed to handle the flue gas equivalent to 100 MW from the boiler (Figure 9).

Flue gas containing SO₂ and fly ash passes into the first stage of a two stage venturi scrubber where fly ash is removed using recirculated water as the scrubbing media. A bleed stream from the scrubber is thickened to concentrate the fly ash as a slurry underflow which is pumped to a disposal area. Overflow from the thickener is returned to the scrubber circuit for reuse. A bypass flue gas duct has been installed around the precipitator to the scrubber absorber. This will allow the introduction of clean flue gas containing little fly ash into the first stage. Dampers have been provided in these ducts which will allow the scrubber absorber to handle either flue gas partially cleaned in the precipitators or flue gas coming directly from the air preheaters. Thus the operation will provide the means of evaluating wide ranges of particulate emissions on the magnesia slurry system for the design of new plants and retrofit systems.

Flue gas leaving the particulate removal system enters the second stage of the two stage venturi where it is contacted with the aqueous slurry containing magnesium oxide, magnesium sulfite and magnesium sulfate and from that point follows the process description of an oil fired magnesium oxide system.

In addition to the incorporation of additional size reduction equipment in this operation the principal difference is in the design of the dryer for the system. The dryer supplied is a co-current unit, equipped with flights of internal chains, some external rappers, toothed lifter flights and a diameter sufficient to reduce the gas velocity to one half that obtained at the Mystic Station.

While it is anticipated that any additional advantages incorporated at Boston Edison will be added to the Potomac Electric facility it appears at this time that they will be minor ones.

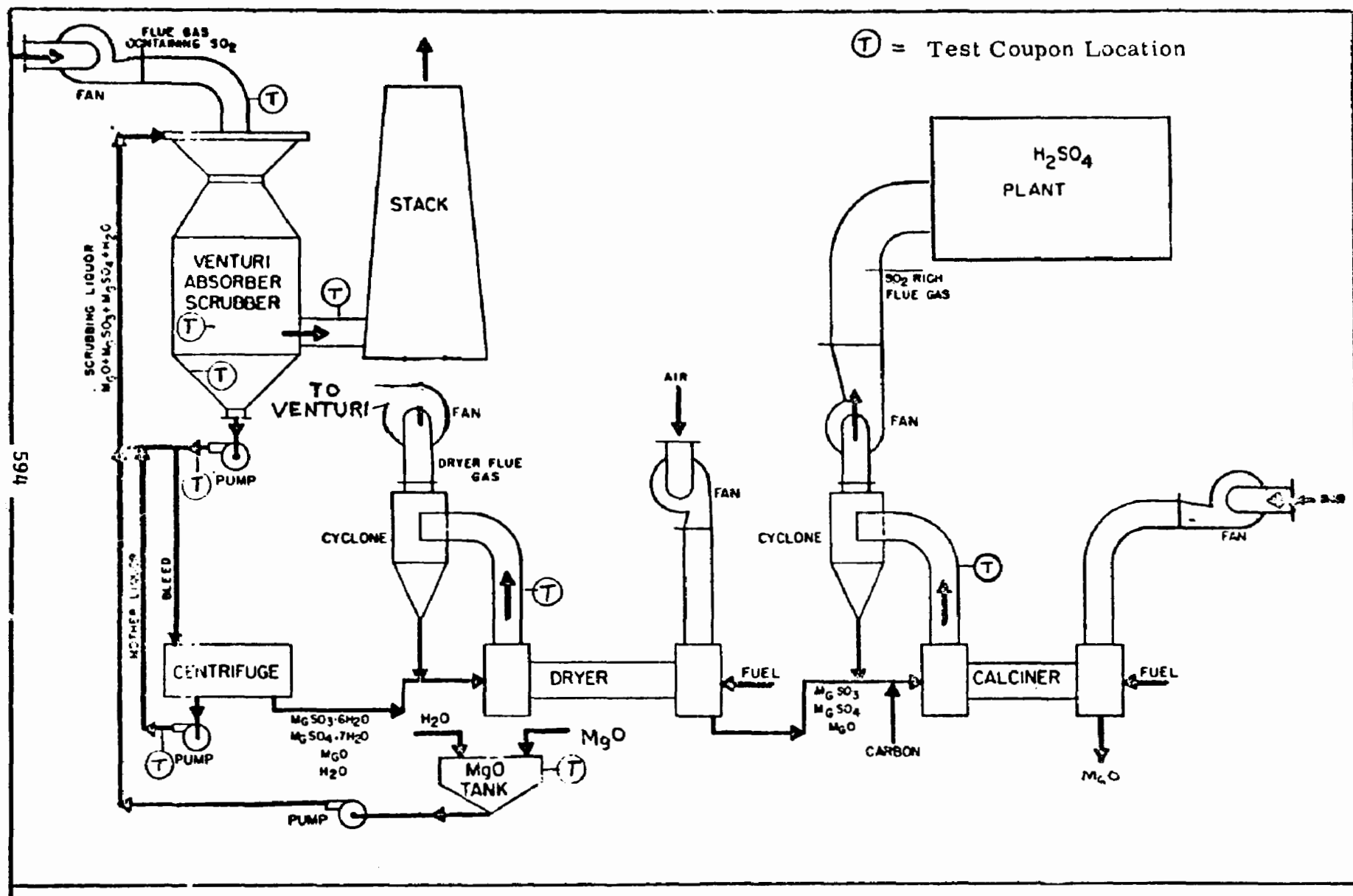


FIGURE 1

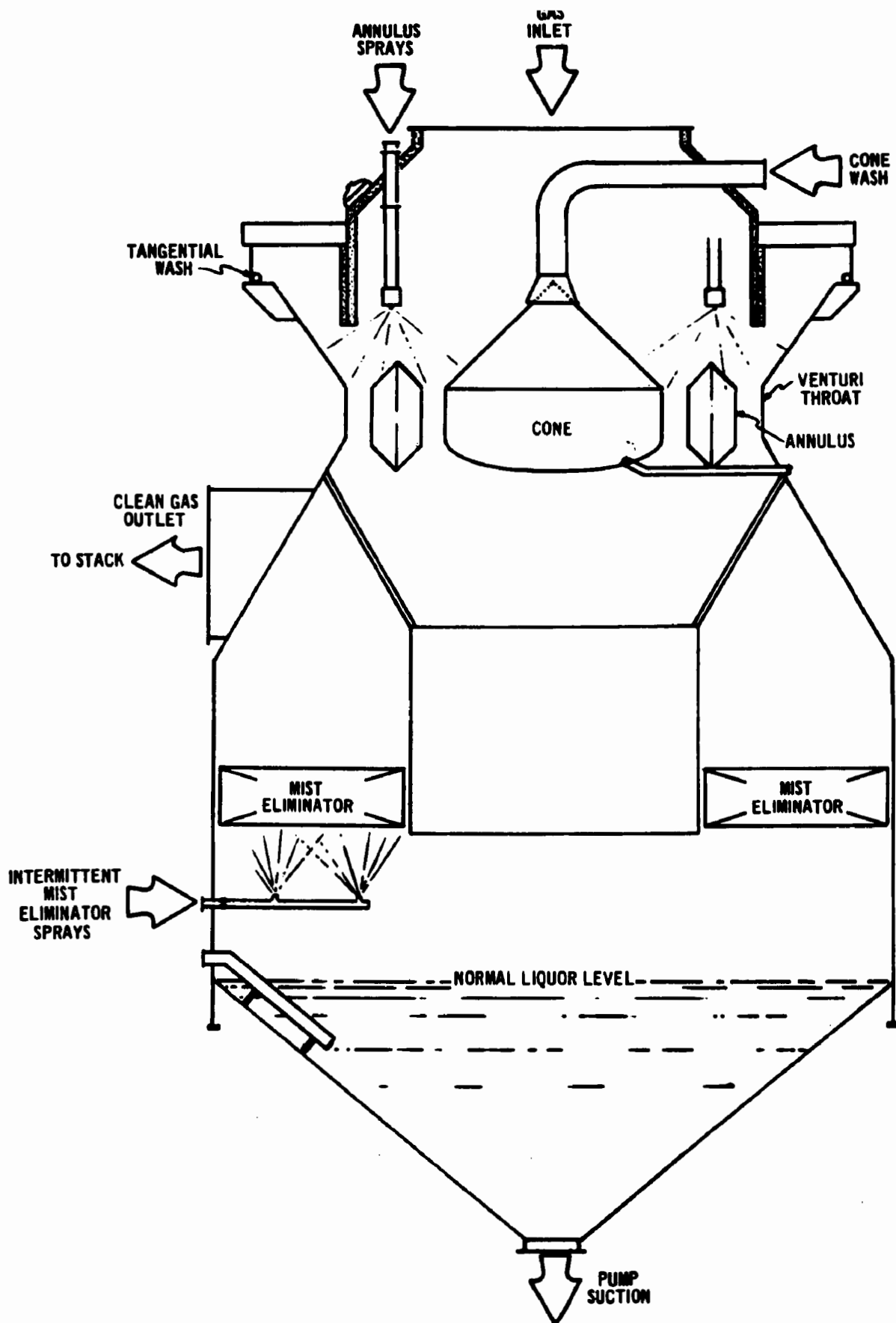


Figure 2. Sectional view of absorber at Boston Edison Company, Boston, Mass.

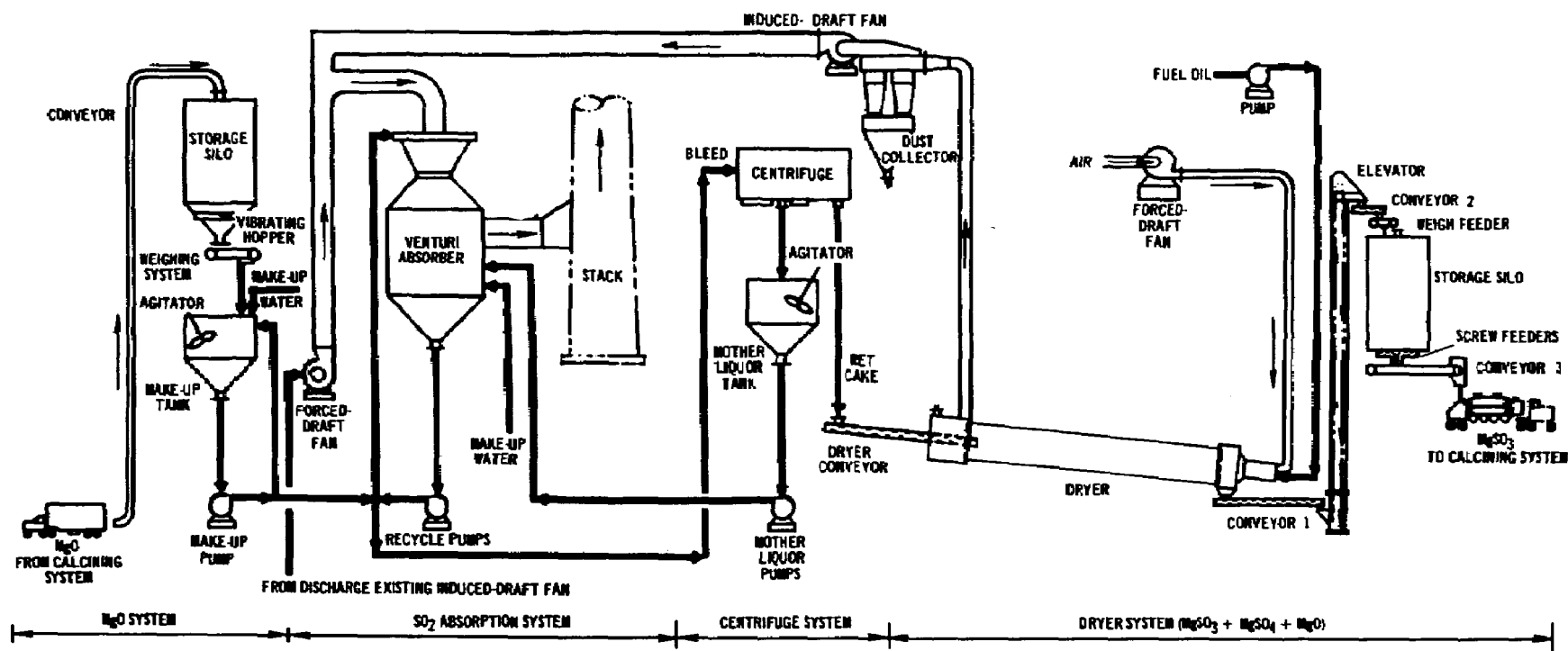
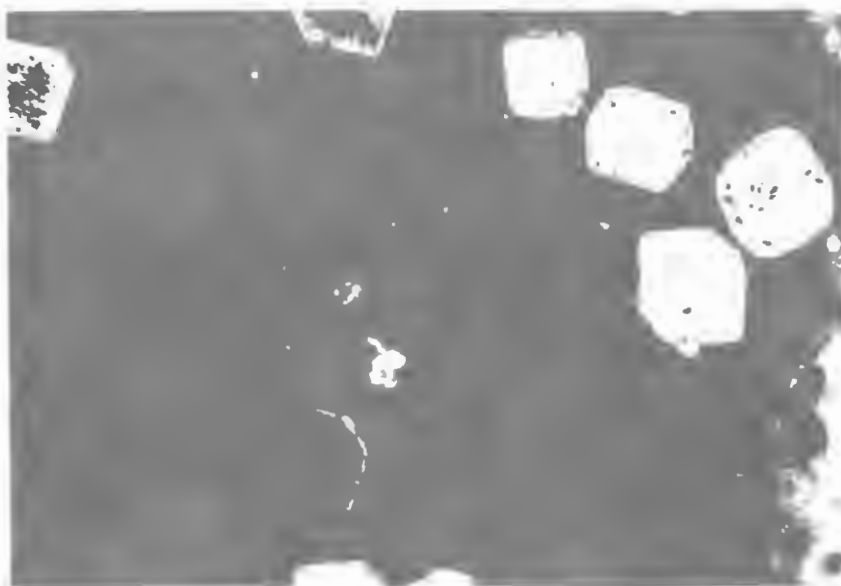
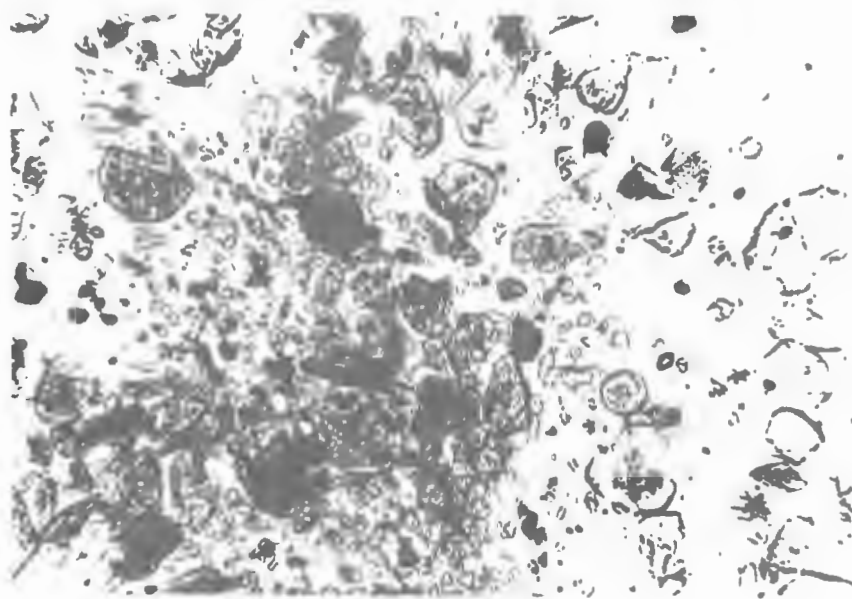


Figure 3. Process flow diagram for magnesia slurry SO_2 recovery system at Boston Edison Co., Boston, Mass.



$\text{MgSC}_3 \cdot 6\text{H}_2\text{O}$ Crystals - plus 200 mesh fraction
100X



Anhydrous MgSC_3 - plus 200 mesh fraction dried
100X

Figure 4

865

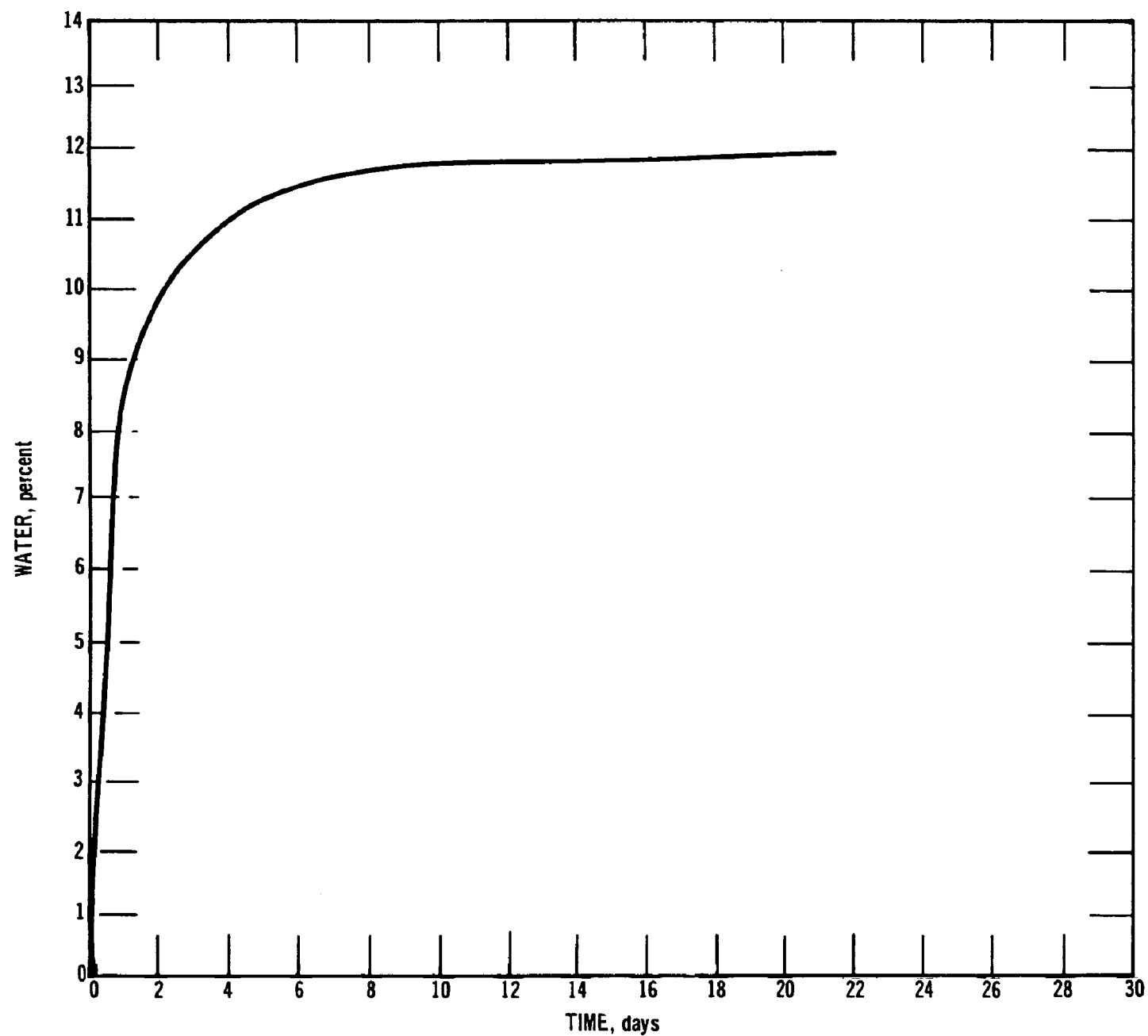


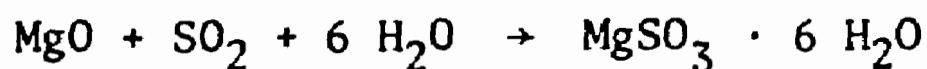
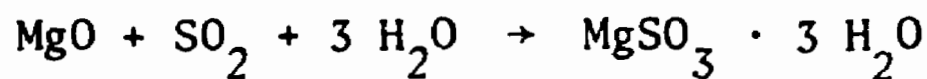
Figure 5. Percent water absorbed by anhydrous MgSO_3 on exposure to air.

CHEMISTRY OF MAGNESIA SLURRY SO_2

RECOVERY PROCESS

ABSORPTION

MAIN REACTIONS



SIDE REACTIONS

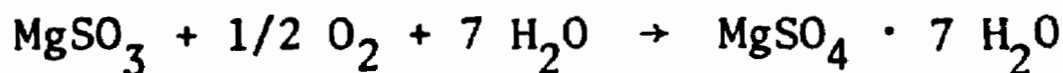
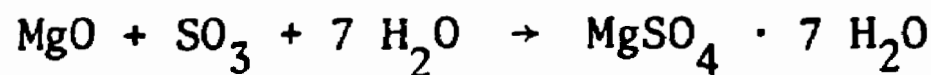
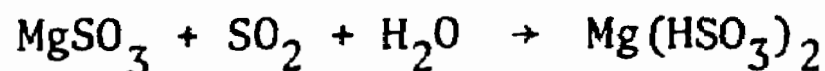


Figure 6

POTOMAC ELECTRIC POWER CO. PROTOTYPE
PRECIPITATOR/SCRUBBER - ABSORBER
MgO ADDITIVE SYSTEM FOR SO₂ RECOVERY

SCHEMATIC PROCESS FLOW SHEET

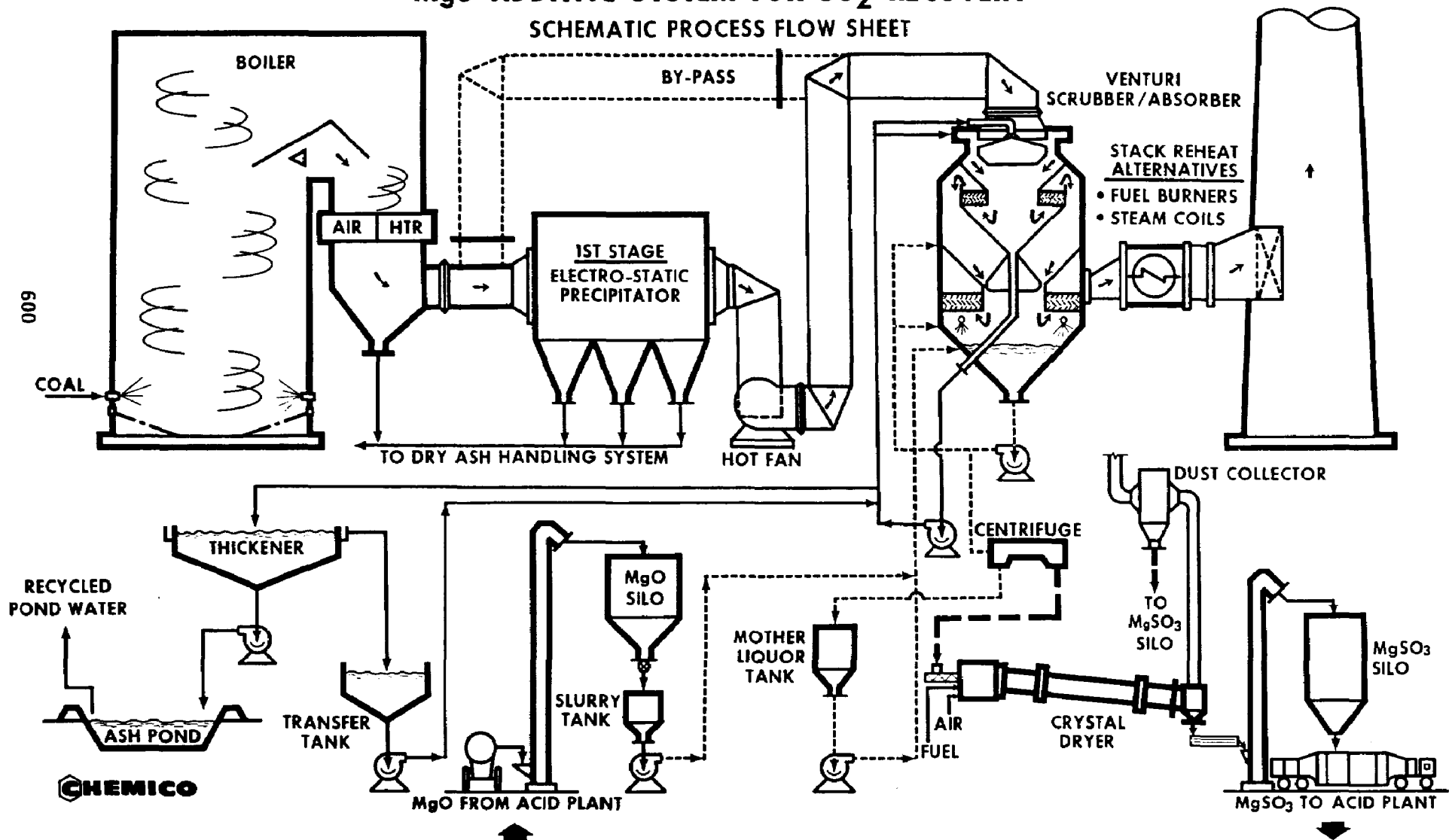


TABLE 1

Effect of slaking temperature on recycle MgO utilization

Slurry Tank Temperature	MgO Bulk Density	Unreacted MgO in Centrifuge Cake
58° F	34.4 lb/ft ³	17%
108°	34.4 "	5.4%
180°	32.3 "	1.4%

TABLE 2

Effect of coke addition (4 day continuous operation with coke feed interrupted for 12 hours.)

	Product Bulk Density	SO ₂ Rating
With coke addition	24.7 lb/ft ³	55.4
Without coke addition	68.2 lb/ft ³	21.9

Table 3

UNIT NO. 6 SO₂ RECOVERY SYSTEM

OPERATING CRITERIA

GAS FLOW, ACFM	425,000
GAS TEMPERATURE, °F	300
DRY GAS, LB/MIN	21,369
WATER VAPOR, LB/MIN	1,620
SO ₂ , LB/MIN	63.2
FLY ASH, LB/MIN	0.91
SO ₂ , PPM (DRY BASIS)	1,410
FLY ASH, GR/SCFD (DRY BASIS)	0.0228
FUEL OIL, CONSUMPTION, GAL/HR	9,700
FUEL OIL SULFUR CONTENT, %	2.5

Table 4 OBSERVATION OF CRYSTAL SPECIES DISTRIBUTION

Sample	% Solids	‡ 200 Mesh (Vol. %)	Composition (%) - 200 Mesh			% Moisture	
			MgSO ₃ Tri	Hex	MgSO ₄	Centrifuge Cake	Dryer Product
07202-05-AT08	4.39	0	100			20	8
07202-09-AT08	6.52	0.65	50	50			
603 07202-11-AT08	8.03	1.45	51	34.6	4.4	12	
07202-14-AT08	8.82	1.05	56	24.3	6.4	16.2	
07212-02-AT08	6.25	0.65	43.3	40.9	4.0	14.0	24
0712-06-AT08	6.3	0.55	49.5	36.5	6.2	18.0	13

Table 5 STREAM ANALYSISSO₂ Abatement System, Mystic Station #6

<u>Average Compositions (%)</u>		
	Fresh MgO Feed	Recycle MgO Feed
Slurry		
<u>Solids</u>	10.8	11.9
MgO	6.2	6.83
MgSO ₃	55.51	59.61
MgSO ₄	5.0	2.34
<u>Filtrate</u>		
MgSO ₄	16.54	10.8
Centrifuge Cake		
<u>Solids</u>	85.0	88.0
MgO	1.36	5.55
MgSO ₃	57.85	58.03
MgSO ₄	4.12	2.59
<u>Centrate</u>		
Solids		3.67
Dryer Product		
<u>Solids</u>	87.2	95.66
MgO	2.6	
MgSO ₃	84.63	88.17
MgSO ₄	14.7	7.68
Acid Insoluble		0.55

OPERATIONAL PERFORMANCE OF THE
CHEMICO MAGNESIUM OXIDE SYSTEM
AT THE BOSTON EDISON COMPANY
PART II

by

Christopher P. Quigley
Boston Edison Company
Boston, Massachusetts

This paper is Part II of a two part paper and supplements Part I of this paper being presented by Mr. G. Koehler of Chemical Construction Corporation.

OPERATIONAL PERFORMANCE OF THE
CHEMICO MAGNESIUM OXIDE SYSTEM
AT THE BOSTON EDISON COMPANY
PART II

C. P. Quigley

INTRODUCTION

The magnesia scrubbing system on Boston Edison Company's Mystic Unit #6 has now been in operation for over a year. From the utility company's point of view we consider the results obtained to date to be a combination of successes and failures.

Success has been achieved in that the process has been demonstrated chemically. The scrubber can consistently remove high levels of SO_2 from the flue gas. The sulfites produced have been successfully calcined at the acid plant. The SO_2 liberated in the calciner has been used to make 98% commercial grade acid. The regenerated magnesium oxide has been reused successfully in the scrubber for short periods of time. Further, the scrubber itself has remained free of the scaling and plugging problems that have so seriously hindered the development of calcium scrubbing systems in this country.

In spite of these successes in demonstrating the chemistry of the process on this large scale, the equipment and the process have failed to demonstrate a reasonable availability commensurate with power plant equipment needs. In this first year, total scrubber operating time has not exceeded 1200 hours. Availability has been a very low 17% of the Unit #6 operating hours. The longest sustained run has been four and one half days. On regenerated magnesium oxide, the longest run has been limited to two days.

OPERATING EXPERIENCE

Process Chemistry

Of the problems encountered in the past year, the most serious have been

1) related to the crystal size produced in the scrubber, 2) the inability to date to

line out the calciner operation so as to produce an acceptable absorbent in terms of sulfate content and magnesium oxide reactivity and 3) the scaling of dryer internals currently occurring when scrubbing with recycled magnesium oxide. These problems are addressed in detail in a supplement to this paper presented at this symposium by Mr. George Koehler of the Chemical Construction Corporation.

Beyond these process problems, other problems have occurred although they must be considered relatively minor and more readily correctible in nature. The following outlines some of the experience with equipment components during this initial running period.

Corrosion/Erosion Experience

The equipment components and piping of the scrubbing system are fabricated mainly of carbon steel. Therefore, considerable attention was paid to corrosion control. The internals of the scrubber and the flue gas ductwork have been coated with corrosion resistant materials. pH of the slurry is maintained normally above 7.0 with only a few short duration tests being conducted at about 6.0 during the year. A few excursions to 4.5- 5.0 pH have occurred for very short periods.

The internals of the scrubber and the flue gas ductwork leaving the scrubber have been coated with a spray-applied polyester lining. This lining has stood up well. Erosion has been noted only at the leading edge of the venturi annulus. This annulus is subject to direct impingement by slurry crystals on its relatively sharp-edged top surface. Some metal wastage has occurred where this coating has been eroded. A cladding of the top surfaces of the annulus ring with stainless steel should correct this problem.

The flue gas ductwork to the scrubber has been protected with a 1" lining of a corrosion inhibiting gunite. During this first year, no corrosion of this ductwork has been experienced although the uncoated fan casings of the new scrubber booster fans were corroding severely in the same environment. Subsequent guniting of these fan casings has eliminated this problem.

Viton expansion joints were installed in the flue gas ductwork as a corrosion protection measure and have stood up well to date.

Severe corrosion/erosion of cast iron pump impellers occurred in the slurry recirculating pumps. These impellers required replacement within the first six months of intermittent operation. New 316 stainless steel impellers have been installed and show no corrosive attack at this time.

Ring header piping at the top of the absorber feeds slurry to several tangential wash nozzles above the venturi throat. Piping in this header has experienced heavy wall thinning at points where slurry sharply changes flow direction, such as at reducers and at tees. Several leaks have resulted requiring maintenance welding. No metallurgical evaluation has yet been made to determine the cause but erosion due to slurry impingement is believed to be responsible.

Scaling and Plugging Experience

A small ring of scale has deposited at the interface between the entering flue gas and the slurry liquor at the top of the scrubber. This scale deposit has been too small to affect the flows of slurry or flue gas and does not appear to increase in size. No maintenance work for removal has been required. The remainder of the scrubber, a rather open vessel and the demisters have shown no evidence of scale or deposit buildups. The pressure drop across the demister has not increased since initial operation.

Scale like deposits have been experienced in dead end legs of magnesium oxide recirculating piping. This occurrence resulted when steam piping used for freeze protection was activated this winter. It is believed that over heating of this static slurry accelerated hydration and resulted in the buildup of hard scale-like deposits plugging the line. Provisions for rodding at pipe ends and provisions for bleed piping to prevent static slurry buildups have been installed.

Slurry settling to the bottom of inactive vertical discharge lines at the slurry recirculating pumps resulted in plugging of these lines. The material deposited and built up at the closed pump discharge valves. Small bleed piping was

installed above each valve to a point of lower hydraulic pressure at the common suction header to the pumps. The problem has been alleviated somewhat by providing a continuous flow path for the settling slurry. In addition, when the system is shutdown, one of the recirculating pumps is operated continuously to move the slurry in the recirculating lines.

The tendency of the centrifuged wet cake to scale has been the process phenomena that has inhibited continuous operation of the scrubber system. Hard scale deposits in the centrifuge, the ribbon conveyor feeding the dryer and the dryer itself have plagued this installation.

Hardened scale deposits left in the centrifuge after shutdown have caused repeated shear pin failures and centrifuge motor overloads on startups. Provisions to backwash the centrifuge were installed and the centrifuge is washed at each shutdown. The problem is still present but appears now to be manageable.

Both rubber housings and steel housings have been tried with relatively poor results in an effort to cope with scale deposits in the dryer feed conveyor. This conveyor continues to be a high maintenance item and a source of many system shutdowns.

The scaling in the rotary dryer of course has been the greatest problem of all and until resolved, a sustained run of this plant cannot be achieved.

Winter Conditions

Winter operation pointed out deficiencies unique to cold weather operation. Freezing and failure of steam traps on steam tracing lines, freezing of control air lines because of inadequate air drying equipment and discomfort for operator and maintenance personnel required to work for long periods on equipment outdoors had to be faced.

Miscellaneous Problems

Flue gas dampers are installed to isolate the scrubber from the gas path to the stack. These dampers are driven by pneumatic power drives. Several occasions of sticking dampers have been experienced and on three occasions,

misoperation of these dampers resulted in an unsafe condition in the boiler requiring emergency tripout of the unit. New more powerful damper drives are about to be installed. In the meantime, operating procedures are in effect to assure proper damper operation so as to prevent the cutoff of a flue gas path to the stack by the failure of dampers to operate.

Spillage and Housekeeping

The conveying and handling of the magnesium sulfite and magnesium oxide material, much of which is of dust size, the removal of scale buildups in the dryer, the occasional spillage of slurry through the scrubber overflow line, and the bleeding of plugged piping have all contributed to a continuing housekeeping problem and an excessive maintenance cost relative to cleanups.

Operation Staffing

Operation at Mystic has been staffed by two Edison operators on a 24 hour basis. Chemico has supplemented this force with one man coverage around the clock for operational guidance and test purposes.

Operation at the calciner facility is covered by two Essex Chemical operators and by one Chemico operator per shift.

Operating Costs

Edison operating costs for the first year of the test and demonstration program at Mystic Station are now projected to be \$525,000. This projection is based on accrued costs for the first eight months and estimated costs for the remainder of the year.

Of these costs, \$235,000 are for Edison operating labor, \$240,000 are for Edison and invoice maintenance labor and materials and \$50,000 are for metered services to the scrubber system such as water, power and fuel.

These costs are heavily unbalanced because of the low operating hours and the many problems encountered during this first year.

A substantial part of the operating labor and maintenance invoice costs are related to cleanup work associated with the dryer scaling and material spillage

problems. These costs would be substantially reduced if the scaling problem were solved and the system was operable for reasonable periods of time.

Maintenance costs, although only 2% of plant investment, must be considered excessive in view of the few operating hours. At this time, we do not have sufficient operating experience to accurately project annual maintenance costs.

The cost for services would increase four fold for the fully operable plant but must be considered high based on actual operating time. This is due to the use of power and fuel through much of the plant standby period this past year.

Magnesium Oxide Requirements

MgO makeup requirements can not yet be ascertained. A sustained run of both plants for at least a few months will be required to get meaningful data in this area.

Operating Constraints On Boiler

There have been no constraints placed on the operation of this unit by the addition of the scrubber system. Whether the scrubber is in service or not, the unit can continue to operate. Through use of a bypass damper system, the scrubber can be put into and taken out of service without influencing boiler operation. When the scrubber is operating, high sulfur residual oil is burned in the boiler. By simple valving, the boiler is changed over to a low sulfur oil supply before the scrubber is taken off the line.

Modifications Dictated By Operating Experience

The following features in hindsight would be of value if available on this prototype:

1. Tank for draining scrubber system, tank to be equipped to assure slurry will stay in suspension.
2. Clean outs at pipe bends and dead ends so as to facilitate rodding lines.
3. Provisions for continuous flow in slurry lines which are valved closed.
4. Careful design of piping to eliminate high velocity impingements of slurry at tees, ells and reducers. Careful selection of piping materials to provide greater erosion resistance when required.
5. Strategic location of crushing systems to handle magnesium sulfite slags.

6. Strategic location of screening and/or crushing equipment to handle contamination of feeds in transport, etc. that have contributed to plugging problems.

LARGE SCALE SCRUBBING STUDY

A recent estimate of the cost to install and operate scrubbers at Mystic Station has been made (Figs. 1 & 2). Under this scheme, four units totaling 1050 MW would be equipped with magnesium oxide scrubbing systems and would burn 2.5% S residual fuel oil. A separate estimate for calciner operating costs was made (Fig. 3). The overall economics of scrubbing and calcining as compared to the present requirement of burning 0.5% maximum sulfur content fuel oil (Figs. 4 & 5) clearly shows a large economic advantage to scrubbing.

Scrubbing costs equate to \$1.00 per barrel of fuel oil burned (\$0.16 per million Btu). Present cost differential between low and high sulfur oil is twice this amount and savings in excess of \$7,000,000 per year are potentially available to our customers who now pay these costs through a fuel adjustment clause.

OVERVIEW

At this writing, we are still attempting to get this process on-stream for a continuous operating period. A continuous run is required to successfully level out the calciner operation. A continuous run is required to develop cost data for the process. A continuous run is required to demonstrate that the process has the reliability necessary for adaptation to power plant equipment.

We are confident that the dryer scaling problem will eventually be overcome. It should be susceptible to solution by equipment modification or by equipment replacement. We are hopeful that a solution to this scaling problem will then result in continuous operation of both plants so that refinement of operation, in particular operation of the calciner, can then be accomplished. Many of the problems now encountered would be eliminated as they relate directly

to our inability to keep the equipment running.

Further, we are confident that this process represents some of the most promising technology today and if successfully developed can assist many utilities who are in a position to combine their operations with a chemical operation for disposal of the SO₂ by-product.

FIGURE 1

Preliminary Estimate
Capital Investment Requirements for
MgO Scrubbing of Stack Gas SO₂ at
Mystic Station

<u>Scrubbing Systems</u>		<u>Capital Investment</u>	
Unit #	MW		
4	150	\$ 2,000,000	
5	150	2,000,000	
6	150	2,000,000	
7	600	<u>5,000,000</u>	
			\$11,000,000
MgSO ₃ Centrifuging, Drying			3,300,000
MgO Storage			400,000
MgSO ₃ Storage			700,000
Media Preparation			100,000
Initial MgO Charge			300,000
 <u>Other Capital Costs</u>			
Services to Battery Limits		\$ 500,000	
Foundations		1,000,000	
Site Work		250,000	
Edison Direct Engineering		<u>250,000</u>	
			<u>2,000,000</u>
Total Capital (1972 \$)			\$17,800,000
Less Existing Unit #6 Base Unit			<u>(2,000,000)</u>
Total Additional Capital			15,800,000
Escalation to 1976			4,200,000
Contingency			<u>1,000,000</u>
Total Additional Investment			\$21,000,000

FIGURE 2

Annual Owning and Operating Costs for
MgO Scrubbing Systems at
Mystic Station

Basis: Mystic Units #4, #5, #6, #7 = 1,050 MW

Fuel Oil Usage = 7,300,000 bbls/year @ 2.5% sulfur

SO₂ removal equivalent to 0.3% sulfur fuel oil

Capital Investment = \$21,000,000

Fixed Charges	\$3,100,000
Maintenance	800,000
Labor	200,000
Supervision	100,000
<u>Utilities</u>	
Electric Power	800,000
Fuel Oil	400,000
Water	100,000
MgO Make-Up	<u>250,000</u>
Total Annual Owning and Operating Cost	\$5,750,000

FIGURE 3

Annual Operating Costs
Calcining Plant

Capital Investment:	\$4,500,000	
Amortization		\$ 450,000
Interest		200,000
Maintenance		200,000
Insurance and Taxes		150,000
Labor + Supervision + Overhead		200,000
General Administration		70,000
<u>Utilities</u>		
Electric Power		50,000
Water (Process, Cooling)		5,000
Fuel Oil		300,000
Chemicals		<u>25,000</u>
Subtotal		\$1,650,000
Management Fee		<u>250,000</u>
Total Annual Operating Cost		\$1,900,000

FIGURE 4

Overall Economics
MgO Processing of Flue Gas SO₂
Annual Operating Costs

MgO Scrubbing	\$5,750,000
Calcining	1,900,000
Transportation	<u>80,000</u>
Gross Scrubbing Costs	7,730,000
Sulfur Credits	<u>400,000</u>
Net Scrubbing Costs	<u><u>\$7,330,000</u></u>
Cost/bbl fuel oil	\$1.00

FIGURE 5

Estimate of Annual Savings
Scrubbers at Mystic Station

Annual Fuel Usage (bbls.)	<u>7,300,000</u>
Annual Cost - LS oil (\$4.70/bbl.)	\$ 34,300,000
Annual Cost - HS oil (\$2.70/bbl.)	<u>-19,700,000</u>
Gross Fuel Savings/yr.	14,600,000
Annual Scrubber Costs	<u>- 7,300,000</u>
Net Annual Scrubber Savings	7,300,000

DESIGN AND INSTALLATION OF A PROTOTYPE
MAGNESIA SCRUBBING INSTALLATION

by

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INTRODUCTION

The design and installation of this prototype magnesia scrubbing installation represent an action of the Philadelphia Electric Company to cope with the problem of stack gas emissions at its Eddystone Generating Station. Although the topic of major interest here today is the removal of SO_2 from flue gas, at Eddystone there was a problem of removal of particulates as well. Because of this and other complications, Philadelphia Electric chose to follow the procedure described in this paper rather than to purchase any package system being offered for SO_2 removal.

The design which will be described here is the result of engineering work by Philadelphia Electric and their Architect-Engineer, United Engineers and Constructors Inc. It had the following three main goals:

1. Build a prototype SO_2 removal system with a capacity equivalent to a 120 megawatt unit.
2. Add equipment which would achieve reduction in the emission of particulates.
3. Minimize the possibility that the operation of this prototype SO_2 scrubber would affect the availability of Eddystone No. 1 to generate power.

This design was based on solid engineering principles which were applied to known chemical process work involving magnesium oxide.

All of this makes it necessary to describe some of the characteristics of Eddystone No. 1, the station to which this magnesia scrubbing

system is being retrofitted. Eddystone No. 2, which is similar to Eddystone No. 1 in general size and some other characteristics, will also have scrubbing units retrofitted to it after the successful operation of this prototype. Both stations burn coal averaging about 2.5% sulfur, 8 to 12% ash and 13,500 Btu/lb. heating value.

Eddystone No. 1, which went into service in November 1959, has a nameplate rating of 325 Mw, but a generating capacity of 360 Mw. Steam conditions are 5000 psi and 1150°F, with two reheats at 1050°F. This pressure and temperature are the highest used in any power station in the U.S., and, as far as we know, in the world. It is a matter of considerable difficulty to start up or to shut down this station. Accordingly, it was essential that special care be taken to prevent any upset condition in the scrubber from reflecting on the generating unit itself. A lot of flexibility was engineered into this scrubbing unit.

The space available for the scrubbing system was severely limited. It was a factor the engineering team always had to keep in mind, and had an effect on the number and sizes of the parallel scrubbing trains. When complete, this overall installation will have essentially three scrubbing trains for each 360 MW boiler unit through which the stack gases from Eddystone No. 1 and Eddystone No. 2 can be passed. Elaborate ducting will permit various combinations of these scrubbing lines to be used. Although particulate scrubbers, ducts and valving will be installed for all three trains for Unit No. 1, only one complete scrubbing line, i.e., both particulate and SO₂ scrubbing, equivalent to 120 MW will be installed in this first phase.

The Eddystone station is exactly in line with the main runways used by jet aircraft at the Philadelphia Airport, and only a few miles away. Obviously no unusual plume could be tolerated. Even if we could have convinced the environmentalists that this steam is harmless, the safety consideration would require that a plume be avoided.

The best approaches to papers for oral presentation with slides, and papers in written form, are not entirely consistent. In order for slides to be read at all by people in the back of the room and to be understood in the short length of time they can be shown, they must be kept very simple. As an aid to describing this process to you, several ultra-simple slides have been prepared. They are included in the written text, because they may help clarify some points, but mostly because the figures had to be prepared anyway. Also, in the written there is provided a process flowsheet with a material balance. It was not originally prepared for this type of use, and there really is given much too much information for the space available. Still, with a low power magnifying glass, you can read it.

Finally, let me repeat that this is not a stripped down plant. In all aspects, the engineering reliability was placed ahead of cost. There are several items of equipment which we might not put in a second generation plant. There is more than liberable interstage storage.

We hope to put this prototype scrubber into operation during the fall of 1973.

PROCESS DESCRIPTION

Humidification and Particulate Removal

Eddystone No. 1 is equipped with mechanical collectors and electrostatic precipitators upstream of the induced draft fans. The collection efficiency is about 93%. This is no longer good enough and the plant design was required to provide for particulate removal as well as SO₂ removal.

Obviously, one approach to additional particulate removal was the installation of wet scrubbers. An early design question was whether to install a separate wet scrubber from the SO₂ scrubbing system or to combine the functions. Clearly the scrubbing device which we have in mind for SO₂ removal would remove enough particulate matter to bring the station into compliance with regulations.

The decision was reached to provide a separate venturi-type wet scrubber using only water for the removal of particulates and for the humidification of the stack gas. There are several reasons for this decision. First, it was expected that the humidification of the stack gas prior to bringing it into contact with any chemical scrubbing medium might assist in avoiding plugging problems. Second, it has been established that some components of fly ash such as vanadium and iron compounds can catalyze the oxidation of magnesium sulfite (MgSO₃) to magnesium sulfate (MgSO₄). The presence of some sulfate in the scrubbing system is, of course, unavoidable because some of the

SO_2 is oxidized to SO_3 before it reaches the scrubber. Nevertheless, it appeared desirable to hold down the quantity of this complicating sulfate as much as possible. Third, there is no easy way to eliminate fly ash from the circulating scrubbing slurry. A blowdown stream might be taken, but this would cause a large loss of magnesium and would add to the solids disposal problem. Finally, there is the matter of general system reliability. In the present design, if difficulties in the operation of the SO_2 scrubber are encountered, particulate removal can be continued by simply by-passing the SO_2 scrubber.

A price was paid for this decision. Not only is there the capital cost of the first scrubber in which only water is used as a scrubbing medium, but there is a serious operating cost. The consumption of electrical power for the entire scrubbing system was almost doubled by the use of this first stage wet scrubber.

SO_2 Scrubbing Step

A fundamental feature of the process being installed at Eddystone is that the chemical compound which reacts in the scrubber to bind the SO_2 is not MgO , or $\text{Mg}(\text{OH})_2$, but MgSO_3 . MgSO_3 reacts with H_2O and SO_2 to produce $\text{Mg}(\text{HSO}_3)_2$. As you know, MgSO_3 (more properly $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ in this system) is not very soluble in H_2O . Accordingly, it is actually used as an approximately 10% slurry of crystals in a dilute solution of $\text{Mg}(\text{HSO}_3)_2$, with a pH of about 6.

On the other hand, $\text{Mg}(\text{HSO}_3)_2$ is very soluble. Thus, the fundamental chemical reaction which occurs in the scrubber tower results in the conversion of a slightly soluble material to a very soluble material. This approach offers a good possibility of avoiding the problem of plugging in the scrubber tower.

A price may be paid for this feature, because the equilibrium vapor pressure of SO_2 over a slurry of MgSO_3 in a slightly acid dilute solution of $\text{Mg}(\text{HSO}_3)_2$ is higher than that for a slurry of MgO or $\text{Mg}(\text{OH})_2$ in H_2O . Accordingly, it is possible that removal of SO_2 from stack gases will not be quite as effective in the Eddystone plant as if an alkaline slurry were used. Precise equilibrium values in the concentration range of interest are not available to us. From the curve relating scrubbing efficiency to the acidity of the scrubbing slurry in a particular experimental unit under consistent operating conditions, it can be seen that the difference between SO_2 removal at a pH of 6 and at pH 8 is not very great.

The equipment in which SO_2 is removed from the stack gases is a commercial device manufactured by Environeering, Inc. known as a Ventri-Rod unit. A simplified sketch of this contactor is shown. Essentially there are two scrubbing stages. In each a slurry of magnesium sulfite is sprayed upward, co-current with the stack gas, through openings between cylindrical rods. A venturi-like effect similar to a fountain is obtained as the streams flow between these rods, assisting in the contacting between the stack gas and the slurry of magnesium sulfite.

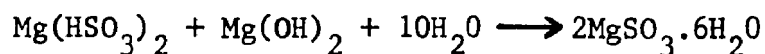
Mist is eliminated by the use of backwash sprays of water onto louvers in the top section of the scrubber.

This scrubber has an overall height of fifty-three feet. It is rectangular in shape, fourteen feet six inches by twenty-five feet.

Magnesium sulfite slurry is circulated to it at a rate of 13,400 gpm, or 133,800 lb/min. The humidified gas rate is 268,000 actual cubic feet per minute or 17,300 lb/min. giving an L/G of 50. This high slurry-to-gas ratio is designed to minimize concentration changes across the SO₂ scrubbing system proper, and to insure a rather constant acidity of the scrubbing medium.

Mg(HSO₃)₂ Neutralization

In the scrubber surge tank the following reaction occurs:



Here we have the first formation of a slightly soluble material. By carrying out this reaction in a large agitated tank - its capacity is 60,000 gallons - having a hold up time of four minutes, any plugging problems should be held to a minimum. The temperature in this tank where the neutralization occurs is close to 129°F, a condition under which the hexahydrate is formed. At higher temperatures the trihydrate can form. Its crystals tend to be smaller than those of the hexahydrate, and might cause more handling problems.

The pH of the slurry in this surge tank is controlled at 6 by regulating the rate of addition of $\text{Mg}(\text{OH})_2$ slurry.

MgSO_3 Recovery

The recovery of the $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ formed in scrubber surge tank is begun by diverting a drag stream from the main scrubber circulation loop. It flows first to a thickener. Here, again, is a piece of equipment which may not be absolutely necessary. The conclusion to include it was based on the desirability for more surge capacity in the recovery portion of the plant and the prospect for improved centrifuge operation.

The thickener has a diameter of forty feet, and a straight side height of twelve feet. It receives 1975 lb./min of slurry containing 165 lb./min $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. The underflow from the thickener going to the centrifuge contains about 25% $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$.

In the stainless steel solid bowl centrifuge, a cake of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ crystals wet with a solution of MgSO_4 is recovered. These wet crystals of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ are discharged from the centrifuge, through a vertical chute into a screw feeder which provides a seal and a continuous flow of wet solids, into a rotary kiln type dryer. Combustion gases from an oil burner, tempered by a side stream of stack gas from the first induced draft fans, flows co-currently with the crystals. Anhydrous MgSO_3 is discharged from the dryer and conveyed to the storage silos.

Some MgSO_4 will also, of course, be present.

Regeneration of MgO

For this prototype facility, the MgSO_3 will be trucked to a sulfuric acid plant about twenty miles from Eddystone. There it will be heated in an oil-fired fluidized bed reactor to decomposition. The MgO formed goes overhead with the SO_2 and the combustion gases, from which it will be separated by cyclones. The stack gas is cleaned up by a combination venturi and a packed scrubber tower before being admitted to the sulfuric acid plant itself.

The selection of an optimum temperature in this fluidized bed regenerator represents a compromise. On the one hand it is desired to reduce the MgSO_4 to MgSO_3 and to insure the substantially complete decomposition of MgSO_3 to MgO and SO_2 , both of which are favored by higher temperatures. On the other hand, excessive temperatures will produce "dead burned" MgO which is not very reactive chemically and is thus not really effective for further SO_2 removal. The final operating temperature for this stage has not been selected, but will probably lie in the range of $1650^\circ - 1750^\circ\text{F}$. Fluidized bed reactors are particularly well suited to precise temperature control. They also allow for precise control of oxygen in the reactor which eliminates the necessity of adding oxygen scavengers such as carbon to the bed so the MgSO_4 can be decomposed.

The regenerated MgO will be trucked back to Eddystone for re-use. For a prototype operation, this sort of thing can be tolerated. For a full

scale operation at a major generating station, however, this trucking will not be practical. The sulfuric acid plant should be located at the station site.

Stack Gas Reheat

When the stack gas emerges from the SO_2 scrubber, its temperature is about 130°F and it is substantially saturated with water vapor. To avoid a billowy white plume from the stack as this mixture emerges and water condenses, some kind of reheat is necessary. In this retrofit unit at Eddystone, the practical way to accomplish this was to install an oil burner mounted directly in the flue gas duct leaving the SO_2 scrubber.

Close to one million Btu/hr. will be required for every one $^\circ\text{F}$ of reheat for the total output of Eddystone No. 1 (all three final scrubbing lines). The fuel cost alone will be close to \$5000 per year per $^\circ\text{F}$ of reheat. Obviously, the amount of reheat used will be held to a minimum, depending on local conditions.

ECONOMICS

Capital Cost

The best estimate we can make now is that the total capital cost for this version of a magnesium oxide scrubber is in the range of \$55 - \$65 per kilowatt. This is for a new unit. For a retrofit, you should add about \$15 per kilowatt.

Of this basic cost, \$45 - \$50/KW is for the scrubbing unit itself. About \$10 - \$15 is for the facility to convert MgSO_3 to MgO for recycle and to carry the liberated SO_2 on to concentrated sulfuric acid. Our thought is that the sulfuric acid plant should be located adjacent to the power station. The hauling of MgSO_3 and MgO to and from a distant regeneration facility and sulfuric acid plant can become very expensive.

This operation of a sulfuric acid plant in conjunction with a power station is not something that will bring universal happiness. To the power station staff it will be an utter nuisance. Its presence may become an upsetting factor in the local sulfuric acid market. This acid which is produced has got to go somewhere, at whatever price can be obtained for it. Moreover, the acid plant which will ultimately be built at Eddystone will be distinctly below the best economic size, since it will have a daily capacity of only about 350 tons. At present, in the Delaware Valley, we do not see any overriding problem in this regard. This brings us on to the matter of operating costs.

Operating Cost

We estimate that the overall operating cost of the final facility at Eddystone, including the scrubbing unit itself, the MgO regenerator and the sulfuric acid plant, will lie between 1.3 and 1.4 mils per kilowatt hour. The factors going into this estimate are as follows:

Fuel cost	\$0.70/MM Btu
Power cost	7 mils/KWH
Fixed charges	15% of capital/yr.
Maintenance	3% of capital/yr.

It was further assumed that there will be a loss of MgO of 5% per cycle. This is probably a very conservative estimate, but in the absence of operating experience, it appeared best to include it.

The operation of this scrubbing facility as described earlier, with a wet scrubber ahead of the SO₂ scrubbing unit, will consume approximately 3% of the power generated by the station. If the wet scrubber were eliminated, power consumption would drop to about 1.75%.

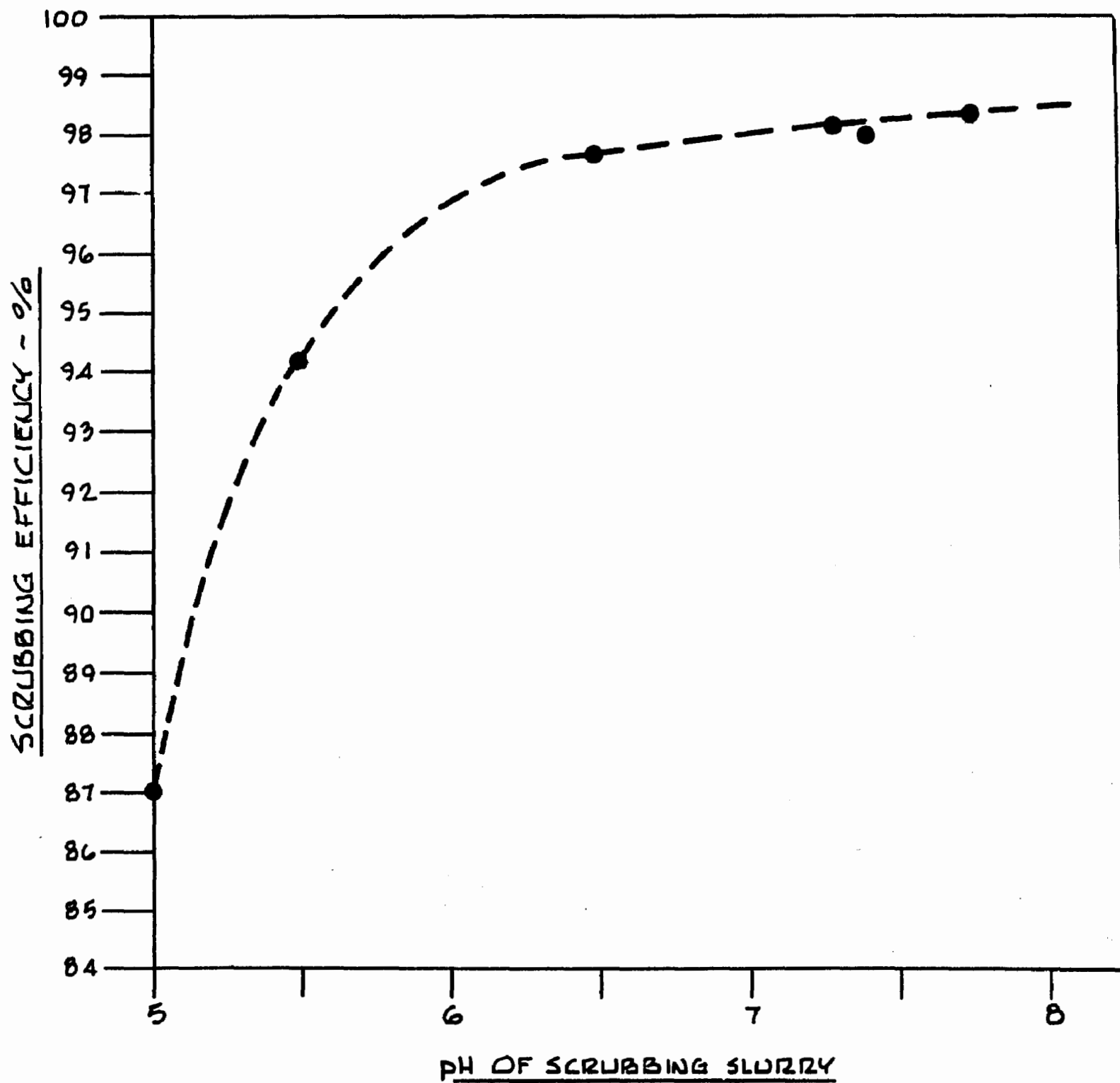
REACTION IN SCRUBBER

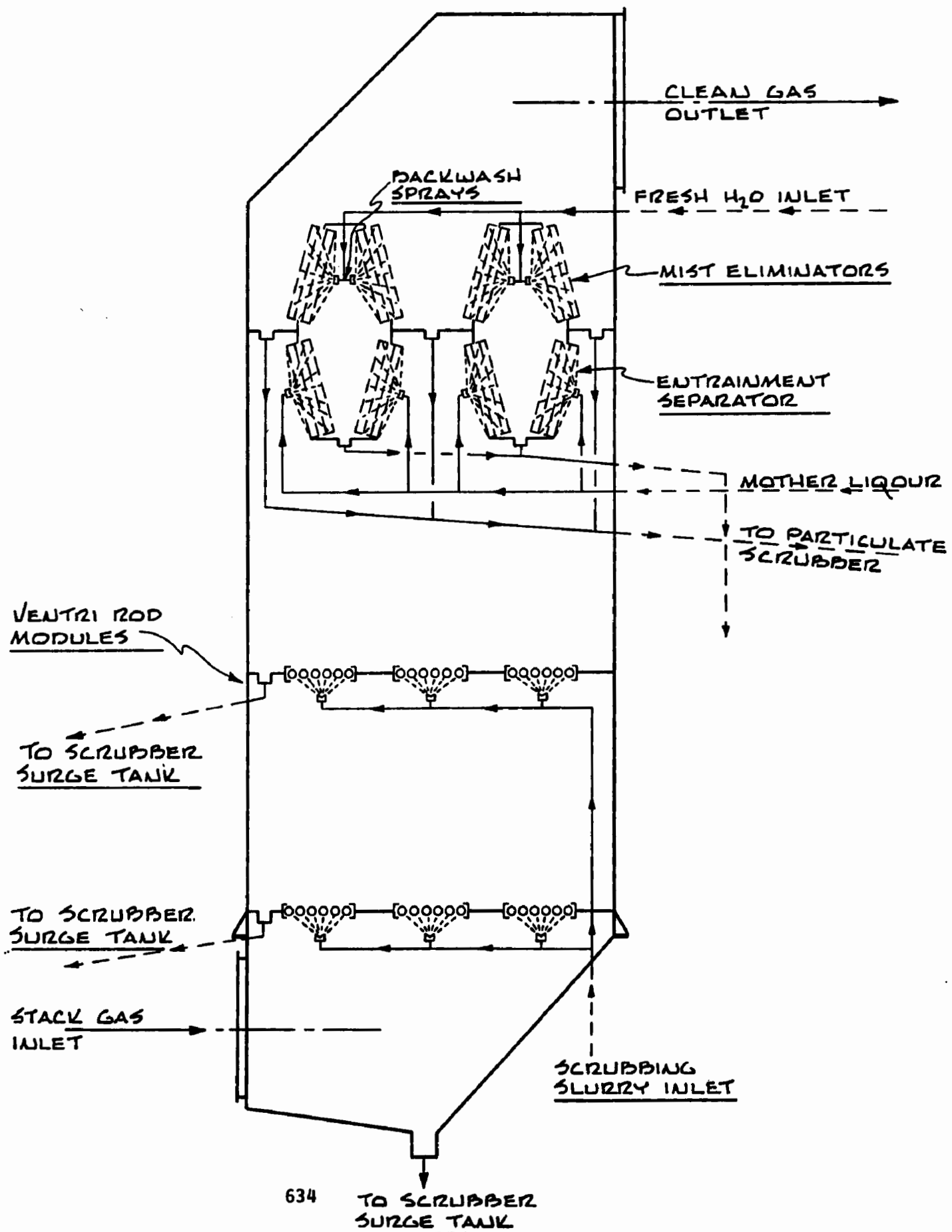
632



SO₂ SCRUBBING EFFICIENCY VS PH

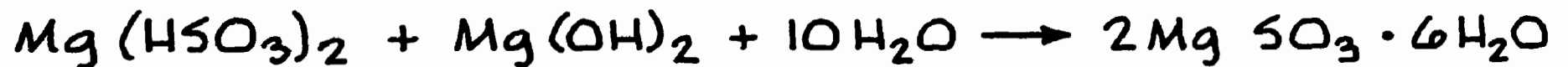
MAGNESIUM SYSTEM

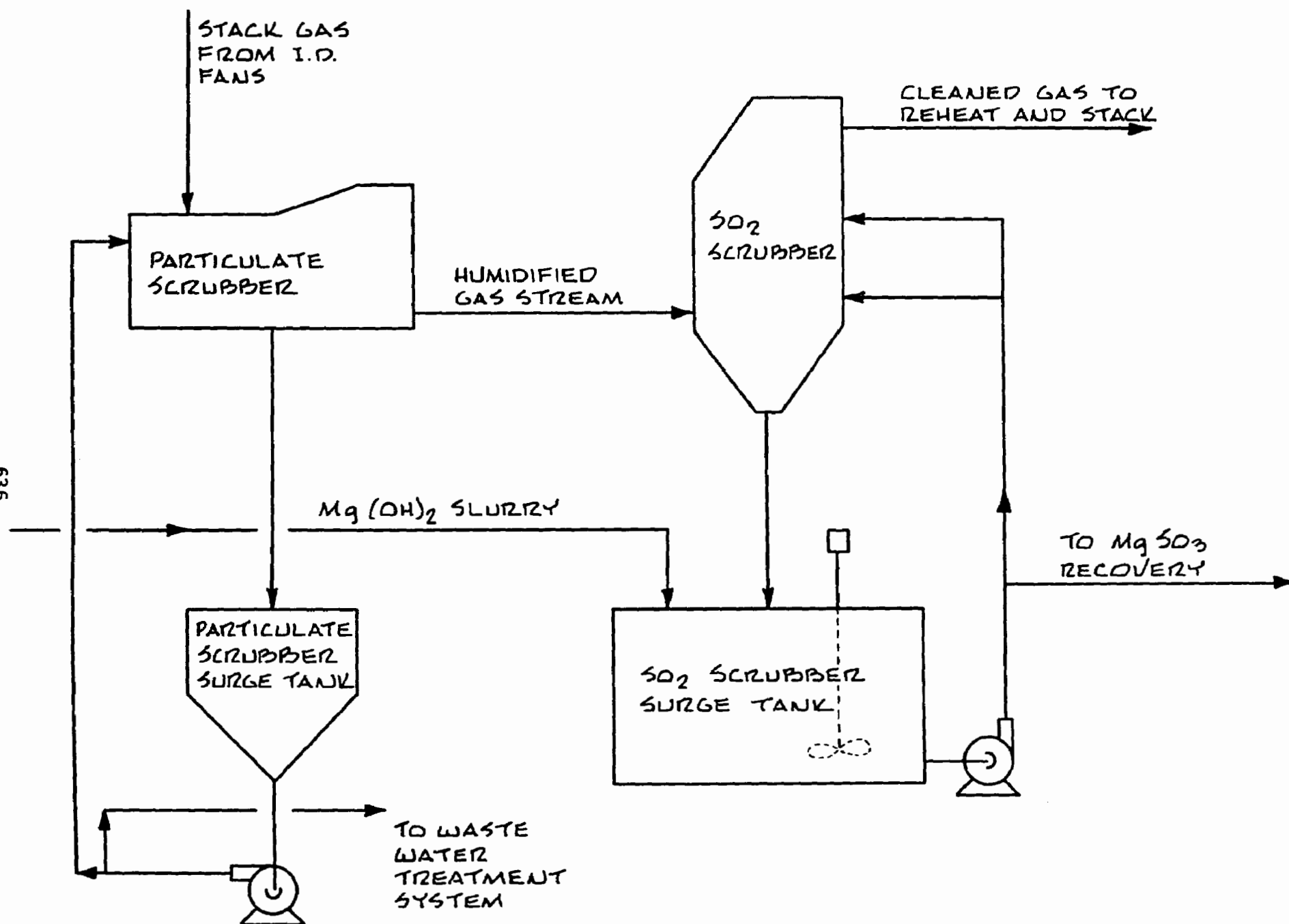


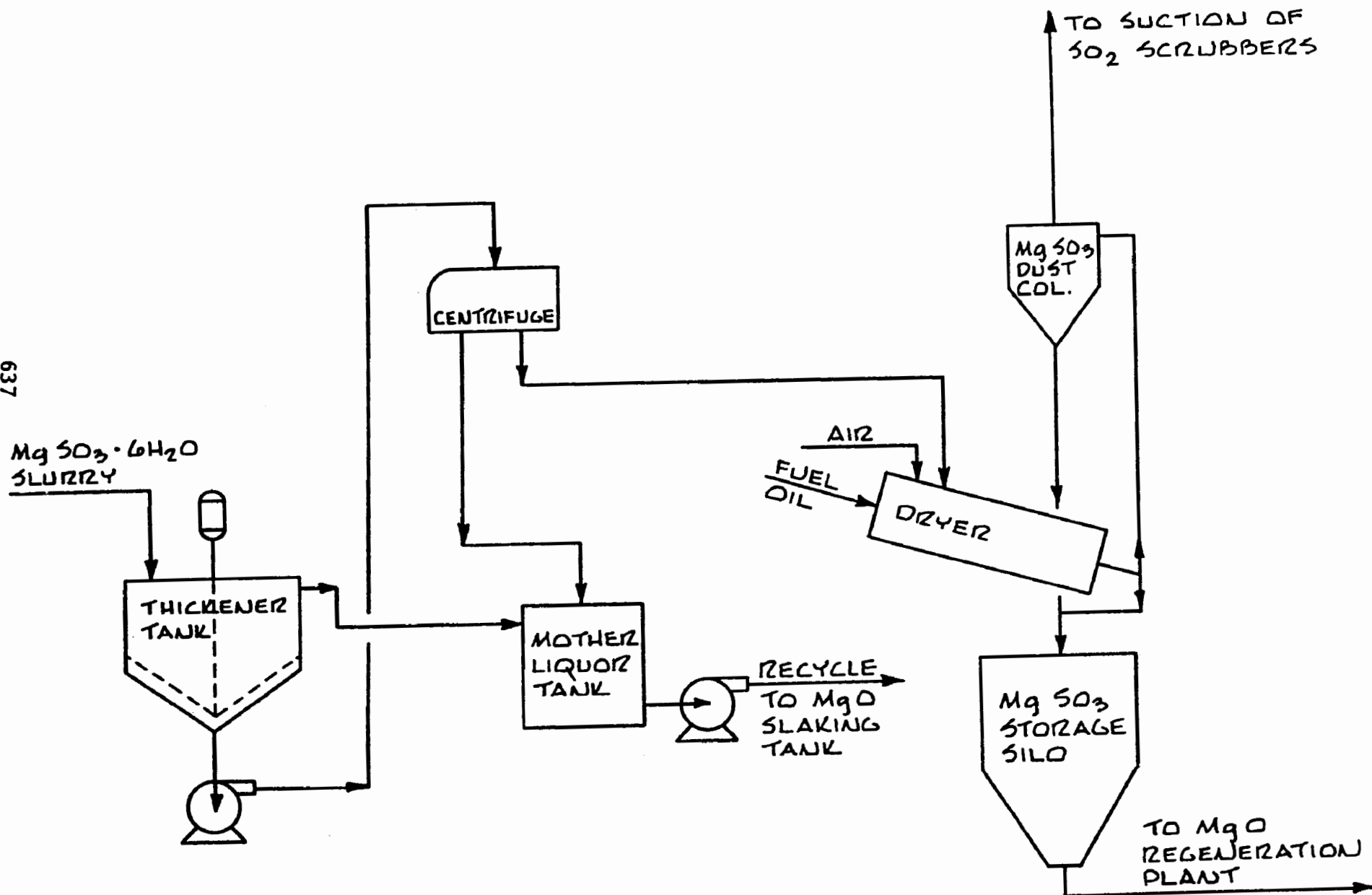


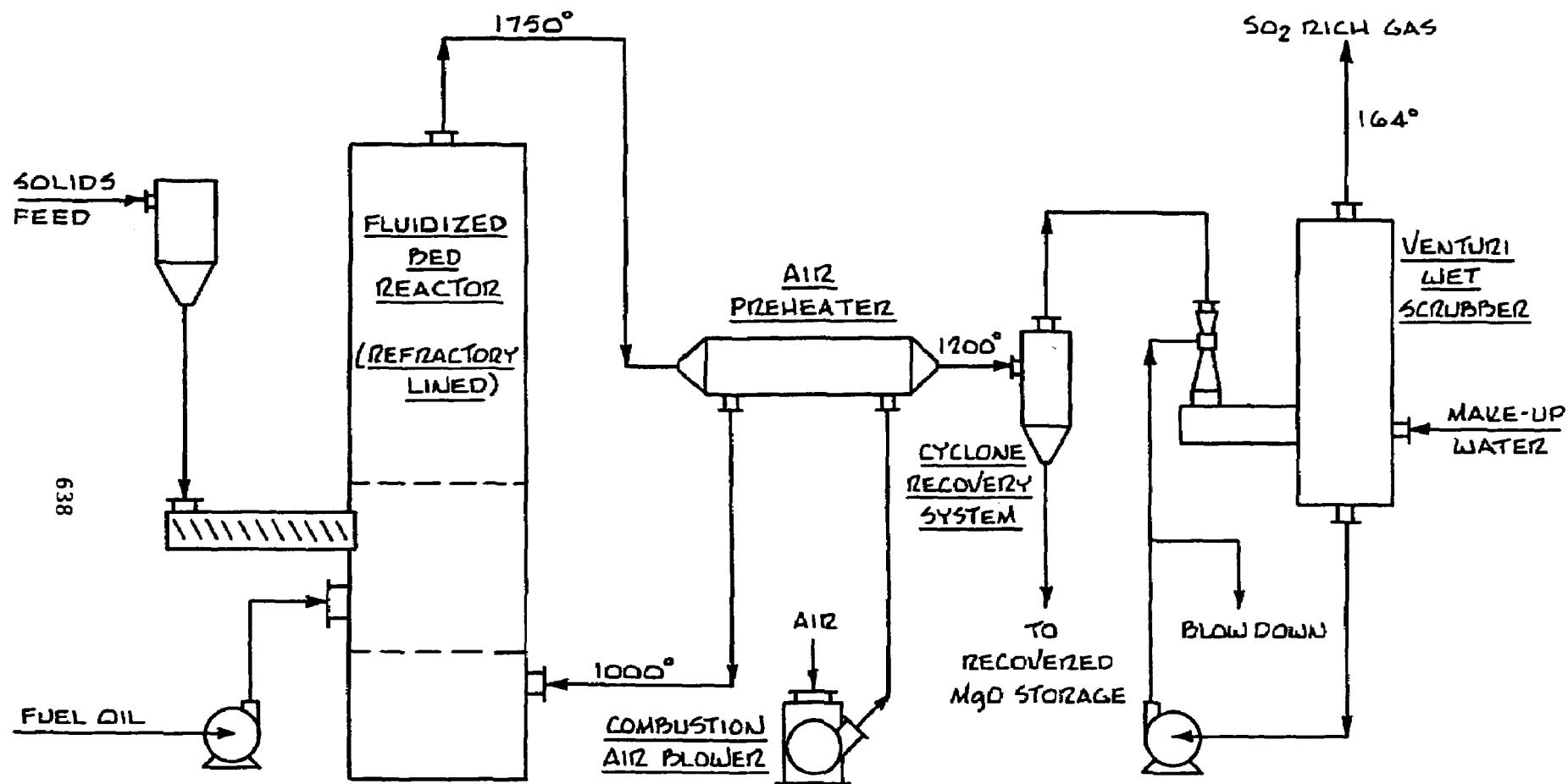
REACTION IN SCRUBBER SURGE TANK

635

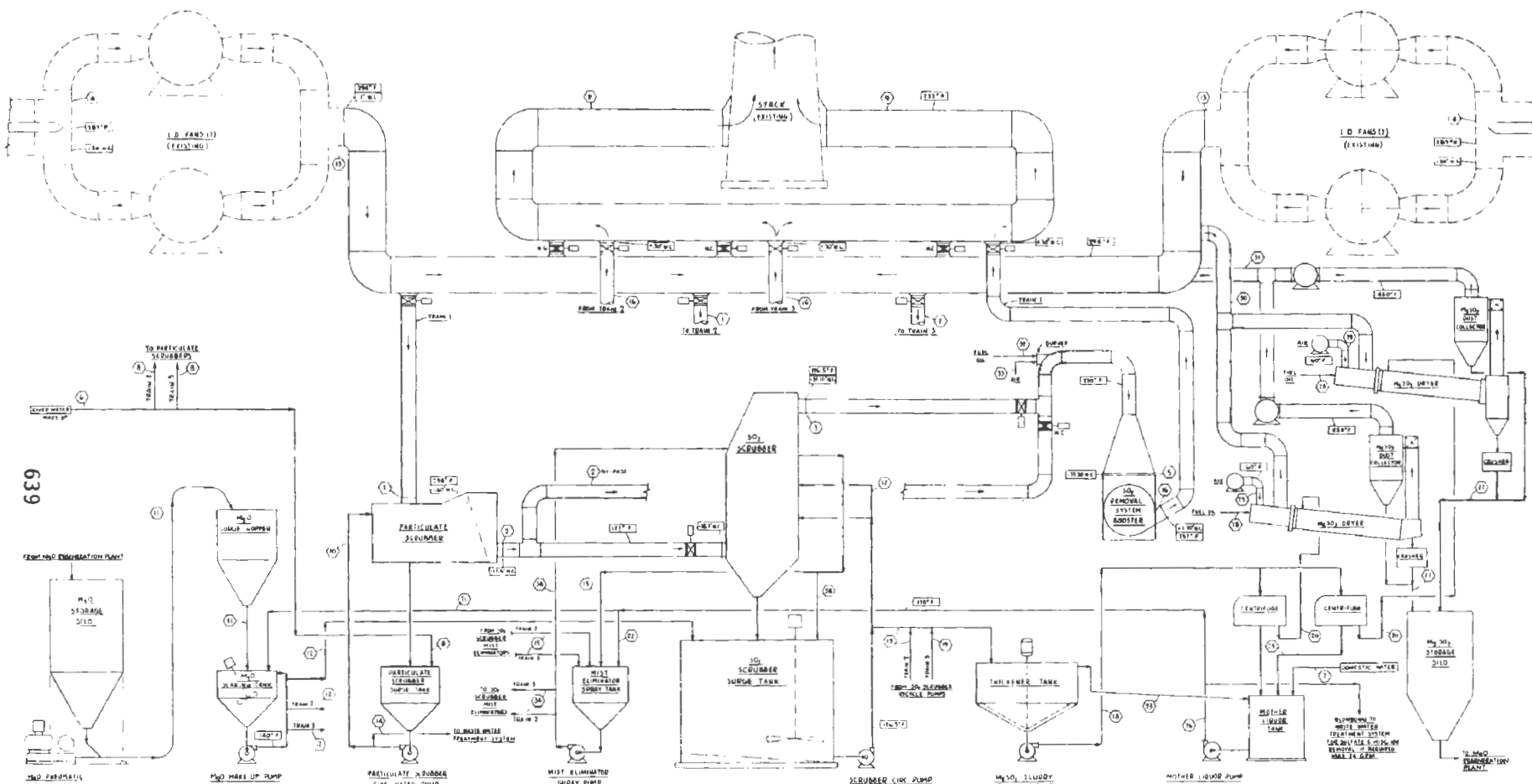








$MgSO_3$ REGENERATION PLANT



639

"PER 1000 GPM"																																		
STREAM NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
DRY GAS	15,000	5,500	5,500	23,111	10,100				24,243																									
H ₂ O VAPOR	4.47	4.47	4.47	18.8	10.9				24.81																									
SO ₂	55.5	55.5	55.5	65	6.6				6.55																									
H ₂ O LIQUID																																		
ASH	3.51	4.7	4.7	5	4.7	2.53	104	9.9		10.81		9.1		2.46	54.74		100,800	174	4.06	25	645	1743	3301	1897	511	4594							475	
MgO																																		
MgSO ₄																																		
MgSO ₄ 6 H ₂ O																																		
AIR																																		
FUEL OIL																																		
MgSO ₄																																		
Mg(OH) ₂																																		
WATER																																		
TOTAL	15,000	11,000	11,000	25,655	13,615	1,232	104	9.9	14,253	10,900	99.9	372.1		266.67	4,999.8	13,840	190.5	1,974	178	1,081	4,910	4,020	25,672	4,726	5,550	114.55	4,805	3,647	146	4,471	14.0	4,408.5	1,850	
UPPER 10 ACFT	300,000	70,000	70,000	615,000	330,000	950	22.5	117	440,000	330,000	1,000	39.8		32	445	12,584	175	197	106	440	415	245	245	70	375	1,946	1,130	813.44	41,000	3.81	8,000	6,000		
UPPER 10 ACFT	24.4	14.7	14.7	29.4	10.7	1.0	1.0	1.0	10.7	1.01		1.23		1.21	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10		
DESIGN FLOW (1000)	371,000	280,000	280,000	495,000	351,000				440,000			121		44.5		132	196	391	154	471	340			90	750	2,950	35,500	28,000	4,700					
MAX FLOW ACFT	345,000	301,000	311,000	555,000	380,000				530,000	14,000		91,000				551,000																		

Revised 10/10

CAPITAL COST

\$45-\$50/KW BASIC NEW SCRUBBING UNIT

\$10-\$15/KW REGENERATION UNIT AND H_2SO_4 PLANT

FOR RETROFIT—ADD ABOUT \$15/KW

OPERATING COST

640

OVERALL OPERATING COST 1.3 - 1.4 mils/KWH

FACTORS CONSIDERED

FUEL

\$0.70/MM Btu

POWER

7 mils/KWH

FIXED CHARGES

15% of Capital Cost/Yr.

MAINTENANCE

3% of Capital/Yr.

APPLICATION OF THE WELLMAN-LORD SO₂
RECOVERY PROCESS TO STACK GAS DESULFURIZATION

by

Raymond T. Scheider
Christopher B. Earl
Davy Powergas, Inc.
Lakeland, Florida

ABSTRACT

The Wellman-Lord SO₂ Recovery Process has been successfully commercialized in the U.S.A. and Japan. Six full-scale installations have now built up an aggregate operating experience of eight years. The fourteen emission sources controlled by the process include sulfuric acid plants, claus plants and oil-fired boilers.

Since the start-up of the original plant at Paulsboro, New Jersey for Olin, the process has demonstrated long-term reliability of operation and its ability to attain SO₂ emission levels as low or lower than required by the regulatory agencies.

This paper describes the basic process and reviews the current status of this technology. The application to large fossil fuel-fired steam generating plants is reviewed, and capital and operating costs for a specific application are included.

THE WELLMAN-LORD SO₂ RECOVERY PROCESS

INTRODUCTION

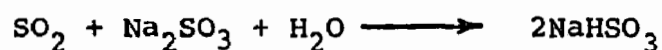
Six commercial installations of the Wellman-Lord SO₂ Recovery Process are operating successfully in the U.S.A. and Japan. These applications include seven sulfuric acid plants, two oil-fired boilers and five claus units (see Table 1).

The SO₂ emission level first envisioned with the use of the process was 500 ppmv since this was a statutory requirement in 1969. The operations of the five plants have demonstrated the process's ability to maintain emission levels at consistently less than 200 ppmv.

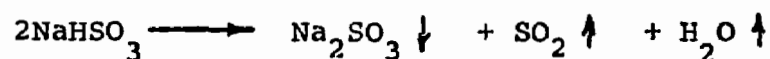
CHEMISTRY OF THE PROCESS

The process is based on a sodium sulfite/bisulfite cycle. The reactions that take place in the process can be abbreviated for simplicity as follows:

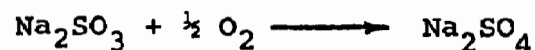
ABSORPTION



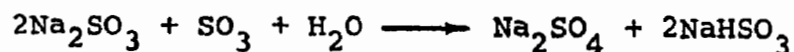
REGENERATION



Apart from the two major reactions above, sodium sulfate (Na₂SO₄), which is nonregenerable in the normal process, is formed in the absorber as a result of solution contact with oxygen and sulfur trioxide as follows:



and



The sodium sulfate so formed is controlled at a level of approximately five percent by weight in the absorber feed stream by maintaining a continuous purge from the system. This purge stream is discussed later.

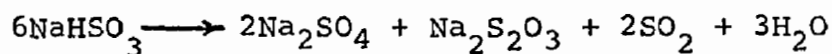
An additional source of sodium sulfate and thiosulfate is the autooxidation or so-called disproportionation reaction which takes place in the regeneration section:

TABLE I

DAVY POWERGAS INC.

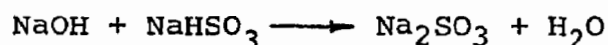
Type Contract
 E - Engineering
 P - Procurement
 C - Construction
 T - Turnkey

WELLMAN-LORD SO ₂ RECOVERY PROCESS							
Project Number	Client	Location	Application Offgas Origin	S C F H Treated	Completion Date	Type of Contract	Remarks
3659	Olin Corporation	Paulsboro, New Jersey	Sulfuric Acid	45,000	July, 1970	T	
	Toa Nenryo	Kawasaki, Japan	Claus Plant	41,000	August, 1971	Process Package	Contract by Licensor
	Japan Synthetic Rubber Co.	Chiba, Japan	Oil Fired Boiler	124,000	August, 1971	Process Package	Contract by Licensor
4120	Standard Oil of California	El Segundo Refinery El Segundo, California	Claus Plants	30,240	June, 1972	E, P	
4126	Allied Chemical Corp.	Calumet Works Chicago, Illinois	Sulfuric Acid	29,580	August, 1972	E, P	
4127	Olin Corporation	Curtis Bay, Maryland	Sulfuric Acid	78,046	In Progress	T	
4137	Northern Indiana Public Service Co. (NIPSCO)	Gary, Indiana	Coal Fired Boiler - 115 MW Power Plant	310,000	In Progress	T	
4144	Sumitomo Chiba Chemical Co.	Chiba, Japan	Oil Fired Boiler	250,000	In Progress	Process Package	Contract by Licensor
4159	Standard Oil of California	Richmond Refinery El Segundo, California	Claus Plants	37,000	In Progress	E, P	
	Japanese Synthetic Rubber	Yokkaichi, Japan	Steam Boiler Plant (SO ₂ converted into sulfuric acid)	270,000	In Progress	Process Package	Contract by Licensor
	Kashima Oil Co.	Kashima, Japan	Claus Plants	20,200	In Progress	Process Package	Contract by Licensor
	Confidential	Kawasaki, Japan	Steam Boiler Plant (SO ₂ converted into sulfuric acid)	412,000	In Progress	Process Package	Contract by Licensor
	Chubu Electric	Nagoya, Japan	Oil Fired Boiler - 220 MW Power Plant	390,000	In Progress	Process Package	Contract by Licensor



Laboratory research and commercial experience have guided the selection of operating conditions which minimize all these sources of sodium sulfate formation.

A make-up of caustic is required to replace that lost in the purge stream. The caustic make-up solution reacts with the sodium bisulfite in the absorber solution to form additional sodium sulfite:



Soda Ash (Na_2CO_3) can also be used as the makeup source of sodium.

The simple regeneration scheme of the patented Wellman-Lord process relies on the favorable solubilities of the sodium system. The bisulfite form has almost twice the solubility of sulfite at the temperatures considered for the process. Because of this it is possible to feed the absorber with a saturated sulfite solution, or even a slurry, without any fear of additional crystallization or scale forming despite considerable evaporation of water. This is due to the fact that as SO_2 absorption proceeds, the composition of the solution is shifted in the direction of increasing solubility.

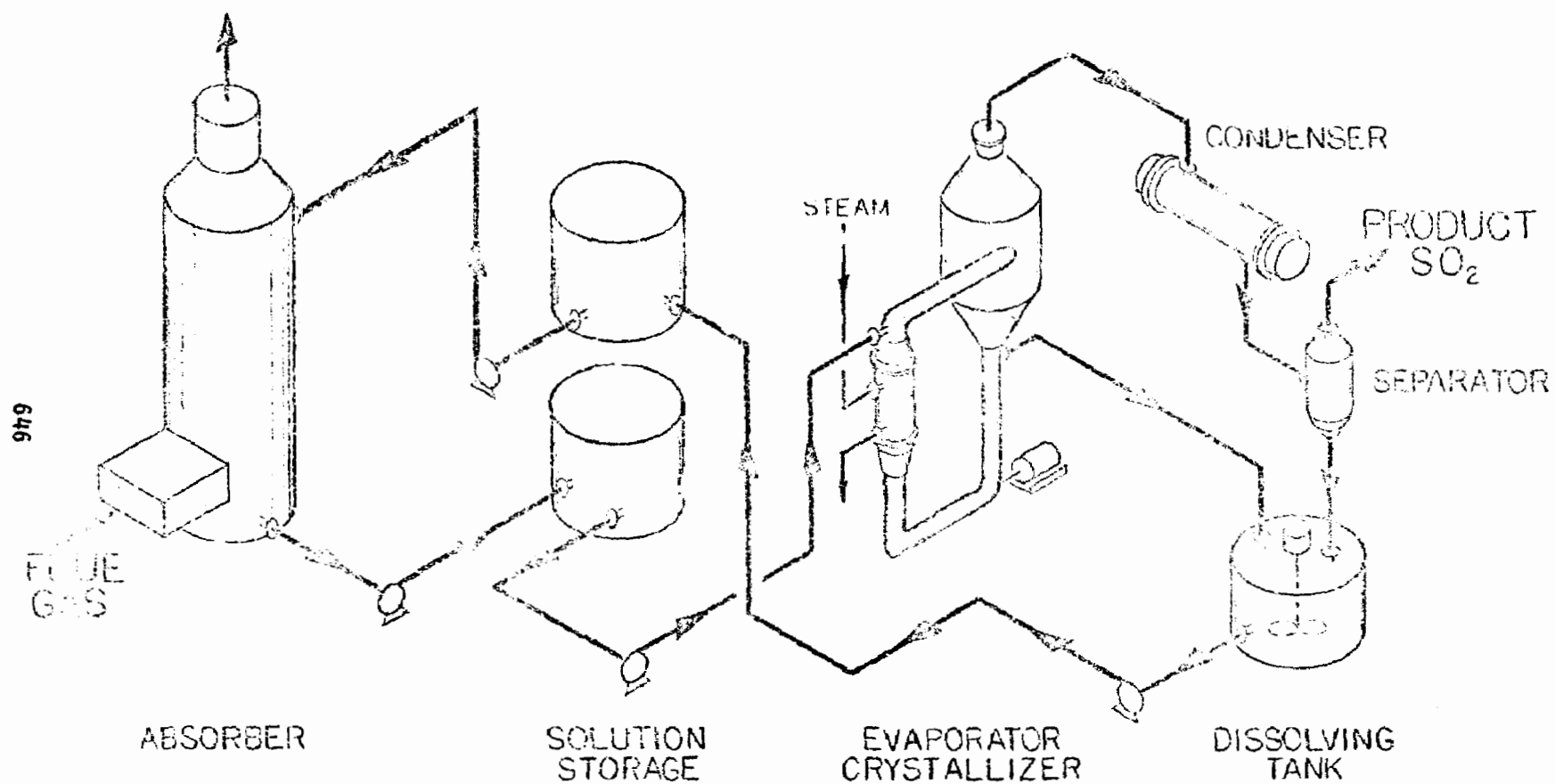
There are several advantages to operating the absorber with highly concentrated solutions. The solubility of oxygen decreases rapidly as salt concentration increases and so the mass transfer of oxygen into the solution is slowed appreciably. This reduces oxidation of the sodium salts to sodium sulfate. The steam requirements of the process are directly related to the quantity of water pumped around the system. Operating at or near saturation with respect to sulfite thus reduces the overall steam consumption.

The same solubility effect is taken advantage of in a revers fashion in the regeneration section. As SO_2 is stripped from the concentrated solution, the sulfite salt is formed and rapidly reaches its solubility limit thus precipitating as crystals. In effect the low vapor pressure component (sodium sulfite) in the solution being regenerated, is removed from the equilibria balance. Thus the regeneration operation can proceed with a constant high percentage of bisulfite in solution permitting a considerable reduction in the stripping steam requirements.

DESCRIPTION OF FLOW

The flow scheme for the basic process is shown in figure 1. The SO_2 rich gas is contacted counter-currently in the absorber by the sodium sulfite solution and passes out the top stripped of SO_2 . The solution leaving the bottom of the tower, now rich in bisulfite,

FIG. 1 BASIC FLOW DIAGRAM



WELLMAN-LORD SO₂ RECOVERY PROCESS

is discharged to a surge tank and then pumped to the regeneration section.

Low pressure steam is used to heat the evaporator and drive off SO_2 and water vapor. The sodium sulfite precipitates as it forms and builds a dense slurry of crystals.

The overhead stream is subjected to a partial condensation to remove the majority of the water vapor. The condensate recycles to the dissolving tank and the product SO_2 is discharged from the process.

A stream of slurry is withdrawn from the evaporator and is redissolved by the overhead condensate. The lean solution is pumped to a surge tank prior to being fed back to the absorber.

GAS PRETREATMENT

Normally the flue-gas from a fossil fuel-fired boiler or a smelter will require cooling and particulate removal prior to absorption of the SO_2 .

In the case of a claus plant, the tail gas must first be incinerated under conditions which destroy the H_2S , COS and CS_2 .

This pretreatment step must be studied on a case-by-case basis to ensure the selection of the optimum design in relation to the overall facility.

The type of pretreatment ultimately chosen will depend on the following parameters:

- Gas Temperature
- Particulate Content
- Organic Sulfur Content
- Sulfur Trioxide Content
- Acid Mist or Vapor Content
- Humidity.

SO_2 ABSORBER

The absorber is a simple two or three stage contacting device. DPG commercial experience with both tray and packed towers permits selection of the design most suited to each specific application.

For most gases treated the absorber will require recirculation around each individual stage, since the quantity of feed solution is insufficient to adequately wet the tray or packing.

During operations the recirculation rate can be throttled until the SO_2 emission increases up to the design point. This will minimize oxidation since the absorption of oxygen is liquid-film controlling and therefore proportional to liquid rate. The absorption of SO_2 is gas film controlled and therefore relatively insensitive to liquid rate.

An inherent advantage of the Wellman-Lord Process is that the absorption system can be physically separated by a large distance from the regeneration system. This also means that it is practical to treat gases from more than one plant by installing separate absorbers for each source of SO_2 , with all the absorbers being supplied by a common regeneration system.

SOLUTION SURGE TANKS

The use of solution storage not only enables the process to operate smoothly during frequent changes of gas flow or SO_2 concentration, but it also permits a complete shutdown of the regeneration section to perform scheduled maintenance activities, without any pause in SO_2 absorption.

This feature minimizes the amount of expensive spare equipment required with no sacrifice in basic pollution control reliability.

CHEMICAL REGENERATION SYSTEM

The heart of the regeneration system is a conventional forced-circulation evaporator/crystallizer. The design parameters of this unit have been developed such that long term continuous operation is assured. The evaporator can be designed to use very low pressure exhaust steam which might otherwise be discharged to the atmosphere.

In very large plants or in case of high cost steam it is practical and economical to operate the regeneration system as a double effect evaporator which will reduce steam consumption by about 40-45%.

PRODUCT SULFUR DIOXIDE

The vapor leaving the evaporator is subjected to one or more stages of partial condensation to remove water. Existing plants are operating with both air and water-cooled condensers

in this service. The final product SO_2 can be delivered at whatever quality is required for further processing. It is suitable for conversion to high grade sulfuric acid, elemental sulfur or liquid SO_2 .

Existing Wellman-Lord plant are recycling the gas back to sulfuric acid and claus plants or sending it to be processed in a satellite sulfuric acid plant.

PURGE TREATMENT

A small amount of the circulating solution is oxidized to a non-regenerable form and a purge stream is removed to control the build-up. This stream can be dried for sale or disposal, or it can be treated to permit its discharge as an innocuous effluent. Other process steps are available which recover the sodium values, thus allowing the system to operate as a closed loop.

OPERATIONS

The first Wellman-Lord plants quickly proved the viability of the process but were not without some start-up problems. Needless to say, the lessons learned in these plants were quickly incorporated in subsequent designs. An indication of this is that three of the first five users already have second plants in operation or in the process of being engineered.

STANDARD OIL OF CALIFORNIA

One of our recent projects for Standard Oil of California started up in September, 1972 and from the first day has operated continuously in a most satisfying manner.

This plant included large surge tanks which if necessary would permit a three day shut-down of the regeneration section, while the absorption section continues to run. The reliability provided by this feature was vital to protect the integrity of this large refinery located close to Los Angeles International Airport and surrounded by a residential area. The regulations governing this situation require full air pollution control 24 hours a day, 365 days per year.

A side benefit of this relatively cheap means of providing reliability was that the plant could handle excursions of SO_2 concentration up to three times the design level while still attaining an SO_2 emission less than design. The unit mentioned above has surpassed the performance guarantees, and has been officially accepted by Standard Oil of California.

JAPAN SYNTHETIC RUBBER COMPANY AT CHIBA, JAPAN

This installation is operating on the flue gas from two oil fired boilers each with a capacity of 286,000 lbs/steam per hour. The fuel oil contains 4.0 - 4.2% sulfur and produces a flue gas varying from 1500 to over 2000 ppm SO₂. The plant has consistently reduced the SO₂ emission to below 200 ppm since its start up in June of 1971. The plant currently averages an inlet SO₂ concentration of 1500 ppm with an outlet emission 150 ppm.

During the period June 1971 - March 1973, the boilers operated a total of 12,972 hours. During this same period of time the Wellman-Lord process unit operated 12,533 hours for a 97% on-stream factor. During the period May 9, 1972 - March 1, 1973, the boilers operated a total of 6,978 hours, and the Wellman-Lord process unit was in operation during all of these for a 100% on-stream factor.

In this plant each boiler is connected to a five meter square by 21 meter high sieve tray absorption tower, and the recovery section utilizes a double effect evaporator for steam economy. The tail gas after the absorber is reheated to 130°C for plume dispersal.

The product SO₂ gas is processed in a slightly modified, conventional contact sulfuric acid plant, and produces high grade, merchant quality, 98% sulfuric acid which is sold in normal markets.

APPLICATION TO POWER PLANTS

THE NIPSCO DEMONSTRATION PLANT

As a consequence of the successful operating units mentioned above, Davy Powergas has been awarded a full scale demonstration plant project for Northern Indiana Public Service Company, funded jointly by the U.S. Environmental Protection Agency and NIPSCO. This facility will treat the total stack gas from a 115 mw coal fire boiler at the Dean H. Mitchell Station in Gary, Indiana. The end product of this plant will be elemental sulfur. SO₂ Removal from the flue gas will be performed by the Wellman-Lord SO₂ Recovery Process, which will deliver the concentrated SO₂ to a reduction facility that uses Allied Chemical Corporation's technology to produce high quality elemental sulfur as the final product.

DEMONSTRATION OBJECTIVES

The broad overall objective of this project is to demonstrate the applicability of the above two commercially proven processes to large scale coal fired boiler plants. In order to meet the overall objectives of the project, specific contractual guarantees are being developed in accordance with the following guidelines:

1. The process will accomplish a minimum of 90% removal sulfur dioxide from the stack gas when firing coal up to 3.5% sulfur content producing an emission of 200 ppm SO₂ or less. 3.5% sulfur content of the coal is equivalent to approximately 2300 ppm by volume sulfur dioxide in the stack gas.
2. The aggregate cost of steam, electric power, water, and natural gas will not exceed a specified amount.
3. The required quantity of make-up chemicals will not exceed a specific amount.
4. No other water or air pollution sources will be created.
5. The sulfur produced will be of a quality suitable for the manufacture of sulfuric acid by the contact process.
6. The plant will comply with all applicable federal, state and local air and water quality regulations in effect at the time detailed engineering is begun.

PHASING AND SCHEDULING OF THE PROJECT

Phase I of the project consists of preliminary engineering and definitive cost estimates. This phase of the project is essentially complete at this writing.

Phase II includes the completion of detailed engineering, procurement, construction and start-up. This phase of the work is scheduled to be completed during the latter half of 1974.

Phase III, following acceptance tests at the conclusion of Phase II, covers a one year period of operation by Allied Chemical and will be funded entirely by NIPSCO.

TRW/EPA TEST PROGRAM

Concurrent with Phase III of the project, a comprehensive emission testing program will be conducted by EPA. To implement this test

and evaluation program the EPA has retained the services of TRW Inc. The primary objectives of the test and evaluation program are:

1. A validation of the emission reduction achieved by the Wellman/Allied process.
2. A validation of the estimated installation and operating costs of the demonstration unit.
3. A determination of the applicability of the Wellman/Allied process to the general population of utility boilers. The test program will include extensive measurements of those parameters that characterize the sulfur removal and economic performance of the Wellman and Allied process units.

In addition to specific test work, TRW will conduct a survey for the purpose of identifying the potential users of the Wellman/ Allied process. User boiler units having applicability potential are selectable based upon considerations such as expected useful life, capacity, average load factor, low sulfur fuel availability and the marketability of sulfur and sodium sulfate in the region where the boiler is located.

PURGE CRYSTALLIZATION SYSTEM

In order to meet the objectives stated above that no additional water or air pollution sources would be created, a purge crystallization section has been included in this project. In this section of the plant the purge stream will be subjected to fractional crystallization in order to concentrate the sodium sulfate and sodium thiosulfate components of the purge. This portion of the purge stream will be dried to produce a solid crystalline byproduct of high sodium sulfate and sodium thiosulfate content. The resulting sulfite/bisulfite stream from which most of the sulfate and thiosulfate has been removed will be recycled to the SO₂ Recover Process.

ALLIED CHEMICAL CORPORATION SO₂ REDUCTION SYSTEM

This project is unique in that it will produce elemental sulfur as a by-product. The Allied Chemical Corp. Process is the subject of the next paper and will not be covered here.

SITE CONSIDERATIONS AT THE D. H. MITCHELL STATION

The demonstration plant will be installed on unit 11 of NIPSCO's

Dean H. Mitchell Station. This slide is a view of this station with unit 11 at the right. Unit 11 is a Babcock and Wilcox pulverized coal feed boiler capable of producing 821,000 lbs/hr of steam. The superheater outlet pressure is 1870 lbs/sq in. gauge at 1005°F. It is equipped with an electrostatic precipitator installation rated at 98% collection efficiency. The coal presently being fired in this unit is from Southern Illinois with an as received average analysis of 3.16% sulfur, 10.5% ash, and 11.8% moisture.

NIPSCO clearly has reason to be interested in a method for removal of sulfur dioxide from the stack gas. Such a method, if effective, reliable, and economically viable, permits NIPSCO to comply with emission limits while continuing to fire coal from assured relatively near by sources.

Stack gas treatment processes can be divided into two classes, those that produce a so-called throw-away product and those that yield a product that can in theory at least be marketed. The throw-away process was rejected by NIPSCO for ecological reasons.

The Dean H. Mitchell Station is located on Lake Michigan in the Northwest corner of Gary, Indiana. As this slide shows, its immediate environs are highly industrial, but farther out the plant community is residential and densely populated. Considerations of land and water use made a throw away process environmentally unacceptable at such a site.

This slide shows an artists rendering of the SO₂ recovery and reduction installation that will be made at the Dean H. Mitchell Station superimposed on a photograph of that station. The red structures are those of the Wellman-Lord process, and the Allied process is housed within the orange building.

CAPITAL AND OPERATING COSTS

Actual costs for power plant flue gas scrubbing and SO₂ recovery will vary considerably depending on the specific application. Local site conditions and the difficulty of retrofit can cause costs to vary over a wide range. It is very misleading to compare estimates that are derived from different bases.

Capital and operating costs for applying the W-L process to two large plants (500 and 1,000 MW) have been projected from the detailed studies made of the 115 MW plant at the Dean H. Mitchell Station of

Northern Indiana Public Service Company. The following table indicates the basic parameters used in estimating these costs:

TABLE 2

	<u>500 MW</u>	<u>1000 MW</u>
Absorber Design Flow SCFM	3 @ 400,000 ea	6 @ 400,000 ea
Regeneration Plant Lb/Hr SO ₂ Product	1 @ 18,000	2 @ 18,000 ea
Sulfur Plant LTPD Sulfur Product	1 @ 92	1 @ 184

The studies of the 500 and 1,000 MW plants are based on 3.2% sulfur coal and the flue gas flows are based on 20% excess air.

The regeneration plant and sulfur dioxide reduction plant sizing correspond to an 80% load factor. Absorber operation at peak capacity would be handled by solution inventory in large surge tanks.

The annual utility costs presented in Table 3 are based on a continuous 80% load factor for 330 days per year which is equivalent to an overall load factor of 72%.

TABLE 3 - CAPITAL AND OPERATING COSTS

	<u>500 MW</u>	<u>1000 MW</u>
<u>Capital Cost</u>	\$18,700,000	\$33,200,000
<u>Annual Costs</u>	<u>\$/Year</u>	<u>\$/Year</u>
Chemicals	956,000	1,912,000
Natural Gas @55¢/MM BTU	336,000	672,000
Electricity @ 7 Mil/KWH	499,000	993,000
Steam @ 50¢/1000 Lb	554,000	1,108,000
Cooling Water @ 2¢/1000 Gal	111,000	222,000
Labor @ \$5.80/hr	169,000	229,000
Supervision	47,000	47,000
Overhead	343,000	506,000
Maintenance @ 4.5% of Capital	842,000	1,494,000
Laboratory	72,000	72,000
Miscellaneous Supplies	45,000	90,000
Capital Charges @ 14.5%	<u>2,712,000</u>	<u>4,814,000</u>
TOTAL	6,686,000	12,159,000
Sulfur Credit @ \$18/LT	<u>(546,000)</u>	<u>(1,092,000)</u>
NET TOTAL	6,140,000	11,067,000
Clean-up Cost mils/KWH	1.9	1.7
¢/MM BTU	20	18

APPLICATION OF SO₂ REDUCTION
IN STACK GAS DESULFURIZATION SYSTEMS

by

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Allied Chemical's experience in the design and operation of a large, single train plant for reduction of SO_2 to elemental sulfur has made possible the application of new technology to emission control in metallurgical operations and fossil fuel combustion.

This Allied Chemical technology has been proven in two years' successful commercial operation where it functioned as the emission control system at a Falconbridge Nickel Mines, Ltd. facility near Sudbury, Ontario, Canada. The quantity of sulfur in the gas stream treated in the Allied unit at Falconbridge (500 long tons per day) is equivalent to that contained in the largest metallurgical sources, or in flue gas from 2000 megawatts of electric generating capacity fired with 3% sulfur coal. As a consequence, future applications of Allied's technology will involve scale down of equipment size with full assurance of optimum plant performance.

Availability of a proven process capable of converting SO_2 to elemental sulfur offers freedom from the problems and cost of disposal of the waste products of neutralization. Likewise, costly storage and transport of by-product sulfuric acid can be avoided at locations remote from acid markets.

The Allied Chemical SO_2 reduction process can be applied directly to gas sources where the SO_2 content is 4-5% or more and where oxygen content is limited. Various metallurgical emissions can, therefore, be processed directly in the Allied system. Since oxygen reacts with the reducing agent in the same manner as the SO_2 , it is desirable in optimizing the system to achieve the lowest oxygen content possible in order to minimize reducing agent consumption. The Allied process has the versatility of being adaptable to feed gases containing any SO_2 concentration up to 100% (dry basis). Hence, in those applications where the oxygen content is too high or SO_2 concentration too low for direct application to the emission source, the Allied SO_2 reduction process may be joined with one of several regenerable flue gas desulfurization process which recovers the SO_2 from the flue gas in a concentrated, low oxygen form.

Adaptability of Allied's SO₂ reduction technology to a feed gas containing 100% SO₂ (dry basis) will be demonstrated at the D. H. Mitchell Station of Northern Indiana Public Service Co. at Gary, Indiana. There, the process will be combined with the Wellman-Lord SO₂ recovery process to provide a flue gas desulfurization system for a 115 megawatt, coal-fired boiler in a project jointly funded by NIPSCO and the Environmental Protection Agency.

Engineering, procurement and construction of the entire facility will be the responsibility of Davy Powergas Inc. Allied is providing the SO₂ reduction process technology as well as technical and start-up services under contract with Davy Powergas. Then, under a separate agreement with NIPSCO, Allied will operate the entire flue gas desulfurization system and will market salable by-products.

The role that will be undertaken with NIPSCO is a familiar one for the Allied organization which has for many years provided services to oil refineries in the design, construction and operation of satellite plants for the conversion of hydrogen sulfide to elemental sulfur and the decomposition of spent sulfuric acids. In addition Allied has performed services to metallurgical industries in the building and operation of facilities for the roasting of sulfide ores, and the production and marketing of sulfuric acid. The development of SO₂ reduction technology enabled Allied to extend the range of its services directed to environmental improvement.

The Falconbridge plant, which involved the fluidized bed roasting of pyrrhotite ore, could only have been built if provisions were made to comply with Canadian regulations requiring the removal of at least 90% of the sulfur values contained in the roaster gases before their release to the atmosphere. Two alternatives were considered: the manufacture of sulfuric acid or reduction of the SO₂ to sulfur. There is no substantial market for either in the immediate area, but the recovery of elemental sulfur offered the advantages of a commercial product that is more easily stored than sulfuric acid and has a much wider economic shipping range.

The Falconbridge installation demonstrated the required capability of removing at least 90% of the SO_2 from roaster gases at a rated capacity of 500 long tons of sulfur per day in the incoming gases. Reliability of performance was established as well as flexibility in turndown to two-thirds and one-third of design capacity with essentially constant operating efficiency at all rates.

At Falconbridge, Allied engineered and constructed the SO_2 reduction plant. The facility was run by Allied supervisors utilizing an operating and maintenance staff assigned Allied by Falconbridge Nickel Mines.

Product sulfur was, for the most part, distributed to Allied's sulfuric acid manufacturing locations serving the U.S. merchant acid market. The Falconbridge product was used interchangeably at these locations with sulfur from Frasch producers and other by-product sulfur sources.

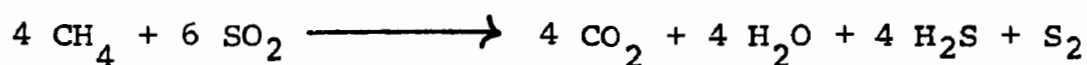
COMMERCIAL PLANT DESCRIPTION

A flow diagram of the Allied Chemical SO_2 reduction process as it is applied to a sulfide ore roasting operation like that at Falconbridge is shown in Figure I. The hot SO_2 gas from the roasters is passed through hot gas heat exchangers (1) and (2) where part of the heat content of the gases is utilized to reheat other process gas streams. These will be described in more detail later. At this point the roaster gas still contains fine dust particles as well as gaseous contaminants which must be removed before the gas reaches the reduction reactor. This gas purification is accomplished in a two-stage aqueous scrubbing system consisting of a two-leg gas cooling tower (3) and a packed condensing tower (4). The bulk of the dust and other contaminants are collected in the gas cooling tower while the gas is cooled and saturated by contact with a recirculated weak sulfuric acid solution. The demister pad at the tower outlet is continuously sprayed with weak acid from the condensing tower. The under-flow from the gas cooling tower is treated with lime to precipitate dissolved metallic impurities removed from the gas, and neutralize the acidity, before being delivered to a waste pond where the solids are allowed to settle.

The process gas is further cooled in the condensing tower (4) by circulating weak acid which is cooled externally in impervious graphite heat exchangers (5). Entrained droplets of acid mist are removed from the gas in electrostatic precipitators (6). Drips from the precipitators are returned to the gas cooling tower.

The temperature of the clean gas is then raised above the dew point of sulfuric acid by admixing with a reheated stream of the same gas in mist tower (7). This recycle gas stream is heated by circulation through hot gas heat exchanger (2). The process gas is drawn through the wet purification system, then forced by a centrifugal blower (8) through the balance of the plant. Natural gas, which serves as the reducing agent, is introduced into the process gas stream at the blower discharge and the mixture passed through hot gas heat exchanger (1) to raise its temperature above the dew point of sulfur before entering the reduction reactor system.

The principal function of the catalytic reduction system is to achieve maximum utilization of the reductant while producing both sulfur and H_2S , so the H_2S/SO_2 ratio in the gas stream leaving the system is essentially that required for the subsequent Claus reaction. Although the chemistry of the primary reaction system is extremely complex and includes reactions involving 11 different elements and compounds, it may be summarized in the following equations:

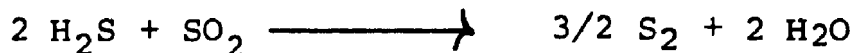


The preheated process and natural gas mixture enters the catalytic reduction system through a four-way flow reversing valve (9) and is further preheated as it flows upward through a packed-bed heat regenerator (10) before entering the catalytic reactor (11). The temperature of the gases entering the reactor is held constant by continuously by-passing a varying quantity of cold process gas around the upflow heat regenerator. The

heat that is generated in reactor (11) by the exothermic reactions serves to sustain the overall heat in the system. Upon leaving the reactor, the main gas flow passes downward through a second heat regenerator (12), giving up its heat to the packing in that vessel before leaving the catalytic reduction system through flow reversing valve (9). A thermal balance is maintained in the system by passing a minor flow of the hot gases from reactor (11) around the downflow regenerator and the flow reversing valve (9) and remixing with the main stream before entering sulfur condenser (17)

The primary function of the heat regenerators (10) and (12), then, is to remove heat from the gases leaving the catalytic reactor (11), and to utilize this heat to raise the temperature of the incoming gases to the point where the SO_2 -natural gas reaction will initiate. The direction of flow through the two regenerators is periodically reversed to interchange their functions of heating and cooling the gases. This is accomplished by the flow reversing valve (9) and four water-cooled butterfly valves (13), (14), (15) and (16). The valve arrangement shown in the flow diagram Figure I is specially designed to maintain the gas flow through the catalytic reactor (11) in one direction only. All five valves are operated from a central control system which synchronizes their movement perfectly so that each flow reversal is completed in less than one second.

The elemental sulfur that is formed in the primary reactor system is condensed in a horizontal shell-and-tube steaming condenser (17). This represents over 40% of the total recovered sulfur. The process gas stream then enters the first stage (18) of a two-stage Claus reactor system where the following exothermic reaction occurs:



After the first stage of Claus conversion, the gas is cooled and additional sulfur condensed by passage through a vertical steaming condenser (19). Further conversion of H_2S and SO_2 to sulfur takes place in the second stage Claus reactor (20). This sulfur is condensed in a third steaming unit (21). A coalescer (22), containing a mesh pad, then removes entrained liquid from the gas stream. Molten sulfur from the three condensers and the coalescer is collected in a sulfur holding pit

(23) from which it is pumped to storage. Residual H_2S in the gas from the process is oxidized to SO_2 in the presence of excess air in an incinerator (24) before being exhausted to the atmosphere through a stack (25).

APPLICATION IN COMBINED SYSTEMS

The versatility of the Allied Chemical SO_2 reduction technology can best be illustrated by considering its application as a component part of several stack gas treatment systems for electric utility generating stations. As was mentioned earlier, the Allied Chemical process can accommodate a wide range of SO_2 concentrations in the feed gas. A process flow diagram of the SO_2 reduction unit as it is applied to flue gas desulfurization systems which produce strong SO_2 gas, say 40% or more (dry basis) is shown in Figure II. Since the gases from SO_2 concentrating systems are generally cleaned by some type of wet scrubbing operation before delivery to the SO_2 reduction unit, and are saturated with water vapor at the scrubbing temperature, it is necessary to raise the temperature of the gases sufficiently above the dew point that no condensation of weak acid occurs in the main blower. After the preheated gases are compressed, the reducing gas is added in the correct proportion and the gas mixture then passed through a feed gas heater where its temperature is raised above the dew point of the sulfur that is formed in the primary reaction system. The purpose of this is to preclude sulfur condensation in the four-way reversing valve mentioned in the earlier process description. The source of this heat will be discussed subsequently.

The functions of the reduction reactor and the heat regenerators are essentially the same when treating gases having high SO_2 concentrations as when treating roaster gases. The exothermic reactions which occur in this primary reactor system result in the gases leaving the system at a substantially higher temperature. A portion of this heat is used to heat the feed gas in a shell and tube heat exchanger. However, because of the excess heat liberated in the reactor system, the exit gases are too hot, and, as a result, are too corrosive to be passed directly through this heat exchanger. Consequently, they are first tempered by diverting a part through a gas cooler, and remixing this side stream with the main stream before entry into the feed gas heater. Some sulfur is condensed in the cooler and withdrawn to a sulfur holding pit. Low pressure steam is generated on the shell side of the cooler.

The two-stage secondary reactor, or Claus converter, system is similar to that used for roaster gases. Residual H_2S in the exit gas from the Claus system is oxidized to SO_2 in the presence of free oxygen in an incinerator. Instead of being released to the atmosphere, however, as in the roaster gas treating process, the incinerator tail gas is recycled to the flue gas desulfurization unit. The SO_2 emission to the atmosphere is thus reduced to the minimum level attainable.

Still another adaptation of the Allied Chemical SO_2 reduction process is represented in the process flow diagram, Figure III. Here, the only significant difference is the quantity of heat generated in the reactor-regenerator system. With an 8% SO_2 , low oxygen gas, the temperature rise in the reduction reactor system is inadequate for the exit gas from the reduction reactor system to be used efficiently in the feed gas heater. This makes it necessary to use the incinerator tail gas for this purpose, as shown in the flow diagram. The remainder of the process is the same as for the more concentrated SO_2 gases. The tail gas is again returned to the front end SO_2 gathering system.

For a given emission control problem, it will be apparent that the fixed amount of sulfur delivered into the Allied SO_2 reduction unit can be contained in greatly differing gas volumes depending upon the choice of flue gas treating system. This is illustrated in Table I.

Note that the quantity of sulfur available for recovery in the case of a 600 MW boiler fired with oil of 4% sulfur content is 130 long tons per day compared to the 500 long tons per day in the roaster gases at Falconbridge when operating at rated capacity. It will also be seen that the volume of gas in which that 130 long tons per day of sulfur is contained may range from as little as 2,500 SCFM to nearly 32,000 SCFM. As an added note of perspective, this latter value is substantially less than one-half of the roaster gas flow entering the SO_2 reduction unit at Falconbridge.

REDUCING AGENT REQUIREMENTS

The reducing agent is the largest single element of operating cost associated with the SO_2 reduction process. The consumption varies directly with the quantity of SO_2 to be reacted, as is illustrated in Figures IV and V.

The natural gas requirements for the reduction of SO_2 recovered from coal burning electric utility stacks is shown in

Figure IV. The sulfur values on the curves are based on the use of 10.6 tons of coal (containing 10% moisture) per megawatt day. Corresponding figures for electric power generation using 2% and 4% sulfur content residual fuel oil are presented in Figure V.

Natural gas was the logical reducing agent for the sulfur recovery facility at Falconbridge because of the proximity of a major trans-Canada pipeline. One phase of Allied's continuing effort in the development of advanced SO₂ reduction technology is focused on the substitution of other gaseous and liquid hydrocarbons for the natural gas utilized in the present process.

CAPITAL COST COMPARISON

The installed cost of an SO₂ reduction plant is primarily a function of the gas volume processed and secondarily the quantity of sulfur contained in that process gas stream. Figure VI shows the comparative relationship of the estimated installed costs of Allied Chemical SO₂ plants applied to the three feed gas concentrations we have examined -- 8%, 40%, and 100% SO₂, dry basis.

The effect of SO₂ concentration on capital cost is readily apparent, as is the fact that SO₂ reduction is strongly favored by increasing system size.

Such a comparison does not, of course, reflect total flue gas desulfurization system installed cost. In fact SO₂ reduction will be a minor fraction of the total installed cost in every case.

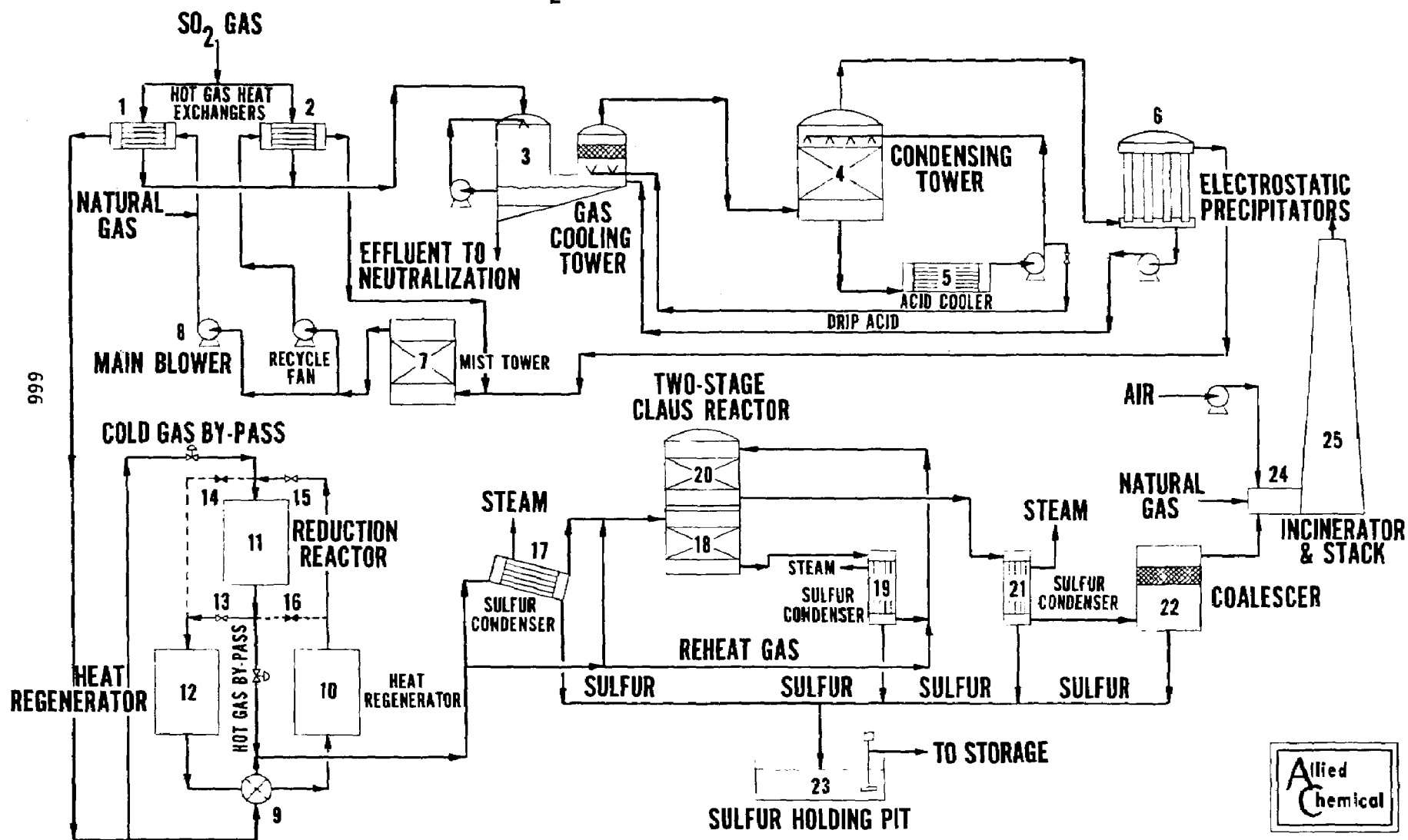
Allied Chemical's studies to date have indicated that location factors have a greater influence on total installed cost than on the cost of the SO₂ reduction component alone. As a consequence, it does not automatically follow that the lowest capital cost SO₂ reduction unit will insure the lowest total system installed cost.

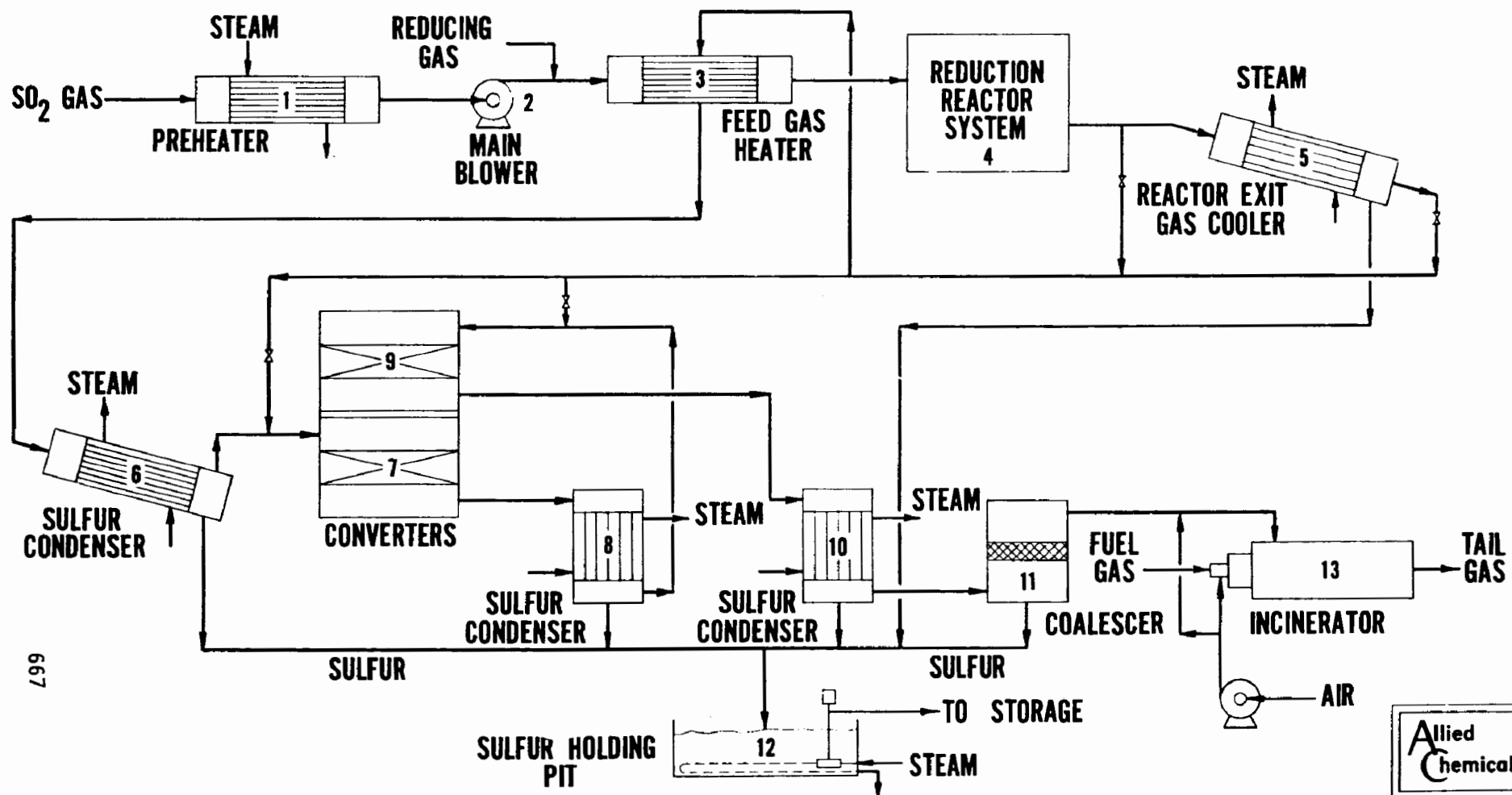
Operating factors, particularly energy requirements and costs, can vary widely among different combinations of flue gas desulfurization systems. The optimization of operating requirements can only be undertaken for the combined SO₂ gathering and SO₂ reduction systems.

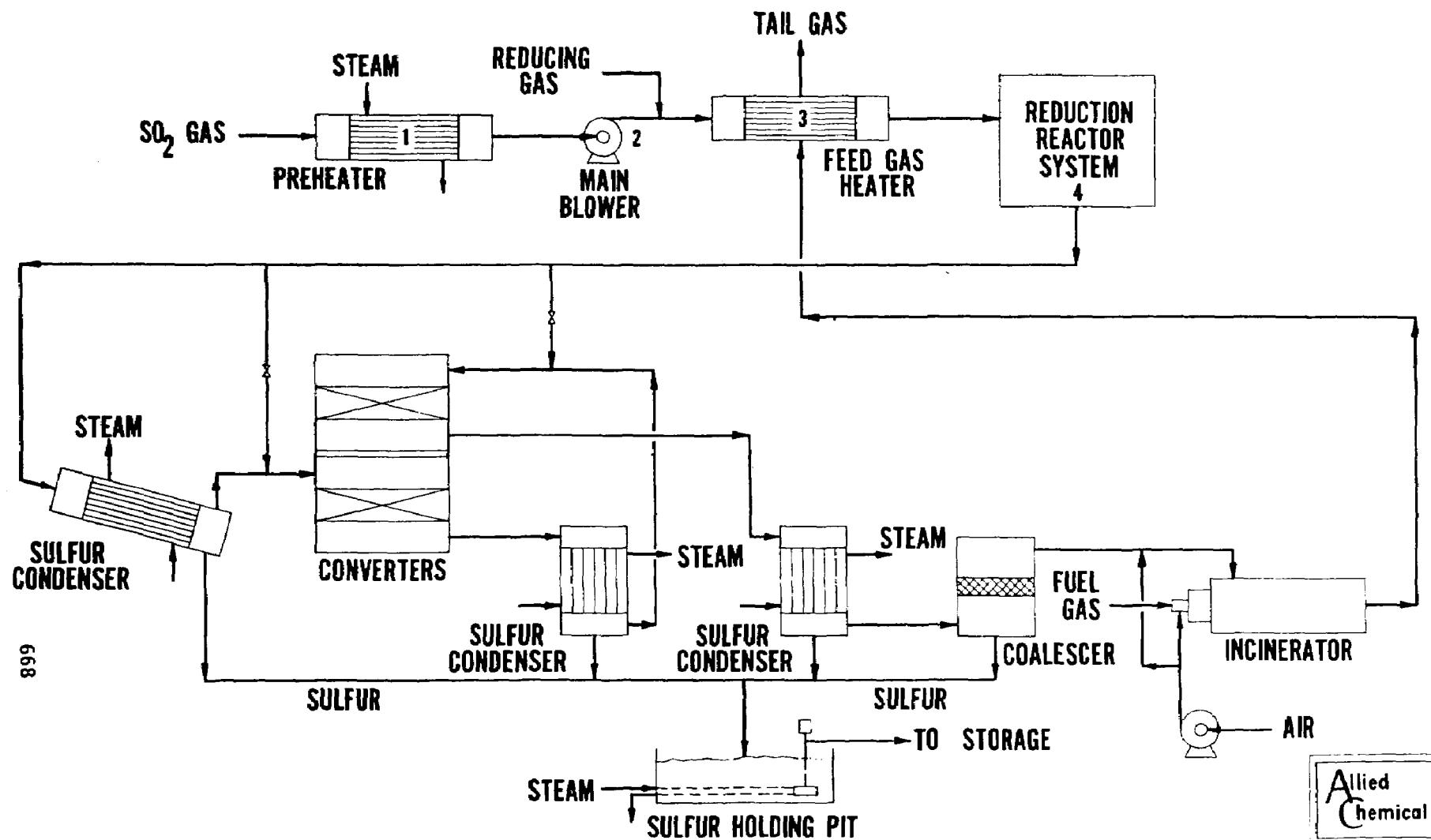
Allied Chemical is prepared to work with organizations having SO₂ emission problems, making its commercially proven SO₂ reduction technology available for direct application or in combination with SO₂ concentration systems provided by others.

ALLIED CHEMICAL SO₂ REDUCTION TECHNOLOGY TYPICAL ROASTER GAS APPLICATION

Fig. 1

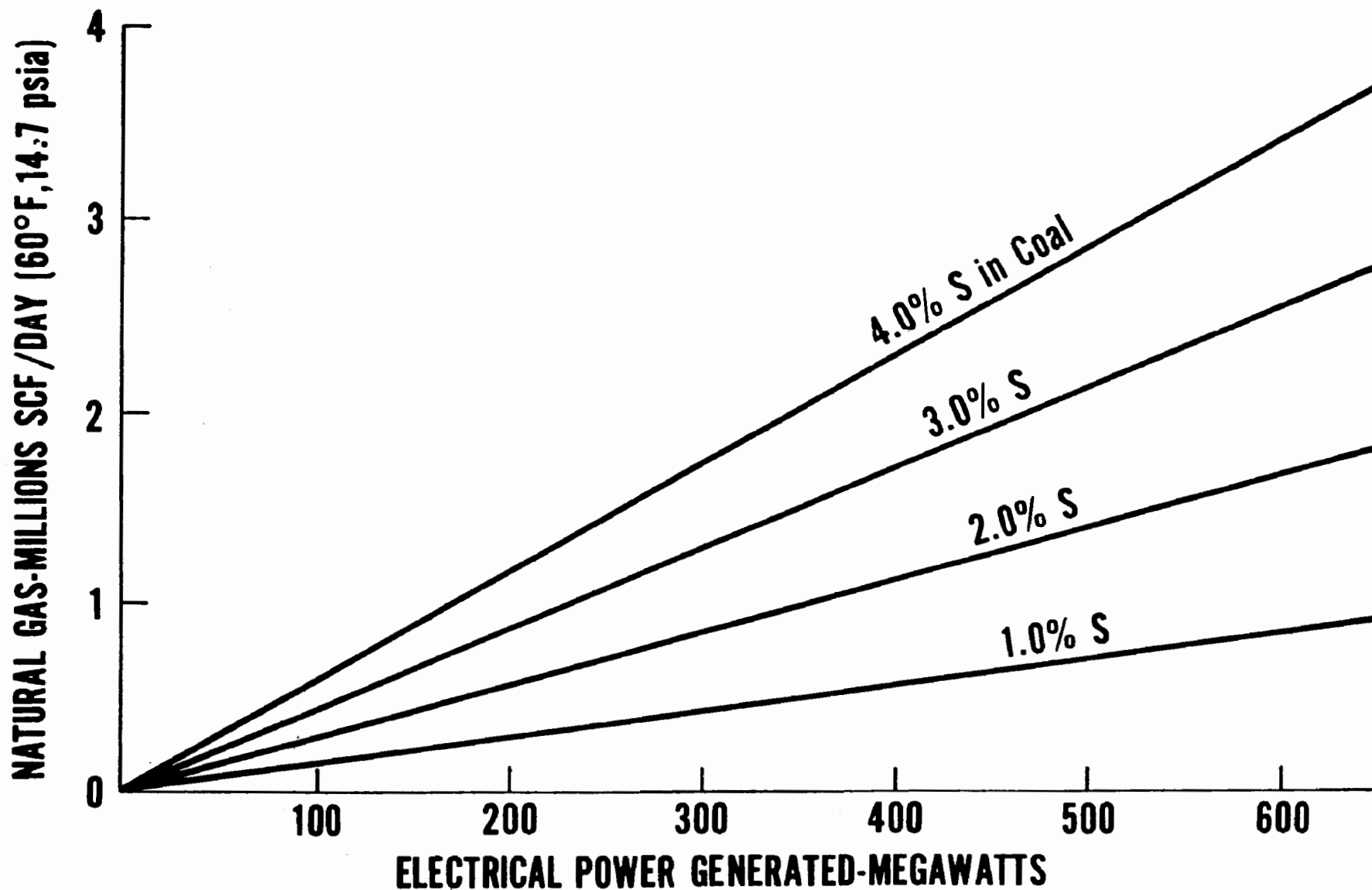






NATURAL GAS REQUIRED FOR SO₂ REDUCTION AT COAL BURNING ELECTRIC UTILITIES

Fig. IV



NATURAL GAS REQUIRED FOR SO₂ REDUCTION AT ELECTRICAL UTILITIES BURNING FUEL OIL

Fig. V

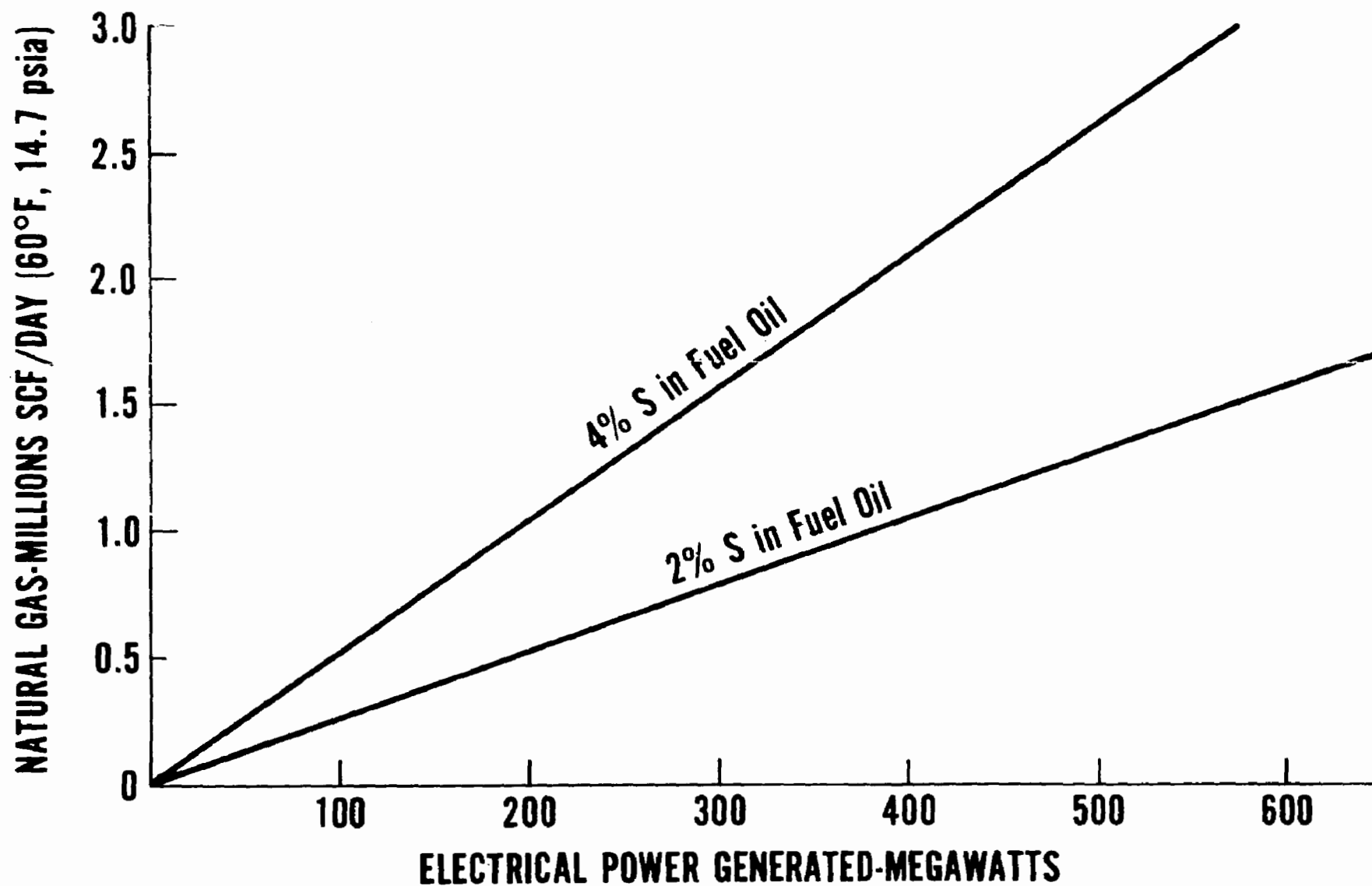
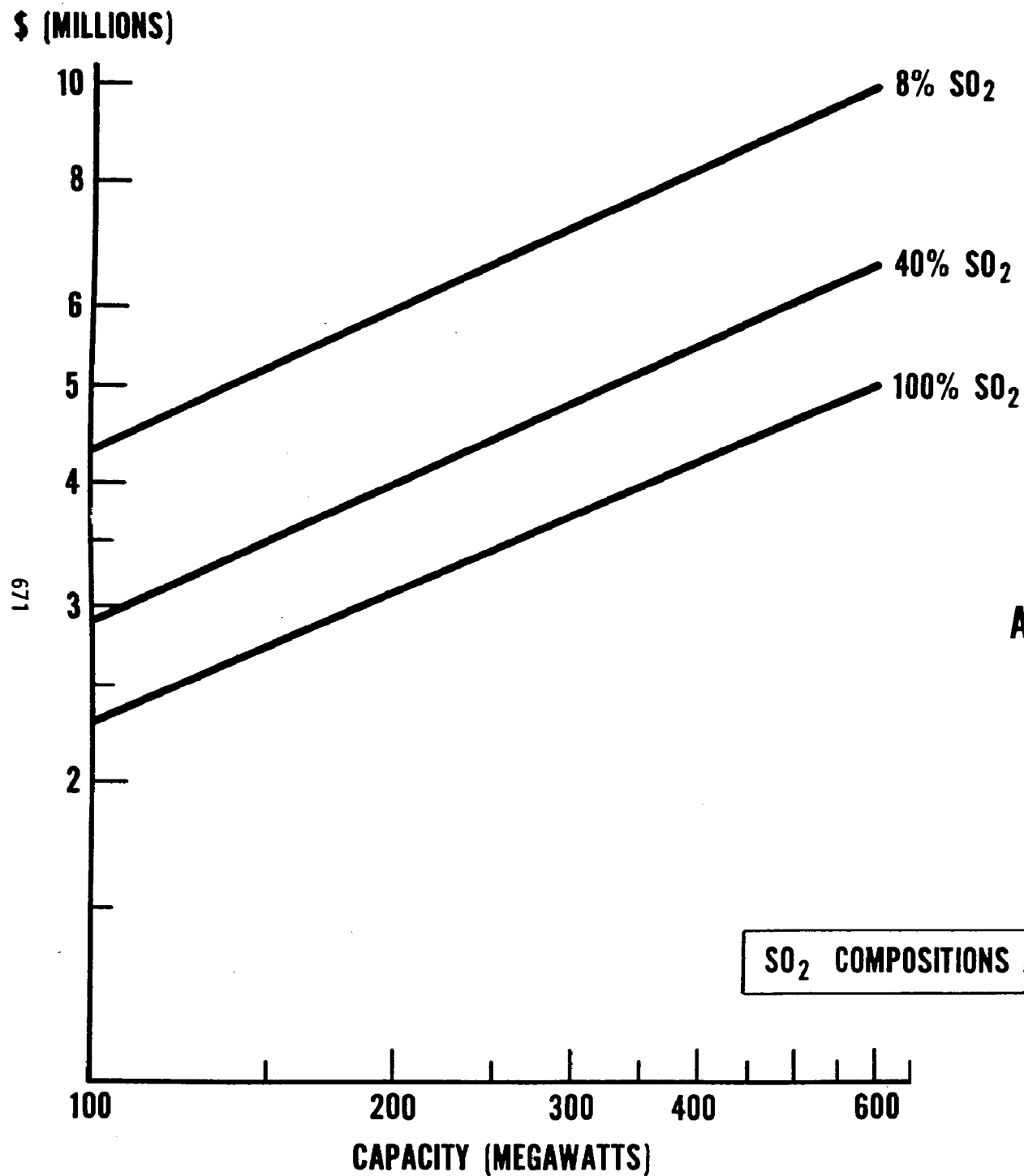


Fig. VI



ALLIED CHEMICAL SO₂ REDUCTION
TOTAL INSTALLED COST
(Battery Limits Plant)

SO₂ COMPOSITIONS ARE DRY BASIS

Table I
FEED GAS TO ALLIED CHEMICAL SO₂ REDUCTION UNIT*

MEGAWATTS GENERATED	100	300	600
EQUIVALENT SULFUR IN GAS (Long Tons/Day)	21.7	65	130
% SO ₂ IN GAS (Dry Basis)	VOLUME OF GAS (MSCFM)		
100%	0.4	1.3	2.5
40%	1.0	3.1	6.3
8%	5.3	15.8	31.6

* Based on 4% sulfur in fuel oil assuming 90% recovery of SO₂ in the associated flue gas desulfurization step.

THE CAT-OX PROJECT AT ILLINOIS POWER

by

W. E. Miller, Director, Environmental Affairs
Illinois Power Company
Decatur, Illinois

THE CAT-OX PROJECT AT ILLINOIS POWER

ABSTRACT

The Catalytic Oxidation method developed by Monsanto Enviro-Chem Systems, Inc. for removing sulfur dioxide from flue gas of fossil fuel generating stations has passed the pilot plant stage. The first commercially sized installation was operated for a short period in September, 1972 on the 100 Mw Wood River #4 unit of Illinois Power Company. The project is being financed jointly by the Control Systems Laboratory of the Office of Research & Monitoring of Federal EPA and by Illinois Power Company. This article describes why Illinois Power Company chose Cat-Ox for a demonstration installation in an attempt to control sulfur oxide emissions and also describes the operation of the Cat-Ox System.

INTRODUCTION

The removal of sulfur dioxide from the flue gas of fossil combustion units is a major concern of public utilities since they rely heavily on fossil fuel for the generation of electricity; therefore, much effort is being expended in close co-operation with the chemical industry in the development of an acceptable method of sulfur removal. At the present time a proven method of removing sulfur dioxide from flue gas is not available although many demonstration installations of the scrubber type are now being installed by utilities. The Cat-Ox System, the chemical conversion method described in this paper, has now been installed on a demonstration basis by Illinois Power Company. A demonstration is considered to be a successful installation whose scale and length of operation are great enough to provide full determination of feasibility for commercial application. It is hoped, therefore, that the Cat-Ox System now installed on a demonstration basis will be successful and can be offered for general use.

ILLINOIS POWER COMPANY

Illinois Power Company is a combination electric and gas investor owned utility serving territories in central and southern Illinois. To supply its electrical needs, the five fossil-fueled generation stations shown in Figure 1 combine to provide a capacity of 2200 Mw.

Baldwin #2, a 600 Mw coal-fired unit has been completed recently and Baldwin #3, another 600 Mw coal unit, will be completed in 1975. With the addition of Baldwin #3, the company capacity will be 3,400 Mw in 1975. Since coal is used for generating the major portion of this capacity, it is vitally important to Illinois Power that reasonable methods of eliminating pollutants from coal either before or after combustion be developed as rapidly as possible.

The Wood River Station of Illinois Power Company is located in Madison County near East Alton, Illinois, which is in the St. Louis Major Metropolitan Area. The Cat-Ox System is being installed on Unit #4 at Wood River which has a nominal rating of 100 Mw; the boiler is a Combustion Engineering reheat, natural circulation, balanced draft, pulverized coal, tangentially fired unit with steam conditions of 1500 psig and 1005°F at the superheater outlet. The Cat-Ox System is designed for a flue gas flow rate of 1,120,000#/hour which is equivalent to a load of about 110 Mw.

The unit burns approximately 275,000 tons of coal per year with a sulfur content of 3.1%. Based on this, the Cat-Ox System theoretically should produce about 19,000 tons per year of equivalent 100% sulfuric acid.

CAPITAL AND OPERATING COSTS

The capital costs involved in the design and construction of the Cat-Ox System were estimated at \$7,300,000, including the costs of providing off-battery services. Of this amount Illinois Power Company contracted to pay \$3,800,000 and the Office of Research and Monitoring of Federal EPA contracted to pay \$3,500,000. The battery limit services include supply facilities for natural gas and fuel oil for reheat burners, cooling water for acid coolers and miscellaneous uses, electric services for ID fans, electrostatic precipitators and pumps and facilities for ash disposal. Final costs now appear to be \$8,150,000, giving us an installed cost of \$74 per Kw based on the 110 megawatt gross capacity of the generating unit.

The Federal EPA will undertake an extensive test and evaluation program to fully characterize the Cat-Ox System and to provide data on its emission reduction capabilities as well as the operating costs for the system to form a basis for comparison with other installations. It is expected that the data will be made available to all interested parties and will be used by EPA, regulatory agencies, and members of the utility industry.

For a period of five years, Enviro-Chem will be responsible for the disposal of the sulfuric acid produced by the system with net revenues from acid sales credited 75% to Illinois Power and 25% to Enviro-Chem. Operating and maintenance costs are expected to run \$600,000 per year after the initial de-bugging period; assuming a price of \$8 per ton of acid, the net operating and maintenance costs should be about \$500,000 per year, excluding fixed charges on capital costs.

THE CAT-OX PROCESS

The operation of the Cat-Ox System consists basically of the following six separate phases:

1. Fly Ash Collection
2. Conversion of SO_2 to SO_3
3. Heat recovery
4. Removal of sulfuric acid
5. Acid mist elimination
6. Acid storage and loading

These basic steps are shown diagrammatically in Figure 2 and are described below.

1. Fly Ash Collection

The existing mechanical collector remains in service on Unit #4 to remove most of the fly ash from the flue gas. A new Research-Cottrell electrostatic precipitator with a design efficiency of 99.6% has been installed to work in series with the mechanical collector to remove essentially all the particulate matter from the flue gas. After leaving the electrostatic precipitator, the cleaned flue gas is heated and passes into the converter of the Cat-Ox System or, during start-up or unusual operation, can be by-passed directly to the stack. The fly ash collected by the precipitators is conveyed pneumatically to the existing ash pit area. The electrostatic precipitator installation was completed in February 1972 and has been operating with Unit #4 since that time.

2. Conversion of SO_2 to SO_3

The temperature of the flue gas leaving the electrostatic precipitator is 310°F and must be reheated to 850°F to allow a 90% conversion of SO_2 to SO_3 . It was proposed that this be done by two in-line reheat burners using natural gas or No. 2 fuel oil and by recovery of sensible heat from the treated

flue gas. The reheat burners were to be designed to maintain the 850°F conversion temperature regardless of boiler load. Modifications are now being made on this re-heat system to permit operation totally on #2 oil. Following reheat to conversion temperature, the flue gas enters the converter where the Cat-Ox [®] catalyst (a vanadium pentoxide catalyst) reacts with the SO₂ to form SO₃. The converter is designed so that the catalyst bed can be emptied onto a conveyor system for transport to a screening process after which the cleaned catalyst is conveyed back to the converter. About 2.5% of the catalyst mass is lost during each cleaning process which is anticipated to occur about four times per year. About forty-eight hours is required for each catalyst cleaning.

3. Heat Recovery

The treated flue gas, now containing SO₃, passes to a Ljungstrom-type heat exchanger where about 400°F sensible heat is recovered to heat the incoming untreated flue gas. As a result of heat recovery in this exchanger, the overall need for fuel usage is to add 150°F of sensible heat in the Cat-Ox process. The temperature of the gas is maintained well above the dew point. Normal flue gas leakage in a regenerative heat exchanger of this type will allow about 5% of the flue gas to by-pass the unit thereby reducing the overall efficiency of SO₂ removal to approximately 85%.

4. Removal of Sulfuric Acid

The flue gas is further cooled in a packed-bed absorbing tower which operates in conjunction with an external shell and tube heat exchanger. During cooling, the H₂O and SO₃ combine to form sulfuric acid which is subsequently condensed. The tower brings a cool stream of sulfuric acid into direct contact with the rising hot flue gas. Exit gas leaves the packed section at about 250°F while hot acid is constantly being removed from the bottom of the tower and cooled

in the external heat exchanger and sent to storage.

5. Acid Mist Elimination

Very fine mist particles of sulfuric acid are formed in the gas as it is cooled in the absorbing tower. These mist particles in the flue gas are removed along with some entrained droplets of circulating acid from the tower by the Brink (R) mist eliminator system. The packed section of the absorbing tower and the mist eliminators are contained within one vessel. The flue gas leaving the mist eliminator to enter the exit stack contains less SO_3 than the amount normally emitted from the combustion process.

6. Acid Storage and Loading

The cooled acid amounting to 12 gallons per minute of 78% H_2SO_4 is collected in two 400,000 gallon steel storage tanks. An acid loading pump and tank car loading facilities are provided adjacent to the storage tanks. Tank trucks may be loaded from this station if desired.

PROJECT TIMETABLE

The time schedule for the Cat-Ox System includes:

Design and Capital Cost Estimates - Initiated June 1970

Detailed Engineering & Equipment Procurement - Initiated November 1970

On Site Construction - Initiated January 1971

Electrostatic Precipitator - Placed in Operation February 1972

Entire Cat-Ox unit scheduled for operation mid-1973

Data Phase including one year operational testing by Federal EPA -
estimated to be completed October 1974.

DELAY IN TIMETABLE

The Research-Cottrell precipitator was completed on schedule and was placed in operation in February, 1972. The Cat-Ox System was scheduled to begin operation

in June, 1972 but, due to construction delays, initial start-up using gas as the in-line heater fuel did not occur until September 4, 1972. Preliminary operations in September and October indicate that the unit is meeting the performance criteria set for the system. Conversion of SO_2 to SO_3 reached 93% which is over the 90% guaranteed. The Cat-Ox unit removed 89% of SO_2 admitted to it which is over the 85% guaranteed. Acid of 78% concentration was produced when operating the absorbing tower at design temperature. Acid mist exiting the system was below 0.3 mg/cu. ft. against a design criterion of 1.0 mg/cu. ft. The system handled the full 1,120,000 lb/hr. of flue gas when meeting these criteria.

Over 1,400 tons of acid were produced during this period and two tank cars of the acid have been sold to a fertilizer manufacturer to assure its acceptability.

In October it became evident that the shortage of natural gas would preclude its use as a reheat fuel for the Cat-Ox unit. The existing burner equipment in the Cat-Ox had to therefore be modified to operate totally on #2 fuel oil. Design modification and equipment changes are in progress. As soon as they are completed, the Cat-Ox System will again be brought on stream.

In a new generating unit, the necessity for reheat would not exist. The flue gas would be taken from the boiler at a point near the economizer or super-heater at a temperature of 850-900°F. A hot precipitator would then remove the particulate matter and let the flue gas enter the converter at the required 850°F. For this reason, based on the limited operation we have had to date, we believe the Cat-Ox System might be a feasible system for installation in a new coal fired station. Retrofit application will be proven or disproven by the Wood River #4 installation.

GUARANTEE AND OPERATING PROGRAM

One or two 24-hour tests by Enviro-Chem will be conducted to assure that the Cat-Ox System meets the following guarantees:

1. The system is capable of operating with a gas flow of 1,120,000#/hour entering the system at 310°F.
2. The system is capable of producing 60° Baume' (77.7% H₂SO₄) sulfuric acid.
3. The exit gas emitted to the stack does not contain, on the average, more than 1.0 milligrams of 100% sulfuric acid mist per actual cubic foot of gas when the system is operated at rated capacity.
4. The conversion of SO₂ to SO₃ of the gas entering the converter is at least 90% at rated capacity.
5. The system operates so that over 99% of the fly ash in the flue gas leaving the boiler is removed when operating at rated capacity.
6. The system removes 85% of the SO₂ in the flue gas entering the system.

Following the 24-hour test period, Illinois Power Company will operate the Cat-Ox System for a minimum of one year as mentioned previously. During this period, and for a subsequent period of four years, if Illinois Power Company decides to continue to operate the system, data will be obtained to evaluate the following items:

1. Operating characteristics and plant performance (relative to SO₂ and fly ash removals and to H₂SO₄ recovery).
2. Maintenance procedures, requirements, and costs.
3. Total process operating costs.

Figures 3 and 4 show the Cat-Ox installation as it nears completion.

SUMMARY

In an attempt to advance the frontiers of knowledge in the science of removing sulfur dioxide from flue gas, Illinois Power, with Battelle Institute, conducted

a comprehensive survey of possible sulfur removal systems. The possibility of using low sulfur Western coal was considered but it was found to be less efficient than local coal, and precipitator efficiency declined with its use; in addition, it cost three times as much. As a result of these studies, Illinois Power Company decided that the Cat-Ox System, after both a pilot installation and prototype installation, was most nearly ready for commercial demonstration. In 1970 the capital costs being considered for Cat-Ox were much higher than those proposed for other SO₂ control systems. However, as more actual experience has been gained since 1970, it seems that the capital costs originally estimated by Enviro-Chem for Cat-Ox were more realistic than those estimated for other systems, primarily because of the decade of research and the advanced stage of development of the Cat-Ox System.

The Cat-Ox System is expected to remove 85% of the sulfur dioxide from the flue gas as 78% sulfuric acid and to remove essentially all of the fly ash. Sale of the sulfuric acid could offset some of the operating costs. Illinois Power Company, by removing the pollutants from the environment and conserving natural resources by recovering a product which is presently being thrown away, is not solving one pollution problem and creating another one. While some start-up difficulties have been encountered with the Cat-Ox System, we are still hopeful it will prove to be a feasible method and that it may solve the sulfur removal problem in a new coal fired generating unit and possibly even in a retrofit installation.

ACKNOWLEDGMENT

We hereby express grateful acknowledgment to the Control Systems Laboratory of the Office of Research and Monitoring of the Federal Environmental Protection Agency for their financial assistance and excellent cooperation in this major project.

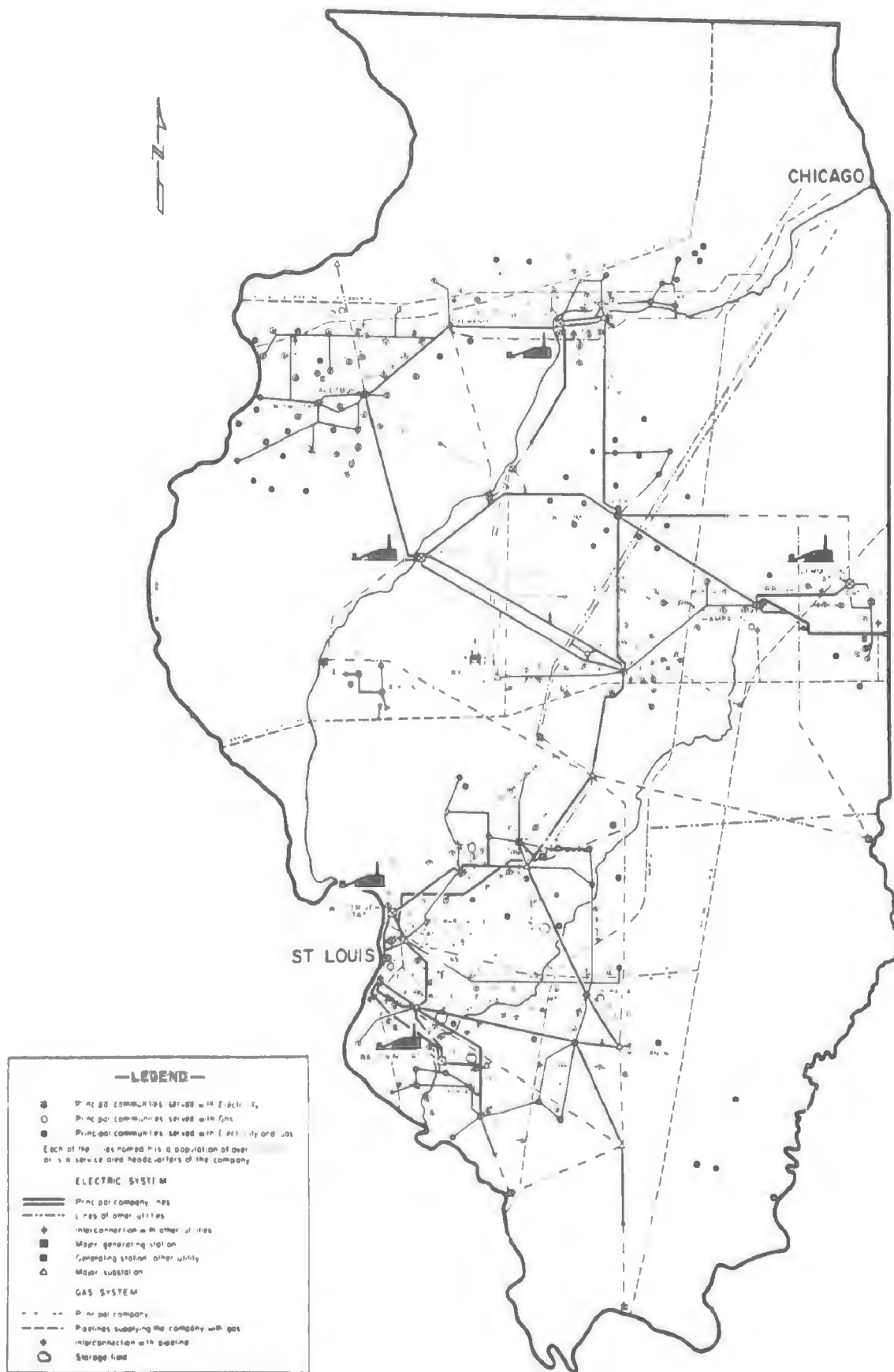


FIGURE 1 TERRITORY SERVED BY ILLINOIS POWER COMPANY

THE REHEAT CAT-OX SYSTEM

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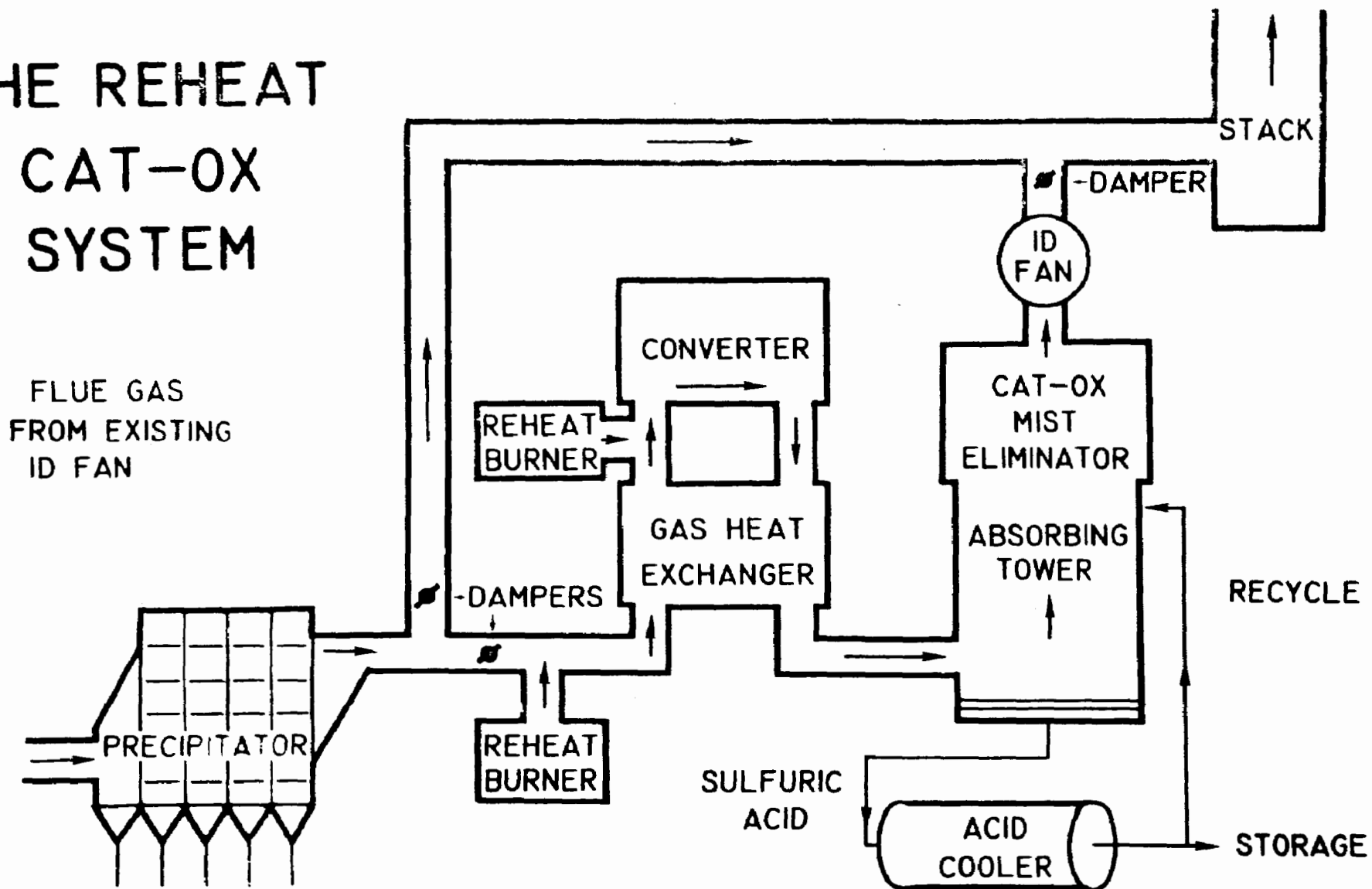
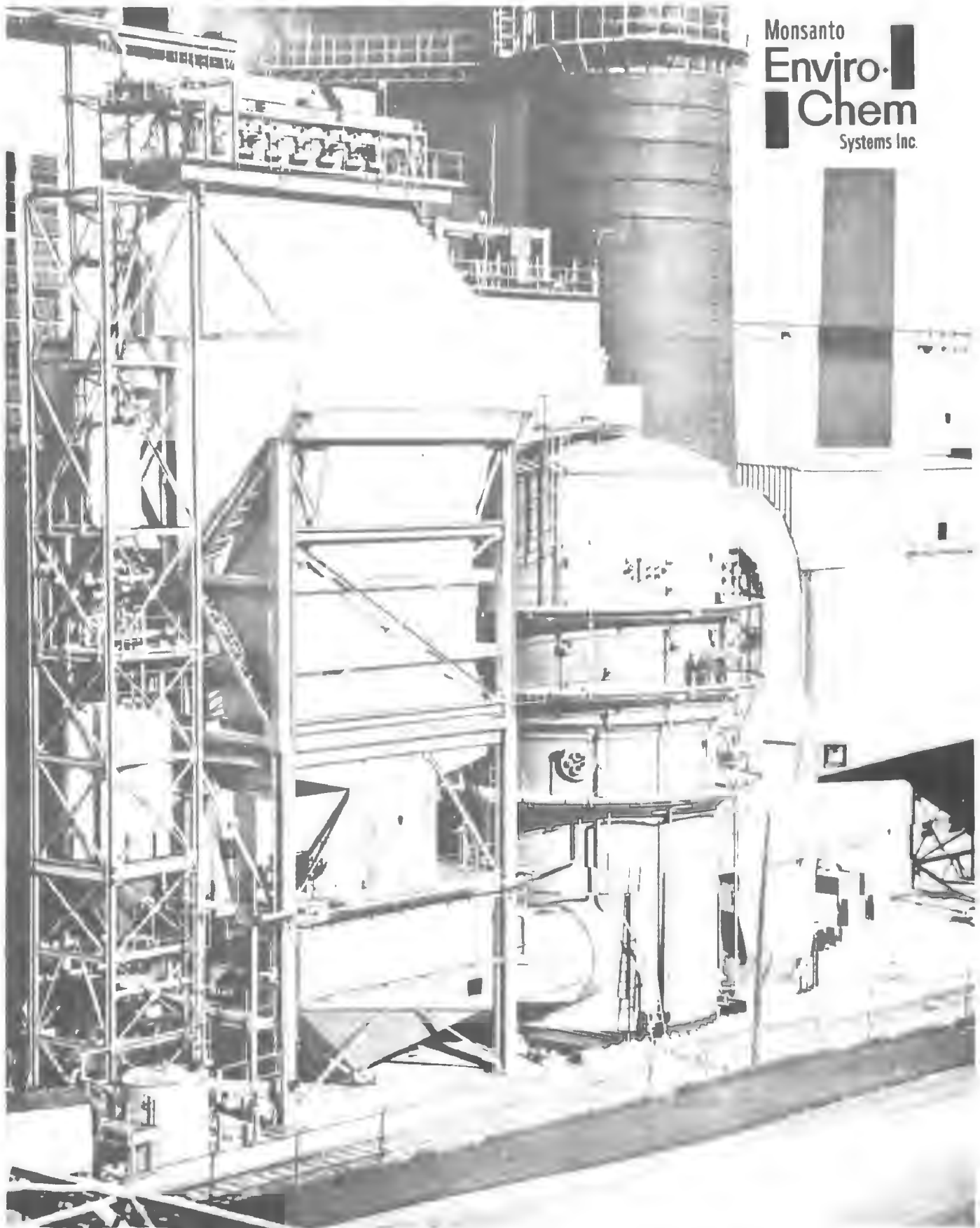


FIGURE 2



REHEAT CAT-OX SYSTEM

Monsanto
Enviro-Chem
Systems Inc.



REHEAT CAT-OX SYSTEM
ILLINOIS POWER — WOOD RIVER UNIT NO. 4

MITRE TEST SUPPORT
FOR THE CAT-OX DEMONSTRATION
PROGRAM

by

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ABSTRACT

This paper describes MITRE test support for the Cat-Ox Demonstration Program. The overall scope of MITRE's test program is outlined, and specific task efforts accomplished to date are presented. A detailed description is provided on the individual tests of the Baseline Measurement Program, and select test results are provided concerning: grain loading measurements, comparisons of continuous and manual measurements of SO_2 with theoretical values, comparisons of continuous and manual measurements of NO_x , sulfur balance measurements, and comparisons of elemental concentrations of coal and ash throughout the steam generator system. The paper further discusses current activity in preparation for the One-Year Demonstration Test Program. In particular, the measurement parameters and design of the continuous measurement instrumentation system for the evaluation of process performance are presented; and the instrumentation and facilities for the measurement of gas concentrations, gas flow, and automatic recording of data are reviewed.

MITRE TEST SUPPORT
FOR THE
CAT-OX DEMONSTRATION PROGRAM

Background

MITRE's contract with the Environmental Protection Agency was initiated in April of 1971. Under this contract, MITRE is required to provide technical support for the Cat-Ox Demonstration Program in terms of: 1) program management assistance, 2) the development of test plans, 3) the design, development, and installation of measurement systems, 4) services related to the implementation of test programs, and 5) evaluation of test results with application of the results to the total industry.

As a first step, a number of program plan alternatives were developed and evaluated. These plans, and the details of the overall program plan which was selected, are described in our Management Plan for Test Support for the Cat-Ox Demonstration Program (MITRE Technical Report No. 6054 dated July 1971). A summary of the MITRE task efforts defined for the program is provided in Figure 1.

Major Task Areas

The first of the task areas concerns the "Definition of Test Requirements," in which MITRE examined the requirements of potential users, reviewed the technical and economic capabilities of the Cat-Ox process, and defined the "window" of test conditions at the steam generator/Cat-Ox interface for the demonstration test (see Figure 2). This task was completed in November of 1971 with the definition of

TASK 1	DEFINE TEST REQUIREMENTS	(COMPLETED)
TASK 2	BASELINE MEASUREMENT PROGRAM	(COMPLETED)
TASK 3	CAT-OX DEMONSTRATION	
	- TEST PREPARATION	TO BE COMPLETED AUGUST 1973
	- ONE-YEAR MEASUREMENT PROGRAM	SEPTEMBER 1973 - SEPTEMBER 1974
TASK 4	EVALUATION OF RESULTS	SEPTEMBER 1974 - MARCH 1975

FIGURE 1
PROGRAM SUMMARY

- EXAMINE REQUIREMENTS OF POTENTIAL USERS
- SPECIFY TECHNICAL & ECONOMIC CAPABILITIES OF CAT-OX PROCESS
- DEFINE "WINDOW" OF TEST CONDITIONS AT STEAM GENERATOR/CAT-OX INTERFACE FOR DEMONSTRATION

FIGURE 2

TASK 1 - DEFINITION OF TEST REQUIREMENTS

interface flue gas conditions (temperature, gas flow rate, SO_2 concentration, and grain loading) for 89 existing steam generators which were categorized as potential users of the reheat Cat-Ox system. Interface flue gas conditions were also determined for 75 steam generators to be constructed by 1976 which were categorized as potential users of the integral design Cat-Ox system.

The second of our task areas concerns the "Baseline Measurement Program." The specific objectives of the Baseline Measurement Program as shown in Figure 3 are to 1) characterize baseline performance in terms of operability, reliability, and emission levels prior to installation of the Cat-Ox process; 2) to determine the relationship between control settings and operating conditions for the steam generator, and flue gas properties at the Cat-Ox steam generator interface; 3) to test and calibrate measurement procedures and hardware to be used in the one year demonstration test; and 4) to obtain quantitative data supporting the establishment of realistic performance standards for pollutants other than SO_2 and particulates.

The third task area concerns the performance of a "One-Year Demonstration Test" wherein a measurement program is conducted which will fully characterize Cat-Ox process emission control performance; quantify the operating economics of the process; establish the operability, reliability, and maintainability of the Cat-Ox process; and determine the resulting effects on the steam generator with which the process is integrated.

- DETERMINE BASELINE EMISSION LEVELS, OPERATING EFFICIENCY, AND RELIABILITY OF STEAM GENERATOR IN ACCORDANCE WITH A.S.M.E. POWER TEST CODES
- DEFINE STEAM GENERATOR CONTROL SETTINGS AND OPERATING CONDITIONS TO PRODUCE DESIRED FLUE GAS PROPERTIES AT THE CAT-OX INTERFACE
- TEST AND CALIBRATE MEASUREMENT PROCEDURES AND HARDWARE TO BE USED IN THE ONE-YEAR DEMONSTRATION
- PROVIDE EMISSION INFORMATION TO EPA TO SUPPORT THE ESTABLISHMENT OF REALISTIC EMISSIONS STANDARDS

FIGURE 3

BASELINE MEASUREMENT OBJECTIVES

The fourth task area concerns the "Demonstration Evaluation" where reduced test data are translated into quantified statements on the technical and economic adequacy of the process.

Scope of Baseline Measurement Program

To meet the objectives of the Baseline Measurement task (Task 2), a test program was initiated with six preliminary tests wherein necessary background information was obtained on isokinetic sampling techniques, rates of particulate loading in sampling equipment, and effects of power plant ambient conditions on the measurements. This information was then used to determine ranges of gas and particulate concentrations to be encountered in the measurement program, to confirm the sampling frequency and sampling positions utilized in the measurement program, and to identify any changes in operating procedures or modifications in test equipment necessary for the primary measurement effort. These preliminary tests were conducted over a two-week period beginning September 28, 1971 (see Figure 4).

The main measurement program was initiated on November 8, 1971 following the completion of the preliminary measurement effort and the completion of all required facility modifications (ports, sheds, and stack access platform). Each of the twenty-one tests of the main measurement program was of approximately 10 hours duration. During the 10 hour period of each test, the major steam generator parameters (load factor, fuel type, soot blowing cycle, excess air, and burner angle) were fixed at a predetermined operating level. The combinations

- 6 PRELIMINARY TESTS BASED ON:
 - LOAD FACTOR: 35%, 100%
 - EXCESS AIR: MINIMUM, MAXIMUM
 - SOOT BLOWERS: NONE, RETRACTABLE AND WALL BLOWERS
 - TEMPERATURE AND VELOCITY TRAVERSE AT ECONOMIZER
 - TEMPERATURE, VELOCITY, AND GRAIN LOADING TRAVERSE AT AIR HEATER

- 21 INDIVIDUAL TESTS BASED ON:
 - LOAD FACTOR: 35%, 50%, 75%, 100%
 - FUEL TYPE: 3 LBS S/M BTU, 1.5 LBS S/M BTU, 1.0 LBS S/M BTU
 - SOOT BLOWING: NONE, RETRACTABLE BLOWER AND WALL BLOWERS
 - EXCESS AIR: MINIMUM, NORMAL, MAXIMUM
 - BURNER ANGLE: NORMAL

- 2 TESTS BASED ON:
 - TEMPERATURE, VELOCITY, AND GAS CONCENTRATION TRAVERSALS AT STACK AND AT AIR HEATER
 - LOAD LEVEL: 100%, 50%
 - FUEL TYPE: 3 LBS S/M BTU, 1.5 LBS S/M BTU

- 1 TEST BASED ON:
 - NO GAS CONCENTRATIONS AT STACK AND ECONOMIZER
 - BURNER ANGLE: MINIMUM THROUGH MAXIMUM

FIGURE 4

BASELINE MEASUREMENT PROGRAM

of operating levels were selected so as to provide the maximum of information in a minimum number of tests, varying the parameters on a "one-at-a-time" basis.

Two supplementary gas traversal tests were also conducted to determine the pattern of leakage at the air heater and the gas flow pattern midway in the stack.

A supplementary test was also conducted in which all factors were held constant except for burner angle, which was varied in steps from the minimum to maximum position.

Baseline Measurement Parameters

For all of the tests, key steam generator operating parameters were monitored, samples of coal and ash were obtained at various points in the steam generator, gas samples were manually obtained, particulate grain loadings were determined by manual sampling, and temperatures, pressures, gas flows and gas concentrations were monitored by a MITRE designed continuous measurement system.

These key parameters were measured as shown on Figure 5 at three locations: 1) Location 1 - Prior to the economizer, was selected to provide data at the relatively high temperatures corresponding to the inlet of an integral Cat-Ox system designed for installation in new steam generators, 2) Location 2 - between the upper and lower sections of the air preheater - selected as representative of a lower temperature condition prior to any existing or planned flue gas treatment system, and 3) Mid stack - approximately 135 feet above the foundation of the

LOCATION 1 PRIOR TO ECONOMIZER

LOCATION 3 MIDWAY IN STACK

- TEMPERATURE
 - PRESSURE
 - FLOW
 - GAS COMPOSITION (SO_2 , CO, CO_2 , HC, NO, NO_2 , O_2 , H_2O VAPOR)
-

LOCATION 2 IN AIR PREHEATER

LOCATION 3 MIDWAY IN STACK

- TEMPERATURE
- PRESSURE
- FLOW
- GRAIN LOADING
- PARTICULATE COMPOSITION
- PARTICLE SIZE DISTRIBUTION
- ADSORBED MATERIALS

FIGURE 5

BASELINE MEASUREMENT PARAMETERS

250 foot stack, selected to provide a condition representative of the flue gas emitted to the atmosphere (and, in this instance, conditions which will be seen at the reheat Cat-Ox/steam generator interface). At all locations, the ports and sampling points were selected so as to provide the proper number and distribution of measurement points in accordance with ASTM Standard D 2928-71 ("Standard Method for Sampling Stack for Particulate Matter").

Results of Baseline Measurement Program

A brief summary of the results of the Baseline Measurement Program is provided in Figure 6. This paper summarizes a few of our major findings, whereas the detailed results of our Baseline program are presented in a report to be distributed by the Office of Research and Monitoring ("Baseline Measurement Test Results for the Cat-Ox Demonstration Program," April 1973, Report No. EPA-R2-73-189).

Representative grain loading measurements are shown in Figure 7. These measurements were taken at our position number 3, midway in the stack. All measurements were taken using the EPA particulate sampling train (with impingers) as described in the Federal Register, Vol. 36, No. 247, December 23, 1971. The upper set of data shown in Figure 7 summarizes the results from a series of tests which were run with coal from the Southwestern Mine of the Peabody Coal Company. Ranges are shown in the data set for the sulfur content, ash content, and the measured grain loading, representing the extremes of the measurement. (As for example, six tests were run at the 100 mw power level

COMPLETE CHARACTERIZATION OF POWER PLANT IN TERMS OF:

- TEMPERATURES, PRESSURES, AND GAS VOLUME FLOWS THROUGHOUT SYSTEM
- GAS CONCENTRATIONS THROUGHOUT SYSTEM AND EMITTED AT STACK
 - SO_2 , O_2 , CO_2 , CO , H_2 , NO , NO_2 , H_2O VAPOR
- GRAIN LOADING AT AIR HEATER AND EMITTED AT STACK
- COAL FEED COMPOSITION: PROXIMATE, ULTIMATE, AND ELEMENTAL ANALYSES
- FLY ASH PARTICLE SIZE, COMPOSITION, ADSORBED MATERIAL
- BOTTOM ASH COMPOSITION
- COMPLETE SULFUR BALANCE
- "MAPPING" OF STRATIFIED GAS FLOW AT AIR HEATER AND STACK
- NO_x EMISSIONS RELATED TO BURNER ANGLE

FIGURE 6

BASELINE MEASUREMENT RESULTS

<u>LOAD FACTOR</u>	<u>FUEL TYPE</u>	<u>ASH CONTENT OF COAL (AS RECEIVED)</u>	<u>GRAIN LOADING (GRAINS/ACF)</u>	<u>EMISSION RATE (LBS/HR)</u>
100 MW	3.24-3.40%S	9.9-10.7%	.6-.95	2,100-3,000
75 MW	2.87-3.37%S	9.8-10.4%	.5-.57	1,000-1,200
50 MW	2.74-3.47%S	9.6-10.8%	.6-.75	650-1,000
100 MW	1.65%S	16.7%	.78-.90	2,500
75 MW	1.83%S	13.6%	.59	1,300
50 MW	1.68%S	16.0%	.76	1,100

FIGURE 7
BASELINE GRAIN LOADING MEASUREMENTS
(MIDWAY IN STACK)

for which the fuel for each individual test ranged from 3.24% sulfur to 3.40%) The lower set of data shown in Figure 7 summarizes the findings from three tests each run at a single power level, using as fuel a mixture of natural gas and coal from the Orient No. 3 mine in Jefferson County, Illinois. The coal and gas were fired in combination so as to simulate fuel with a sulfur content of 1 lbs Sulfur/ 10^6 BTU. The values shown in Figure 7 do, however, represent the actual measured percentage sulfur and ash of the coal constituent of the mixture. The data show that although the ash content of the coal in the lower set of data was substantially higher than the upper set, grain loadings and emission rates were comparable because of the diluting effect of the natural gas fired with the coal.

Data from the same tests are shown in Figure 8, compared with respect to measured SO_2 concentration. Again, the lower data set which shows sulfur content of the coal as 1.65%S, 1.83%S, and 1.68%S is fuel equivalent to 1 lbs S/ 10^6 BTU because of the blending with sulfur-free natural gas. The theoretical values shown for SO_2 concentration (and the other measured values shown for SO_2 concentration) are based upon the actual measured excess air, they are not corrected to any standard excess air condition. The manual SO_2 values were obtained using the procedures defined by EPA in the Federal Register for determining sulfur dioxide emissions from stationary sources (Federal Register, Vol. 36, No. 247 - December 23, 1971). The continuous SO_2 values were obtained using MITRE's continuous measurement instrumentation system, which included a Dupont 460 UV analyzer

<u>LOAD FACTOR</u>	<u>FUEL TYPE</u>	<u>MEASURED EXCESS AIR</u>	<u>THEORETICAL SO₂ (PPM)</u>	<u>MANUAL SO₂ (PPM)</u>	<u>CONTINUOUS SO₂ (PPM)</u>
100 MW	3.24-3.40%S	36-64%	1760-1990	1300-1850	1755-2040
75 MW	2.87-3.37%S	27-52%	1780-2170	1300-1430	1740-2080
50 MW	2.74-3.47%S	38-69%	1760-2110	860	1780-1815
100 MW	1.65%S	41%	580	425	535
75 MW	1.83%S	35%	755	445	630
50 MW	1.68%S	34%	533	385	565

FIGURE 8

COMPARISONS OF CONTINUOUS & MANUAL
MEASUREMENTS OF SO₂ WITH THEORETICAL VALUES
(MIDWAY IN STACK)

for SO_2 measurement. Both the upper and lower data sets shown in Figure 8 are typical of the results of the total test effort where good agreement was found between the continuous measurements and the theoretical measurements, whereas the manual measurements were generally lower than the theoretical values (averaged 76% of the theoretical values).

Figure 9 shows a comparison between continuous and manual measurements of NO_x for the same set of tests. The manual measurements were obtained using the standard EPA method for determination of nitrogen oxide emissions from stationary sources as described in the previously cited Federal Register. The continuous measurement results were obtained using a Dupont 461-C UV instrument which measured both NO and NO_2 . The results shown in the continuous measurement column are primarily NO . No consistent patterns were found with respect to the effect of test conditions on NO_x concentrations, except for the tests performed with gas and coal fuel firing which produced NO_x levels significantly lower than in the tests performed with the other fuel types.

Representative sulfur balance calculations are shown in Figure 10. For each of the tests, the average coal consumption rate was determined utilizing coal scale readings. The average sulfur content of the coal (as determined by chemical analysis) was then used with the coal scale readings to determine the rate of sulfur feed to the steam generator. Average SO_2 mass flow readings from the continuous measurement system were then used to determine the average sulfur flow from the stack. The results are based upon measurement of SO_2 concentrations in the

<u>LOAD FACTOR</u>	<u>FUEL TYPE</u>	<u>MEASURED EXCESS AIR</u>	<u>MANUAL NO (PPM)</u>	<u>CONTINUOUS NO (PPM)</u>
100 MW	3.24-3.40%S	36-64%	320-650	285
75 MW	2.87-3.37%S	27-52%	270-450	330-345
50 MW	2.74-3.47%S	38-69%	325-405	345
100 MW	1.65%S	41%	265-365	105
75 MW	1.83%S	35%	308	240
50 MW	1.68%S	34%	235-260	150

FIGURE 9

COMPARISONS OF CONTINUOUS & MANUAL MEASUREMENTS
OF NO_x (MIDWAY IN STACK)

<u>LOAD FACTOR</u>	<u>FUEL TYPE</u>	<u>AVERAGE SULFUR FEED IN COAL (LBS/MIN)</u>	<u>AVERAGE SULFUR FLOW FROM STACK AS SO₂ (LBS/MIN)</u>
100 MW	3.24-3.40%S	35.8-46.0	31.8-45.5
75 MW	2.87-3.37%S	31.7-36.0	26.5-35.1
50 MW	2.74-3.47%S	21.5-29.2	19.8-22.9
100 MW	1.65%S	10.4	10.0
75 MW	1.83%S	12.8	11.3
50 MW	1.68%S	7.3	6.3

FIGURE 10
SULFUR BALANCE MEASUREMENTS

stack and do not include measurement of the sulfur exhausted from the stack as SO_3 , or the sulfur adsorbed on the surface of the ash throughout the system. The results, however, show good agreement on the sulfur balance leading to the conclusion that the total combined error in SO_2 and gas flow measurements was low. For all except two tests, the sulfur feed rate exceeded the sulfur flow rate measured in the stack indicating that there were, in fact, small unmeasured losses of sulfur.

Trace element concentrations were determined in four tests on the coal feed, pulverizer rejects from the mills, bottom ash, and the fly ash collected from the bottom of the air heater, the mechanical collector, and in the duct at the air heater and at mid stack. Trace element concentrations were also determined for samples of fly ash collected in the duct at the air heater and at mid stack for four additional tests, as well as trace elemental analysis of pulverized coal for six additional tests. In all cases, the analysis was performed for approximately 27 elements using atomic absorption. A sample comparison from these analyses is provided in Figure 11 for thirteen of the elements of special interest as potentially hazardous materials. An exact material balance of the elements cannot be performed because of the fact that certain material flows such as bottom ash and ash from the mechanical separator were not measured and can only be estimated. This type of balance is also precluded by the fact that many elemental concentrations are expressed as "less than" values. The results are, however, of special value in estimating emission rates for a number of elements

<u>ELEMENT</u>	<u>PULVERIZED COAL</u>	<u>PULVERIZER REJECTS</u>	<u>BOTTOM ASH</u>	<u>ASH FROM MECHANICAL SEPARATOR</u>	<u>ASH FROM AIR HEATER DUCT</u>	<u>ASH FROM MID STAGE</u>
Ba	< .03	< .03	----	.03	< .04	< .04
Be	< .0002	< .0002	.0004	.0008	.001	.001
Cd	.0006	.0004	< .005	.002	----	.002
Cr	.002	.002	.016	.013	.05	----
Cu	.002	.003	.007	.007	.010	.020
Hg	< .0002	.00006	.0003	.00004	< .00002	----
Mn	.009	.007	.057	.036	.050	.080
Ni	.009	.0009	.013	.040	.050	----
Pb	< 0.003	< 0.003	.009	< 0.003	0.020	0.020
Se	< .06	< .06	< .05	< .07	< .05	< .05
Sn	< .05	< .05	< .1	< .05	< .05	< .05
V	< .02	< .02	.04	< .02	.02	.03
Zn	.11	.011	.038	.057	----	.090

FIGURE 11

COMPARISONS OF ELEMENTAL CONCENTRATIONS IN COAL
AND ASH THROUGHOUT SYSTEM
(WEIGHT PERCENT)

not usually examined in emission testing programs. For this purpose, the elemental concentrations must be combined with the mass loading measurements to provide the emissions data in useful form. An estimate of the overall accuracy of the measurements can be noted by comparing the values given for the ash from mid stack and with ash from the air heater duct. The values from these two columns should be nearly identical, and as such represent essentially duplicate measurements.

Cat-Ox Demonstration Test

Task 3 of MITRE's support program concerns the Cat-Ox Demonstration Test. Preparation for the demonstration test is currently underway. This preparatory work is scheduled to be completed in August of 1973, after which MITRE will initiate our one-year measurement program in September of 1973.

The major areas of concern which MITRE will investigate in the one-year test program are summarized in Figures 12 and 13. A test plan has been drafted which examines these areas in a systematic step-by-step fashion. The prime area for investigation concerns the overall operating characteristics and performance of the Cat-Ox system relative to the removal of SO_2 and fly ash and the production of sulfuric acid. Other areas, include the effectiveness of the catalyst as a function of time, the effectiveness of the mist eliminator and any special requirements for maintaining its effectiveness, the degree of seal leakage encountered in the Ljungstrom rotary heat exchanger, corrosion rates of the plant equipment, and the response of the Cat-Ox

- OPERATING CHARACTERISTICS AND PLANT PERFORMANCE (RELATIVE TO SO_2 AND FLY ASH REMOVAL AND H_2SO_4 RECOVERY)
- LONGEVITY OF THE CATALYST
- NECESSITY AND FREQUENCY OF MIST ELIMINATOR WASHING OPERATIONS
- DEGREE OF REGENERATIVE HEAT EXCHANGER SEAL LEAKAGE WITH TIME

FIGURE 12

CAT-OX DEMONSTRATION TEST - MAJOR AREAS OF CONCERN

- CORROSION RATES OF PLANT EQUIPMENT (WITH SPECIAL EMPHASIS ON THE ACID LOOP AND HEAT TRANSFER EQUIPMENT)
- RESPONSE OF PROCESS TO FUELS OF VARYING SULFUR CONTENT
- EFFECT OF CAT-OX SYSTEM FAILURE ON POWER PRODUCTION
- COMPONENT PRESSURE DROPS (AS A FUNCTION OF TIME)
- ABILITY OF POWER PLANT PERSONNEL TO OPERATE AND MAINTAIN SYSTEM

FIGURE 13

CAT-OX DEMONSTRATION TEST - MAJOR AREAS OF CONCERN

system to fuels of various sulfur content. Also of interest in our test program is the possible effect of Cat-Ox system failure on power production, pressure drops across system components as a function of time, and the ability of power plant personnel to operate and maintain the Cat-Ox System.

Manual and Continuous Measurements

Both manual and continuous measurement instrumentation will be used for evaluation of the Cat-Ox process performance. Figure 14 states the reasons for utilizing both methods. With regard to the measurement of particulates, sulfur trioxide and sulfuric acid mist, there is presently not available completely automatic continuous measurement instrumentation, and, therefore, manual techniques must be employed.

Continuous recording of data has several advantages. One advantage is the ability to obtain immediate indication of results instead of having to wait for several days until sample solutions are analyzed in the laboratory. Also real-time availability of data provides an early check on the performance of the measuring instrumentation so that necessary repairs can be made quickly, thereby minimizing the loss of data. The installation of continuous measuring instrumentation is cost effective provided the measurement program for which it will be used is particularly long, as it will be for Cat-Ox (one year), so that the initial cost of equipment purchase and installation is offset by reduced manpower requirements during the test itself. Furthermore,

- MANUAL SAMPLING METHODS
 - PROVIDE BASIS FOR COMPARISON
 - SOLE METHOD FOR DETERMINING CERTAIN POLLUTANTS
 - METHOD FOR CALIBRATION

- CONTINUOUS MONITORING SYSTEM
 - CONTINUOUS RECORD OF EMISSIONS
 - AUTOMATIC SAMPLING FROM TWELVE LOCATIONS IN PROCESS
 - AUTOMATIC CALIBRATION ON PERIODIC BASIS
 - IMMEDIATE DATA OUTPUT ON GAUGES, STRIP CHART, AND TELETYPE
 - DATA STORAGE ON MAGNETIC TAPE FOR COMPUTER PROCESSING

FIGURE 14

CAT-OX DEMONSTRATION TEST - MEASUREMENT METHODS

if one is evaluating a complex process as is the case with regard to Cat-Ox where simultaneous measurements are desirable from several locations, continuous measurements provide a particular advantage because of the manpower which would be required to man all the sites if the data were to be obtained manually. Continuous measurement instrumentation also permits test conditions to be changed more quickly, and permits observation of process performance during transitions from one test condition to another. Finally, once it has been decided to utilize continuous recording instrumentation, there is a tremendous advantage to storing the information on magnetic tape so that it can be readily processed by computer. The process of transferring data from strip charts to punched cards is expensive in time and manpower when large quantities of data are involved.

Cat-Ox Process and Measurement Points

The continuous measurement instrumentation represents a major part of the MITRE program so that the discussion which follows will be devoted primarily to that area of the MITRE work. The process itself is discussed by W. Miller in a paper entitled "The Cat-Ox Project at Illinois Power" included in these same proceedings and, therefore, will be reviewed in this paper to the extent required to explain the interfaces to MITRE instrumentation.

Figure 15 shows the flow diagram of the steam generator and Cat-Ox process. In this Figure, the dashed line separates the steam generator from the process. The Cat-Ox process, which is of

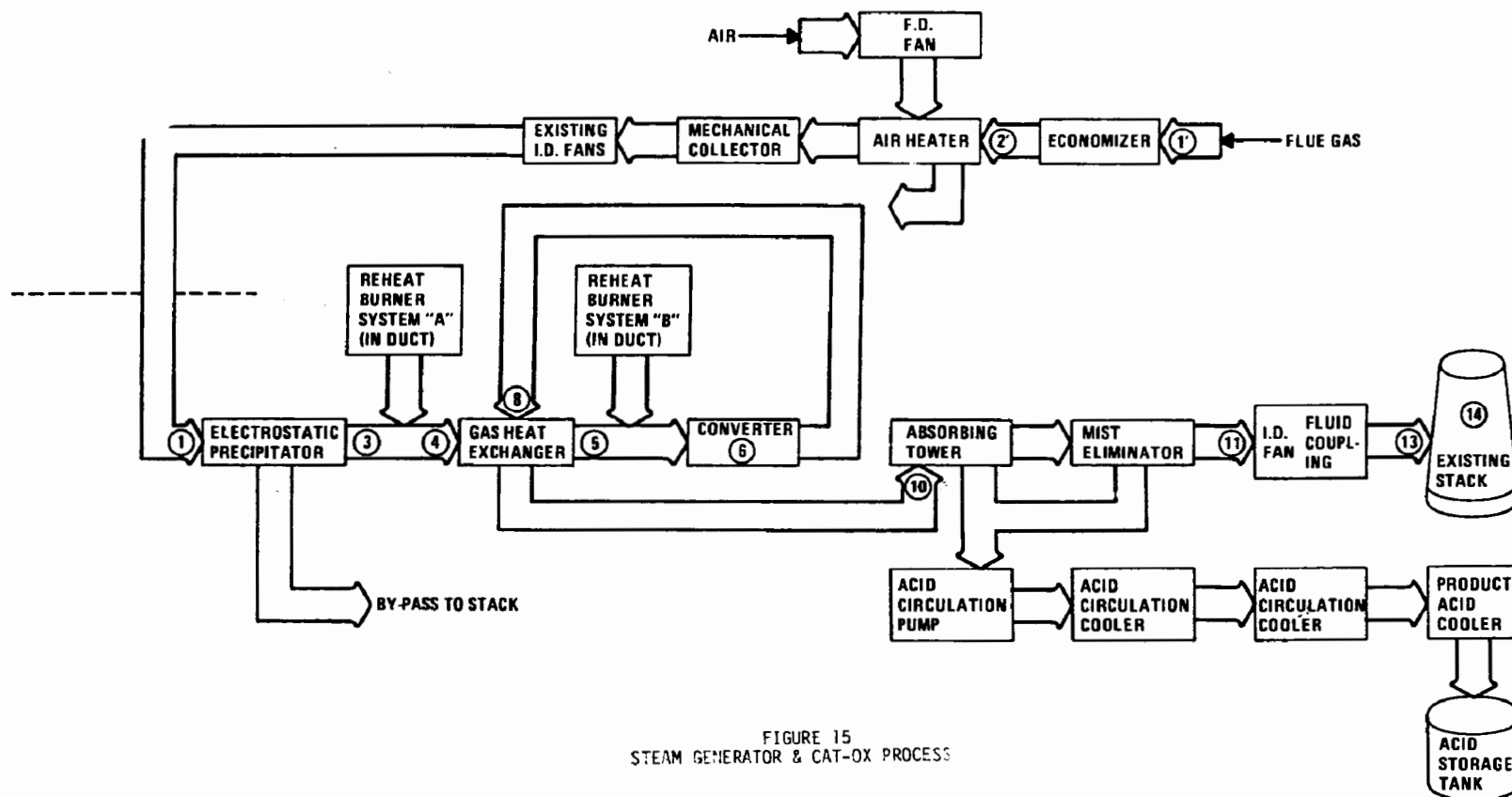


FIGURE 15
STEAM GENERATOR & CAT-OX PROCESS

the reheat type, has been installed between the existing I.D. fans and stack. The electrostatic precipitator is regarded as part of the process because it was installed with the process, and is required by the process to minimize contamination of the catalyst in the converter.

Flue gas from the boiler passes through the economizer and air heater, and then enters the mechanical collectors where particulates are initially removed. Particulates are further reduced to a very low level by the electrostatic precipitator. During the course of this flow, the gas temperature has dropped approximately 400°F and therefore must be reheated prior to entering the converter. The reheating is accomplished by burners "A" and "B" and the heat exchanger. The SO_2 in the flue gas is then converted to SO_3 and combined with water vapor in the absorbing tower to formulate sulfuric acid. The mist eliminator removes sulfuric acid mist which may escape from the absorbing tower with the flue gas. Because of the pressure drop throughout the process, a second I.D. fan is required to make up the losses and restore flow to the stack. Acid from the absorbing tower and mist eliminator are pumped, cooled, and finally stored in a large tank from which it can be periodically removed.

The numbers shown in the flow diagram identify the locations at which measurements will be made. Points 1', 2', and 14 are locations where measurements were made during the baseline measurement program. Measurements will be repeated at these three locations to permit

correlation with the baseline results and to reevaluate improvements which have been made in the operational efficiency of the mechanical collector. The other measurement points identified are pertinent to the evaluation of the overall Cat-Ox process and major subsystems of the process.

Purpose of Measurements

Figure 16 shows the measurement points which have been identified, the parameters which will be measured at each point, and the purposes for making particular measurements. The significant parameters which will be measured by continuous recording instrumentation are gaseous concentrations of SO_2 , H_2O vapor, O_2 , CO_2 , NO_x , NO_2 , and THC. Also differential pressure, static pressure, and temperature will be recorded continuously to obtain gaseous volume flow, system pressure drops, and gas temperatures. In addition, manual measurements will be made of gaseous SO_3 , H_2SO_4 mist, and particulates.

These measurements will be utilized to determine subsystem performance of the power plant and Cat-Ox process as follows:

- Efficiency of the mechanical collector
- Efficiency of the electrostatic precipitator
- Pressure drops across process subsystems and overall system
- Efficiency of the heat exchanger
- Percent leakage of heat exchanger
- Efficiency of converter
- Gas distribution in converter

<u>POINT</u>	<u>LOCATION</u>	<u>PARAMETERS</u>	<u>PURPOSE</u>
1'	INPUT ECONOMIZER	SO ₂ , O ₂ , CO ₂ , ΔP, P, T	CONFIRMATION BASELINE TEST; NON-REHEAT PROCESS CONDITIONS
2'	AIR HEATER	MASS LOADING*	EFF. MECHANICAL COLLECTOR
1	INPUT ESP	MASS LOADING*, ΔP, P, T	EFFICIENCY ESP; PRESSURE DROP ESP/CAT-OX
3	OUTPUT ESP	MASS LOADING*, ΔP, P, T	EFFICIENCY ESP;PRESSURE DROP ESP

*MANUAL MEASUREMENT

FIGURE 16
MEASUREMENT POINTS ONE-YEAR DEMONSTRATION TEST

<u>POINT</u>	<u>LOCATION</u>	<u>PARAMETERS</u>	<u>PURPOSE</u>
4	INPUT HEAT EXCHANGER	SO ₂ , H ₂ O, O ₂ , CO ₂ , ΔP, P, T	EFFICIENCY/PERCENT LEAKAGE HEAT EXCHANGER
5	OUTPUT GAS HEAT EXCHANGER (INPUT CONVERTER)	SO ₂ , SO ₃ [*] , H ₂ O, O ₂ , CO ₂ , ΔP, P, T	EFFICIENCY/PERCENT LEAKAGE HEAT EXCHANGER; EFFICIENCY CONVERTER
6	CONVERTER	SO ₃ [*] , SO ₂ , O ₂ , CO ₂	GAS DISTRIBUTION
8	OUTPUT CONVERTER	SO ₂ , SO ₃ [*] , H ₂ O, O ₂ , CO ₂ , MASS LOADING [*] , ΔP, P, T	EFFICIENCY CONVERTER VS. FLOW RATE, T, AND TIME; ASH ACCUMULATION; EFFICIENCY/ PERCENT LEAKAGE HEAT EXCHANGER

* MANUAL MEASUREMENT

FIGURE 16 (CONTINUED)

MEASUREMENT POINTS ONE-YEAR DEMONSTRATION TEST

<u>POINT</u>	<u>LOCATION</u>	<u>PARAMETERS</u>	<u>PURPOSE</u>
10	INPUT ABSORBING TOWER	SO ₂ , SO ₃ [*] , H ₂ O, O ₂ , CO ₂ , ΔP, P, T	EFFICIENCY/PERCENT LEAKAGE HEAT EXCHANGER; H ₂ SO ₄ IN ABSORBING TOWER
11	OUTPUT MIST ELIMINATOR	H ₂ SO ₄ MIST [*] , ΔP, P, T	PERFORMANCE MIST ELIMINATOR
13	INPUT STACK	P, T	PRESSURE DROP ACROSS CAT-OX
14	MIDWAY IN STACK	SO ₂ , H ₂ SO ₄ MIST [*] , CO ₂ , O ₂ , NO ₂ , NO _x , THC, H ₂ O, MASS LOADING [*] , ΔP, P, T	EMISSIONS

* MANUAL MEASUREMENT

FIGURE 16 (CONCLUDED)

MEASUREMENT POINTS ONE-YEAR DEMONSTRATION TEST

- Ash accumulation in converter
- Formation of H_2SO_4 in absorbing tower
- Performance of mist eliminator
- Emissions from the stack

The measurements performed at point 1' will be used to confirm the baseline test conditions and to obtain data at a location in the steam generator which is typical of that to which an integral type Cat-Ox process would be connected.

Overall Continuous Measurement System

Figure 17 shows the overall continuous measurement system. The system consists of four subsystems: the time-shared gas measurement subsystem, the flow measurement subsystem, the continuous gas measurement subsystem, and the data recording/control subsystem. The measurement points identified previously are shown inputting to each of the major subsystems. There are additional locations which have not been identified in this flow diagram where temperature, pressure, and humidity are measured continuously as individual parameters. Some of these locations are discussed in subsequent text.

Gas concentrations are measured on a time-shared basis at seven different locations by the time-shared gas measurement subsystem. One of these locations is the stack (point 14) where a second gas measurement subsystem is dedicated to measuring gas concentrations at this one point alone. There is a common time slot when both the time-shared subsystem and the dedicated subsystem both measure gas concentrations in the stack simultaneously so that data from both subsystems can be correlated.

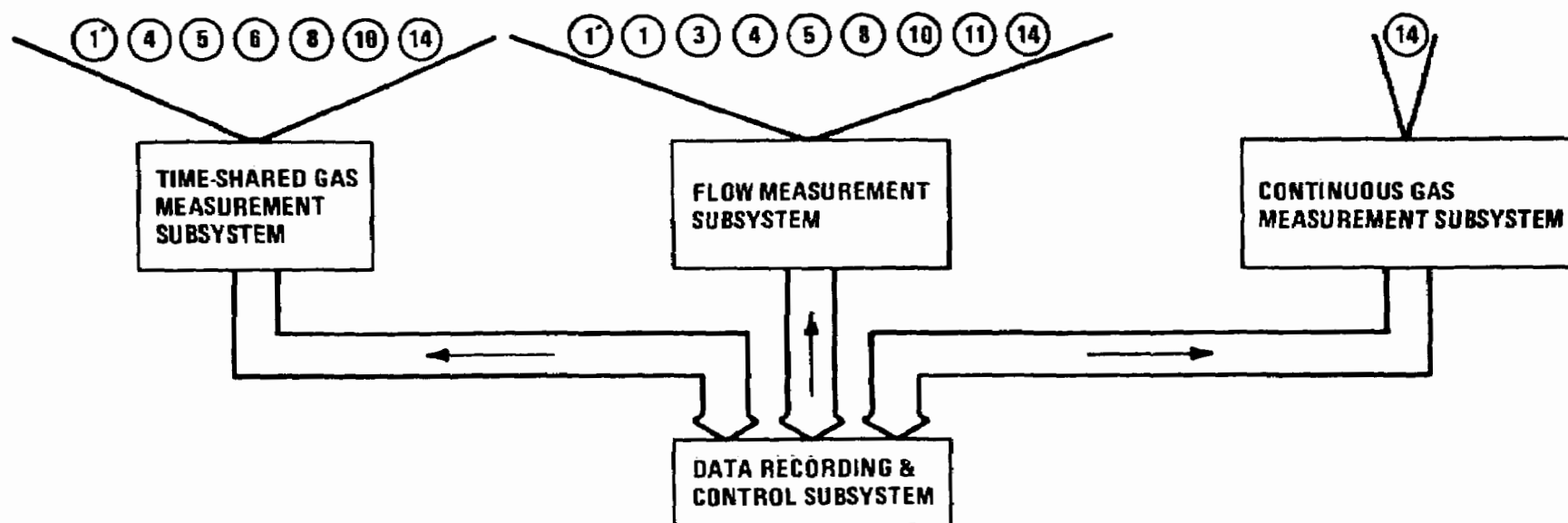


FIGURE 17
OVERALL INSTRUMENTATION SYSTEM

With the exception of point 6 which permits access within the converter, flow measurements are made at every point where gas concentration measurements are made so that mass flow rates can be computed. In addition, there are several points where continuous flow measurements are made without corresponding continuous gas measurements. At these points flow measurements are combined with manually measured gas concentrations or are used of themselves for subsystem evaluation.

Data from the gas and flow measurement subsystems are automatically recorded on strip charts, by printer, and on magnetic tape. Strip chart and printer data are utilized in real-time to assure that the instrumentation is functioning properly. Data recorded on magnetic tape is used for subsequent computer processing eliminating the tedious task of transferring data from strip charts to punched cards. In addition, the system is designed to perform certain automatic control functions such as switching of the time-shared gas subsystem, gas analyzer calibration, and blowback of sampling lines.

Time-Shared Gas Measurement Subsystem

Figure 18 shows the flow diagram of the time-shared gas measurement subsystem. Flue gas is drawn into the analyzers through a filtered probe which may be either an in-the-duct filter or an external heated filter. The gas from the probe is passed through a heated water trap and then through a heated teflon gas line (Dekoron line). The gas lines are heated to prevent condensation of water vapor and hydrocarbons.

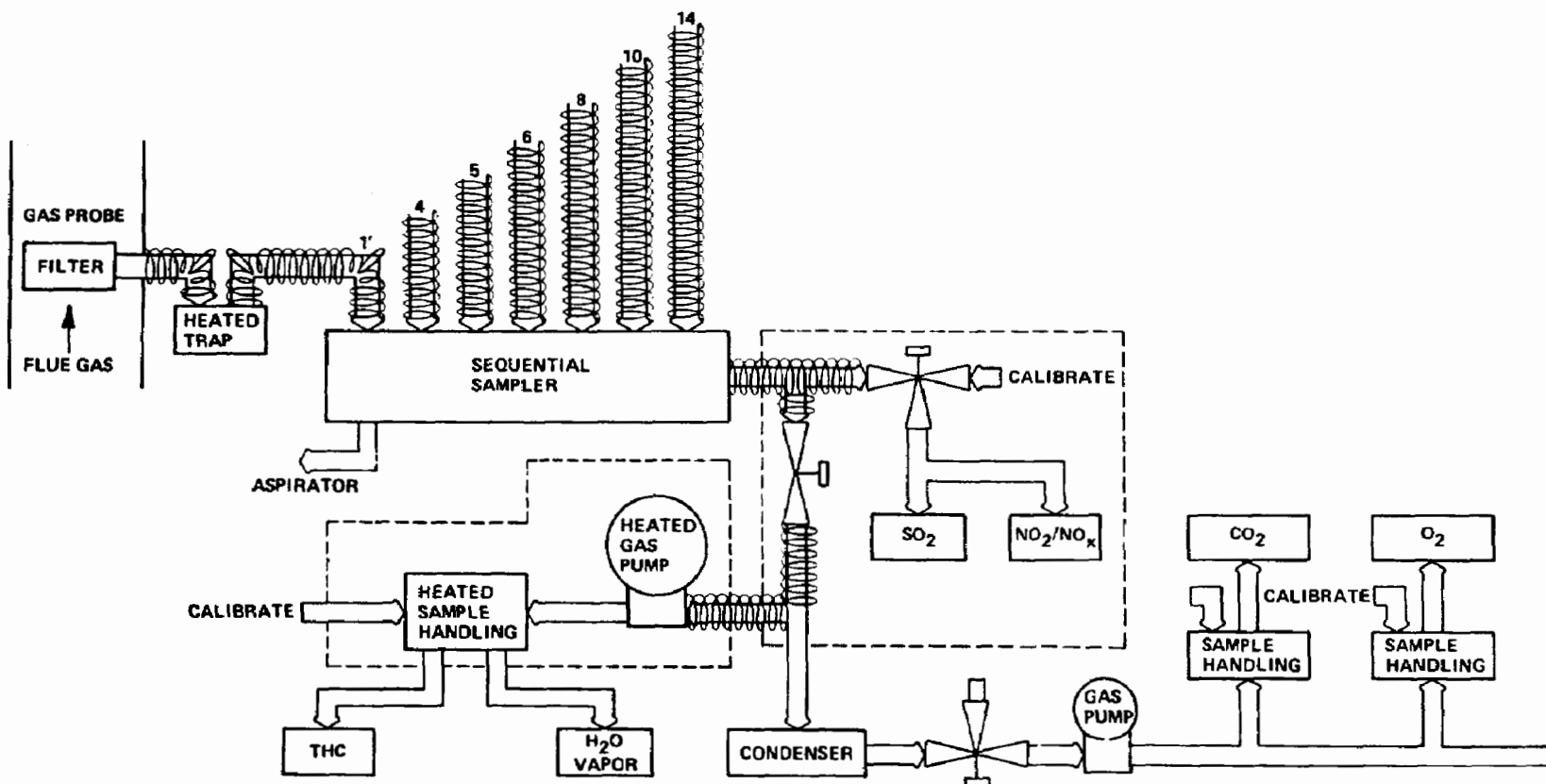


FIGURE 18
TIME-SHARED GAS MEASUREMENT SUBSYSTEM

Gas is sampled from seven different locations by a multi-point sequential sampler. The gas is aspirated through the seven lines continuously except during blowback. Each line is then selected sequentially by switching pneumatic valves drawing a fraction of the gas into the analyzers. The gas lines from the sequential sampler to the combined $\text{SO}_2\text{-NO}_2/\text{NO}_x$ analyzer and the THC and water vapor analyzers are also heated for the same reasons given above. The flue gas to the CO_2 and O_2 analyzers is first passed through a refrigerator-condenser in order to remove the water vapor, thereby preventing water vapor interference in the CO_2 analyzer and corrosion in the O_2 analyzer.

Operation of the time-shared gas measurement subsystem is shown in Figure 19. The subsystem is sequenced automatically on a one hour time base by the control subsystem. Flue gas is drawn into the analyzers from one particular line for a period approximately 7 minutes, and then that same line is blown back by high pressure air for approximately 1 minute to remove particulates from the ceramic filter. Subsequently, each of the remaining lines are sampled in succession in the same manner until the sequence is completed. Then all of the analyzers are automatically zeroed against nitrogen (except for the $\text{SO}_2\text{-NO}_2/\text{NO}_x$ analyzer), and then spanned against a calibration gas. The $\text{SO}_2\text{-NO}_2/\text{NO}_x$ analyzer provides the blowback air and is also designed to zero on the blowback air which is passed through the sample cells of the analyzer.

<u>POINT</u>	<u>OPERATION</u>	<u>TIME PERIOD (MINS.)</u>
1'	SAMPLE	7
	BLOWBACK	1
4	SAMPLE	7
	BLOWBACK	1
5	SAMPLE	7
	BLOWBACK	1
6	SAMPLE	7
	BLOWBACK	1
8	SAMPLE	7
	BLOWBACK	1
10	SAMPLE	7
	BLOWBACK	1
14	SAMPLE	7
	BLOWBACK	1
ALL ANALYZERS	ZERO	2
	SPAN	2
		<hr/> 60

FIGURE 19
OPERATION OF TIME-SHARED SUBSYSTEM

Continuous Gas Measurement Subsystem

Figure 20 shows the flow diagram of the continuous gas measurement subsystem which samples gas continuously from the stack. The principle gas sampled is SO_2 so that a continuous record of SO_2 emission from the stack is obtained. For purposes of illustration, an external heated filter is shown as opposed to an in-the-duct filter which was shown in the flow diagram of the time-shared subsystem. In addition, a multi-point gas probe is shown which will be used at several of sampling locations where gas concentration is expected to be non-uniform. The advantage of the external filter is that the filter element can be removed for cleaning without removal of the probe itself. The continuous gas measurement subsystem is synchronized with the time-shared gas measurement subsystem so that both subsystems overlap in time while sampling gas from the stack permitting correlation of data from both systems.

Flow Measurement Subsystem

The flow measurement subsystem is shown in Figure 21. Gas flow is determined by measuring differential pressure, static pressure, and temperature which are combined in an analytical relationship to calculate flow. As the cross-section of ducting is very large throughout the steam generator and Cat-Ox process, it is necessary to measure these parameters at a number of points within any particular duct in order to obtain a representative measurement. Therefore, the cross-section of the duct is divided into a number of sampling points based on the ASMA

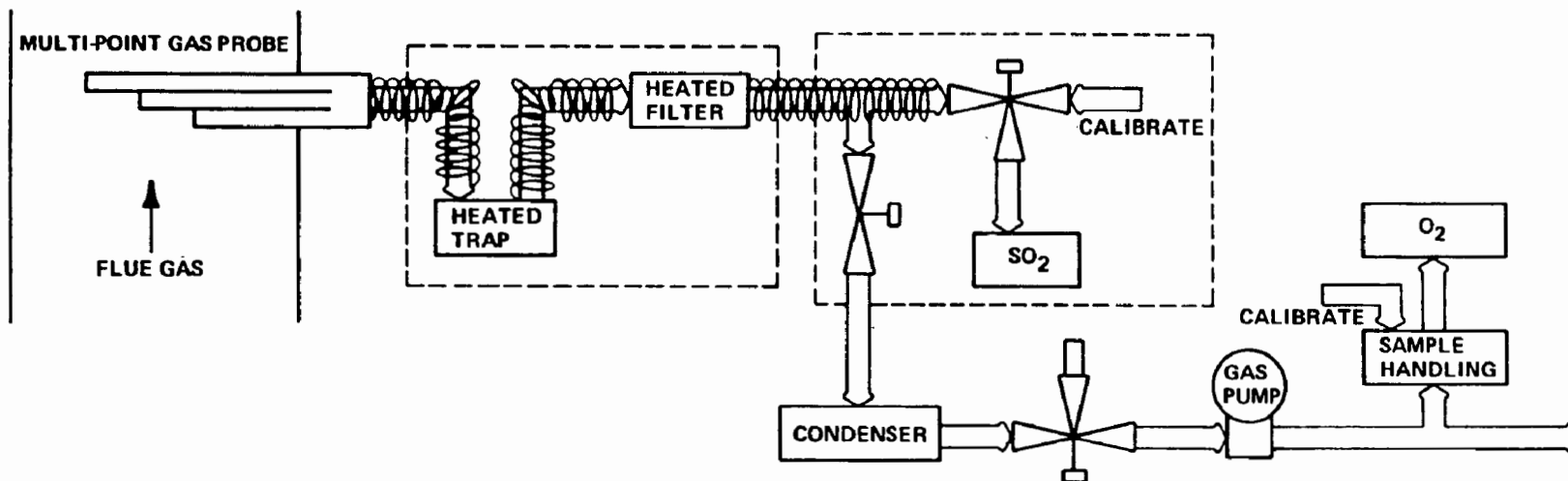


FIGURE 20
CONTINUOUS GAS MEASUREMENT SUBSYSTEM

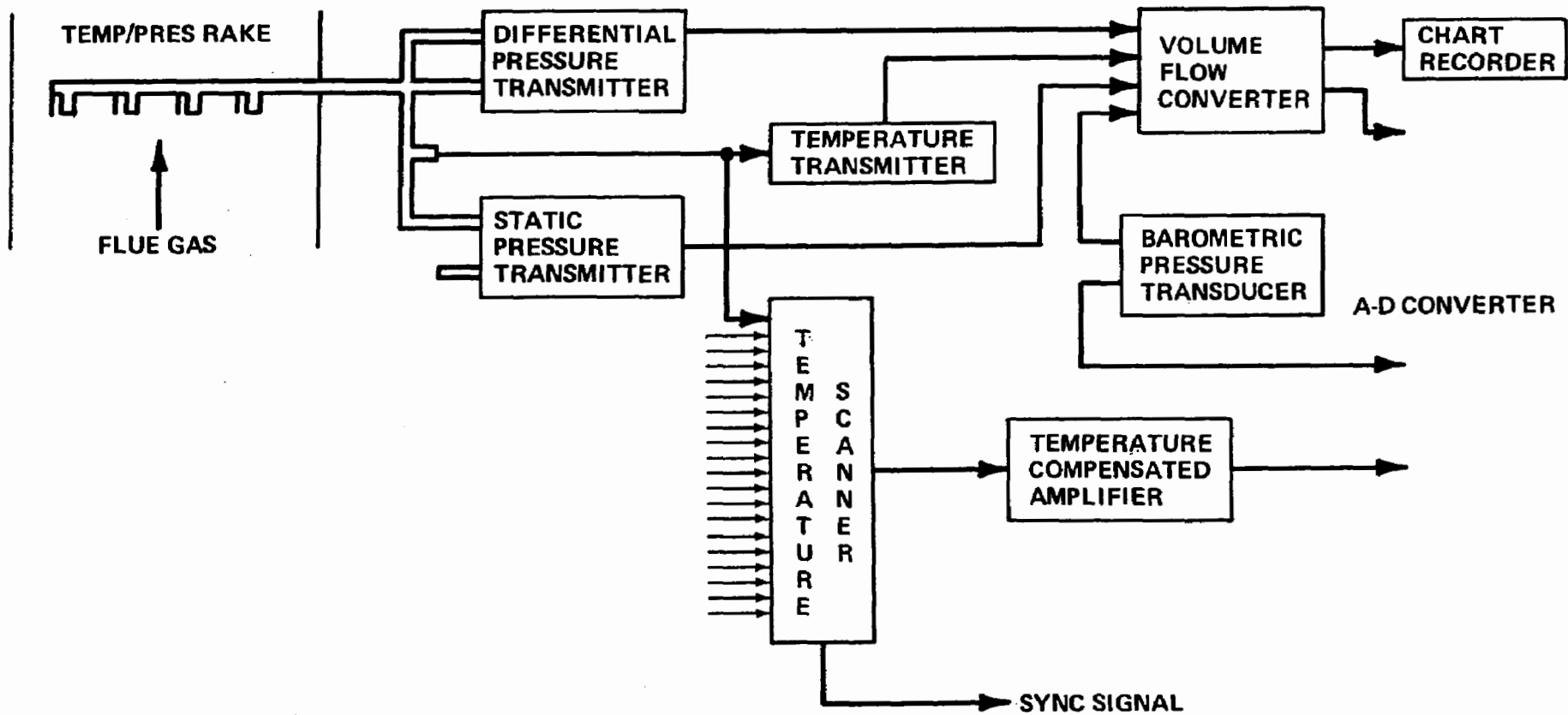


FIGURE 21
FLOW MEASUREMENT SUBSYSTEM

power test codes, and an array of combined temperature/pressure rakes are used to sense differential pressure, static pressure and temperature at the sampling points selected.

The magnitudes of the differential pressure and static pressure are measured by pressure transmitters and are normally recorded directly on strip charts and magnetic tape. As temperature is measured at many more locations in the system than is required for flow measurements, the temperature sensor, which is an iron-constantan thermocouple, is inputted through a constant temperature enclosure to a scanner. The scanner acts as a switch to connect thermocouples from various locations to a temperature-compensated amplifier which amplifies, linearizes, and temperature compensates the signal prior to entry into the A-D converter. The constant temperature enclosure, which is not shown in the flow diagram, maintains the connector junctions at constant temperature so that emfs which are generated cancel out.

In addition to recording the three parameters directly, a specialized analog computer identified as the volume flow converter is used to calculate the volume flow in real-time. The volume flow converter can be utilized at the output of any of the flow measurement instrumentation. Gas volume flow is of particular interest because it is one of the design parameters of the Cat-Ox process.

There are nine flow measurement locations which are nearly identical. However, at two of the locations, the economizer and stack, where differential pressures are particularly low, it has been necessary to use an electronic manometer in place of the differential pressure transmitter.

Data Recording and Control Subsystem

The outputs of the analyzers, transmitters, and other sensors are recorded on magnetic tape as shown in Figure 22. The data acquisition system proper has a capacity of fifty channels, which has been expanded, as discussed previously, with an additional twenty channels by means of a low noise temperature scanner. Eight channels are assigned to gas concentration measurements, 10 to static pressure, 9 to differential pressure, 1 to gas volume flow, 3 to channel identification and ambient measurements, and 14 to additional temperature measurements. The last 14 channels are tentatively assigned depending on time available to integrate the necessary electronics.

The scanner connects the analog signal from each channel in sequence to the A-D converter which digitizes the analog signal. The data from the A-D converter is transmitted to the coupler which formats it for recording on magnetic tape. A printer is utilized for visual recording of selected data. In addition, a teletypewriter (TTY) is employed as an input/output device. As an input device, the TTY writes directly onto the magnetic tape via the keyboard.

The scanner will normally be operated at 1 scan/minute but is capable of being operated at better than 1 scan/5 seconds. The digital clock will generate time in days, hours, and minutes and will provide reference signals to the function controller. The function controller will initiate start-stop commands to perform remote control functions such as sequencing of the time-shared gas measurement subsystem, calibration of the analyzers, and blowback of the probes.

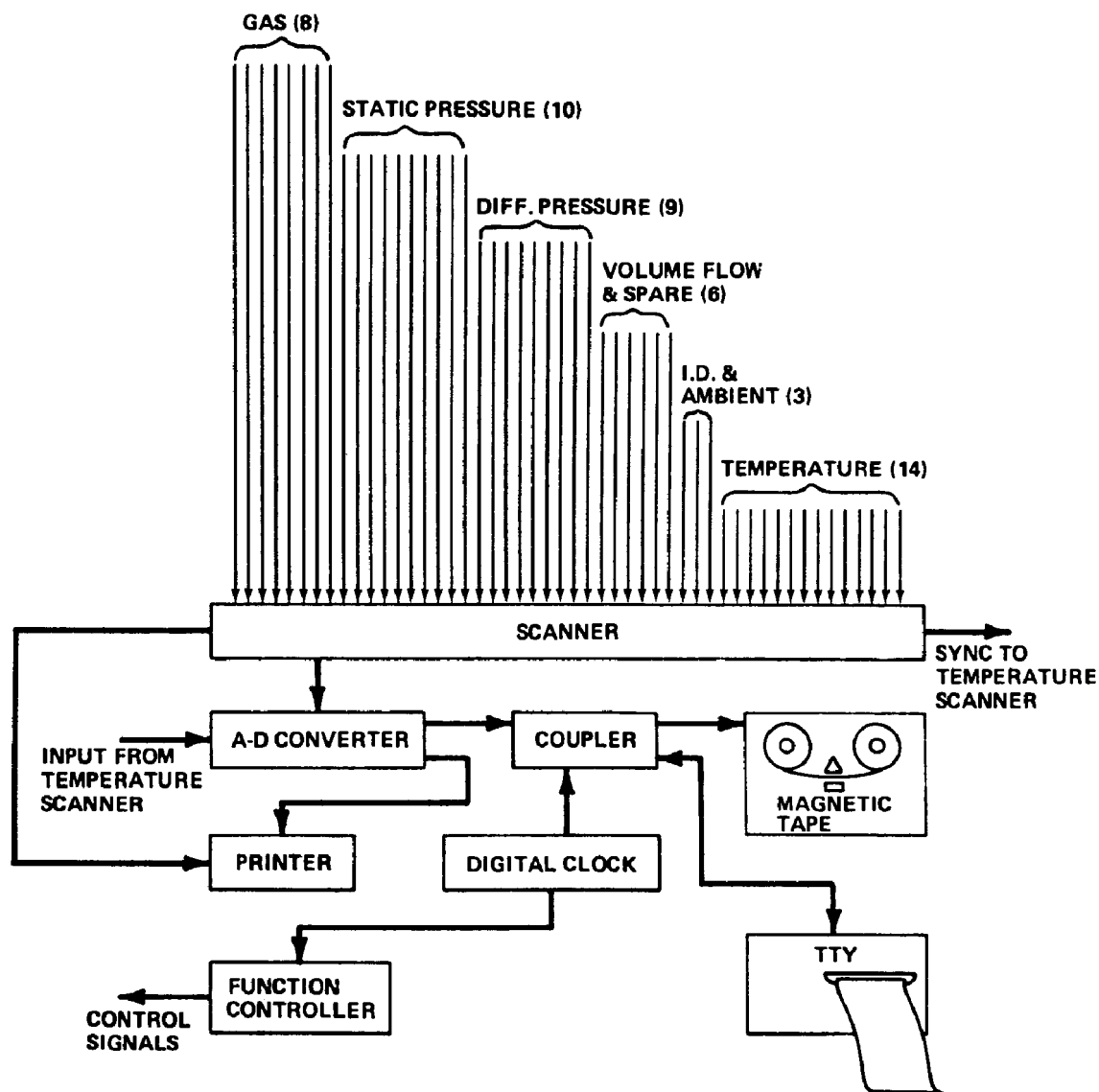


FIGURE 22
DATA RECORDING AND CONTROL SUBSYSTEM

Status of the Instrumentation

Figures 23, 24, 25, and 26 list the equipment previously discussed for each of the major subsystems and identify the manufacturer and model number. If the equipment is specialized to MITRE specifications, model numbers have not been provided by the manufacturer.

Installation of the continuous measurement instrumentation is near completion and will be on line prior to start of the one-year demonstration test program. Some of the hardware is shown in the following photographs. Figure 27 shows two types of gas probes. The probe on the left uses a heated water trap with an external heated filter, whereas the probe on the right uses an in-the-duct filter with an external heated water trap. Figure 28 shows the interior of the multi-point sequential gas sampler. The gas from each of the 7 Dekoron lines is passed through teflon water traps shown in the center of the photograph and then from the top of the traps through pneumatic valves to the analyzer. The center cabinet is heated to prevent condensation of water vapor. Figure 29 shows the interior of the $\text{SO}_2\text{-NO}_2/\text{NO}_x$ analyzer. The center cabinet is heated and contains the NO_2/NO_x gas cell. The SO_2 cell is attached to the side of the cabinet and is not in view. Figure 30 shows the refrigerator-condenser in the foreground with parallel gas pumps. The rack in the rear contains the O_2 and CO_2 analyzers with sample handling and flow balancing instrumentation.

<u>FUNCTION</u>	<u>EQUIPMENT</u>
SEQUENTIAL SAMPLER	DUPONT
SO ₂ - NO ₂ /NO _x ANALYZER	DUPONT 461C
THC ANALYZER	BECKMAN 400
H ₂ GENERATOR	MILTON ROY ELHYGEN R 8320
H ₂ O VAPOR ANALYZER	MSA LIRA M202 (MODIFIED)
HEATED SAMPLE HANDLING	MSA
REFRIGERATOR-CONDENSER	BENDIX
SAMPLE HANDLING	BENDIX
O ₂ ANALYZER	BECKMAN F-3
CO ₂ ANALYZER	BENDIX UNOR-6

FIGURE 23

TIME-SHARED GAS MEASUREMENT SUBSYSTEM

<u>FUNCTION</u>	<u>EQUIPMENT</u>
SO ₂ ANALYZER	DUPONT 460
REFRIGERATOR-CONDENSER	BENDIX
SAMPLE HANDLING	BENDIX
O ₂ ANALYZER	BECKMAN F3

FIGURE 24
CONTINUOUS GAS MEASUREMENT SUBSYSTEM

<u>FUNCTION</u>	<u>EQUIPMENT</u>
TEMP./PRES. RAKES	UNITED SENSOR & CONTROL
DIFFERENTIAL PRESSURE TRANSMITTERS	LEEDS & NORTHRUP 1912
STATIC PRESSURE TRANSMITTERS	LEEDS & NORTHRUP 1912/1970
TEMPERATURE TRANSMITTER	LEEDS & NORTHRUP 1992
VOLUME FLOW CONVERTER	LEEDS & NORTHRUP
TEMPERATURE SCANNER	MONITOR LABS 1100
TEMPERATURE COMPENSATED AMPLIFIER	IRCON DATA SYSTEMS 3J16F
BAROMETRIC PRESSURE TRANSDUCER	ROSEMOUNT ENGINEERING 1331
ELECTRONIC MANOMETER	CGS DATAMETRICS 1023

FIGURE 25
FLOW MEASUREMENT SUBSYSTEM

<u>FUNCTION</u>	<u>EQUIPMENT</u>
DATA ACQUISITION SYSTEM	DATA GRAPHICS CAT-12
FUNCTION CONTROLLER	DATA GRAPHICS DGC-100
STRIP CHART RECORDERS	MFE M26 CAHA L & N SPEEDOMAX M MARK II

FIGURE 26

DATA RECORDING AND CONTROL SUBSYSTEM

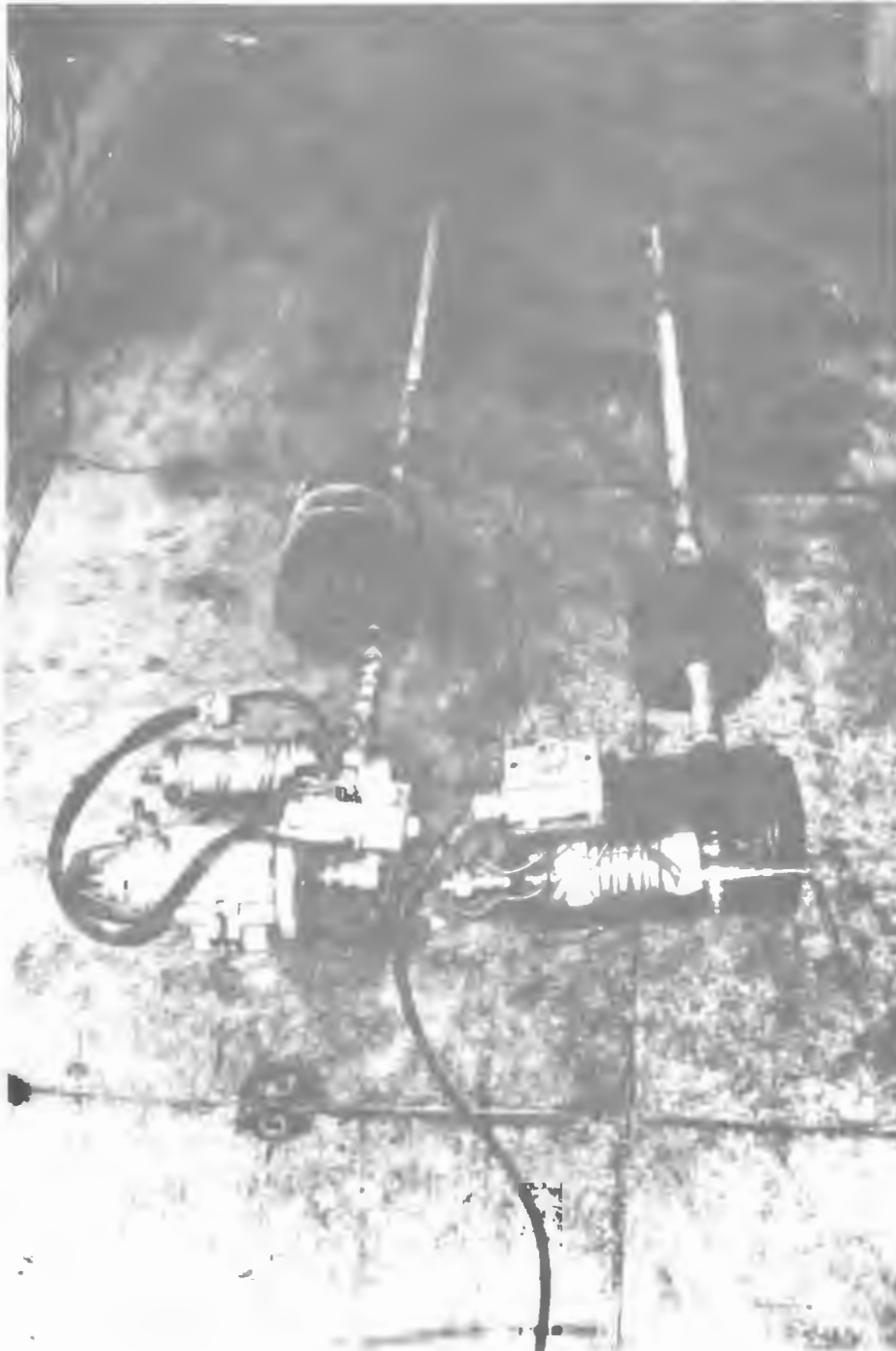


FIGURE 27
GAS PROBES WITH EXTERNAL AND
IN-THE-DUCT FILTERS



FIGURE 28
MULTI-CHANNEL SAMPLER



FIGURE 29
 $\text{SO}_2\text{-NO}_2/\text{NO}_x$ ANALYZER



FIGURE 30
REFRIGERATOR-CONDENSER, O₂ ANALYZER, AND CO₂ ANALYZER

Figure 31 shows a photograph of the temperature/pressure rake. The support for the temperature/pressure sensors is aerodynamically shaped to minimize turbulence effects at the pressure sensor. This particular rake shows two sets of sensors. The longer of the two sensors is the pressure sensor and is a conventional pitot-static probe. The temperature sensor is an iron-constantan thermocouple encased in stainless steel protective tubing. Figure 32 shows the rakes mounted in six inch ports with manifolding to the pressure transmitters. Figure 33 shows the differential pressure transmitter on the left and the static pressure transmitter on the right with the zero/blocking valve and drip pots below.

Figure 34 shows the data acquisition subsystem and function controller. The TTY is on the extreme left. The data acquisition subsystem is in the rack next to the TTY. The lowest panel of this rack is the temperature compensated amplifier. The next rack is the function controller and the last rack shows strip chart recorders and the volume flow converter mounted in the top panel.

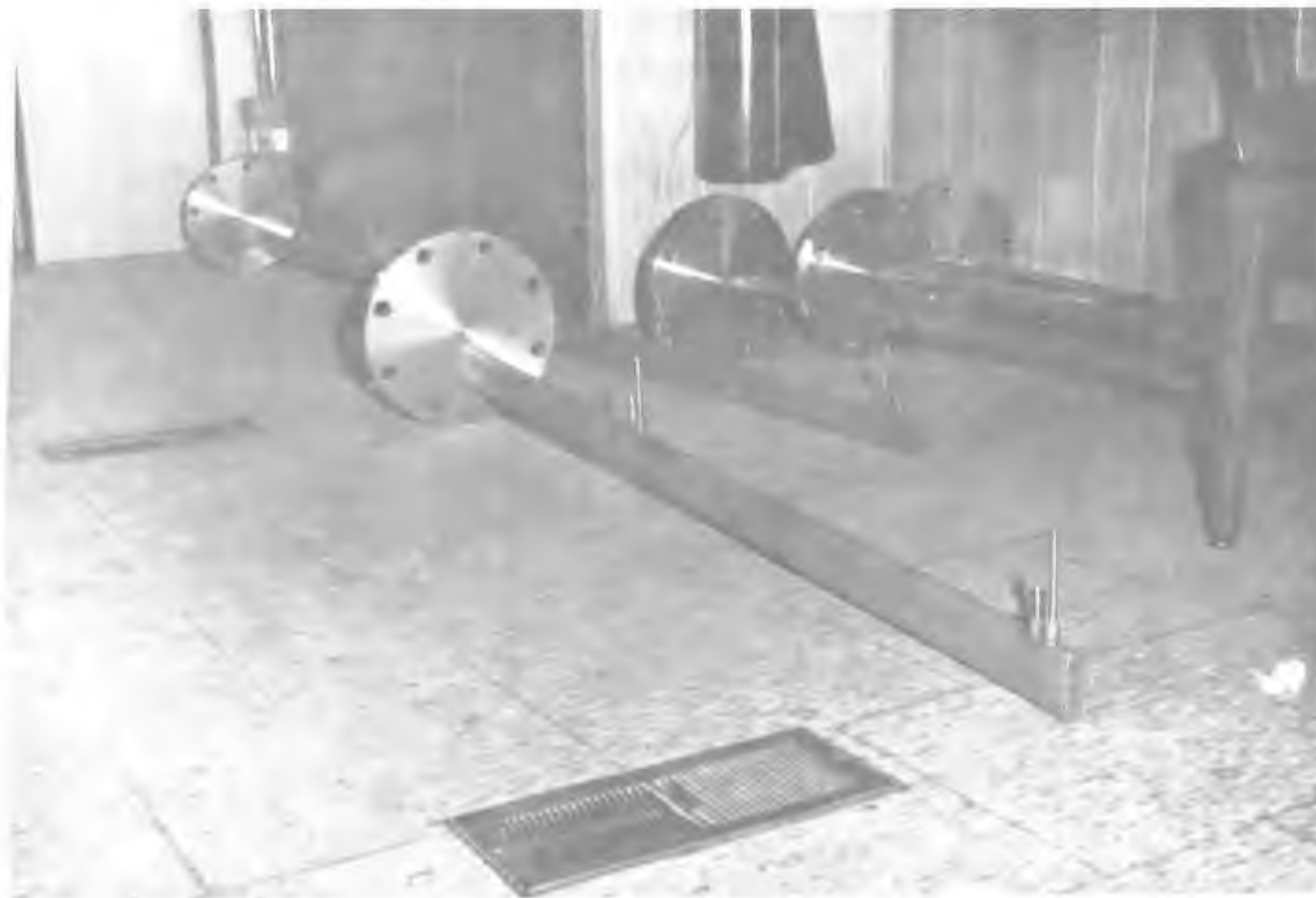


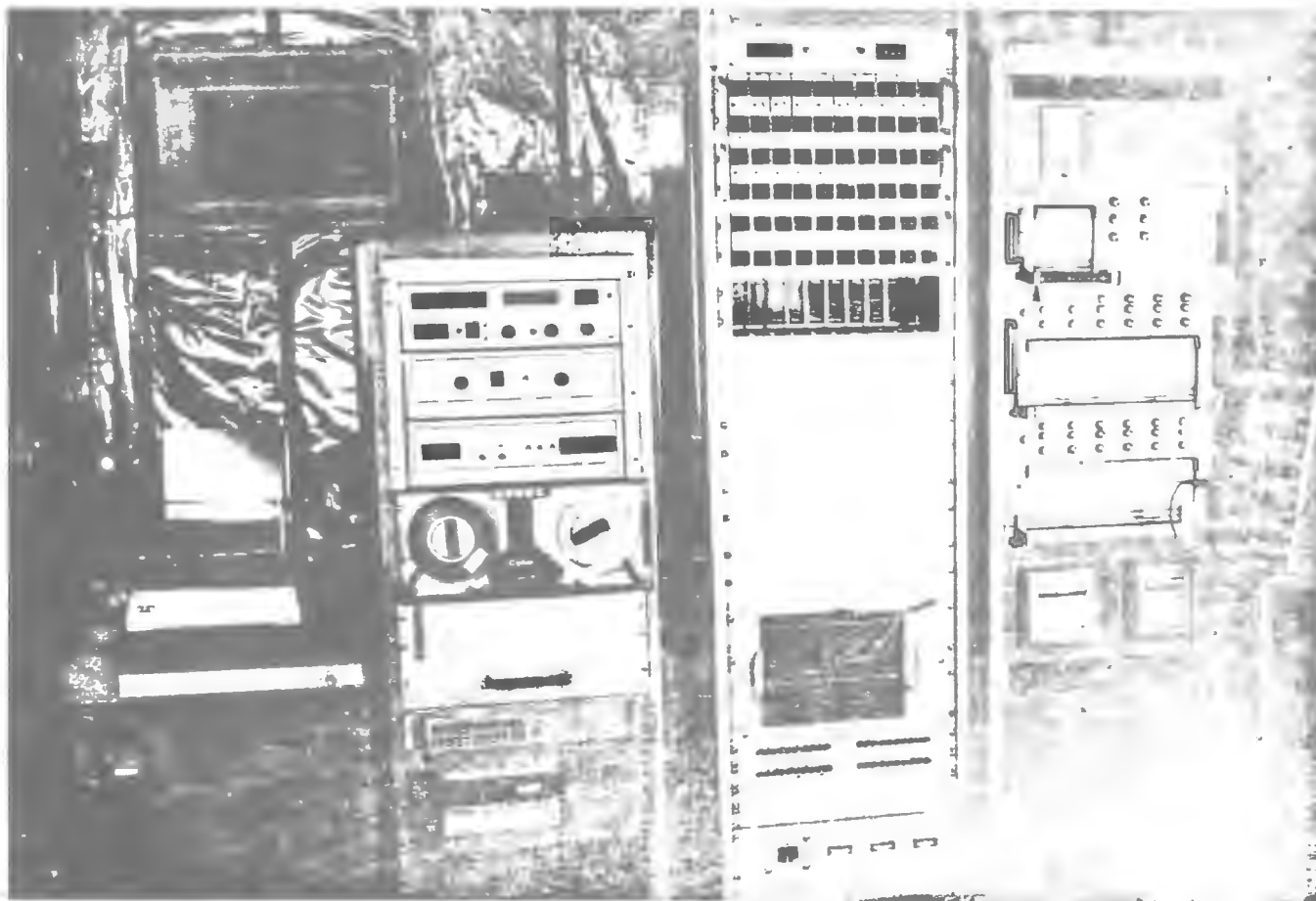
FIGURE 31
TEMPERATURE/PRESSURE RAKE



FIGURE 32
6 INCH PORTS SHOWING MANIFOLDING OF RAKES



FIGURE 33
DIFFERENTIAL AND STATIC PRESSURE TRANSMITTERS



F1, U

DATA ACQUISITION SUBSYSTEM UNIT I

DISPOSAL AND USE OF BYPRODUCTS
FROM FLUE GAS DESULFURIZATION PROCESSES
INTRODUCTION AND OVERVIEW

by

A. V. Slack and J. M. Potts
Office of Agricultural and Chemical Development
Tennessee Valley Authority
Muscle Shoals, Alabama

DISPOSAL AND USE OF BYPRODUCTS FROM FLUE GAS DESULFURIZATION PROCESSES

INTRODUCTION AND OVERVIEW

By

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The removal of sulfur oxides from flue gases poses several very difficult problems to the owner of the emitting plant--whether the operation involved is power production, smelting, sulfuric acid production or a Claus plant. The overriding consideration in many situations may be the difficulty in disposing of the sulfur once it has been gathered from the gas and concentrated in some solid or liquid material. Whatever the product--a waste solid or a salable material such as sulfuric acid, elemental sulfur, or a fertilizer--there must be the assurance that it can be moved away from the plant as fast as it is produced, except to the extent that surge storage may allow fluctuations. Since it is a byproduct rather than the primary one, production cannot be planned in accordance with market demand. Instead, the byproduct flow must be disposed of in the best way possible, even though it may vary widely with production of the main product.

For a new plant the problem is not as troublesome because byproduct disposal is part of the overall planning involved in determining project feasibility. For an existing plant, however, finding a way to dispose of a byproduct that was never considered in the original project planning can be quite difficult or perhaps in some cases impossible.

One of the difficulties, both from the country-wide viewpoint and that of the local plant, is the very large tonnage involved. Various estimates have been published on the amount of sulfur oxide emission in the United States; a reasonable order-of-magnitude figure for 1980 appears to be 50 million tons of sulfur dioxide from sources amenable to stack gas cleaning--and if it is assumed that emission from the other sources will be reduced by fuel cleaning, about 10 million tons would be added to the total recoverable sulfur dioxide. Since complete removal is unlikely, a factor must be applied; assuming 80% removal, the total is 48 million tons as SO_2 --or 24 million tons of sulfur.

Obviously this amount of sulfur, or anything approaching it, would produce an almost overwhelming disposal problem no matter what the product. If converted to a waste solid by CaO-CaCO_3 scrubbing the resulting tonnage (wet basis) would be on the order of 300 million tons per year or, more importantly, the sludge accumulation over the next 20 years would cover an area of almost 5000 square miles a foot deep. Or if converted to salable materials, the amount of sulfur involved would be about 1.7 times the expected 1980 consumption in the United States.

The local situation is even more difficult. Assuming a modern large plant such as TVA's Paradise station (2530 mw; about 4.2% S in coal), sludge production could be as high as 8500 tons per day and the disposal volume about 1600 acre-feet per year (at 70% capacity factor). If the sulfur were recovered in useful form the annual tonnage (as H_2SO_4) would be on the order of 600,000 tons, which would generate such a sales problem that for the particular location involved it might be necessary to ship the acid so far that shipping cost would be higher than sales revenue.

Thus the problem of byproduct disposal looms as a major obstacle in the future of sulfur oxide emission control. In this symposium an effort will be made to explore the problem from all angles and in depth. One paper will describe in detail the situation regarding disposal or use of the waste solids from $CaO-CaCO_3$ scrubbing and others are concerned with the future market for sulfur products, including new uses that are under development. Finally, one paper will describe the overall situation in Japan, where both throwaway and recovery methods have been carried farther than perhaps anywhere else in the world.

The present paper introduces the problem and presents an overview of the current status of the technology, particularly from the viewpoint of a utility such as TVA that is faced with the problem of process selection. Most of the information presented has been abstracted from reports on research work carried out by the TVA Office of Agricultural and Chemical Development for EPA and/or the TVA Office of Power. The work of other organizations is also summarized to the extent that it has been made available to the public.

Most of the producers who operate sulfur dioxide-emitting plants, particularly the utilities, favor discarding a waste solid over recovering a product for sale. Ash disposal is an old technique to power producers whereas sale of chemical products is not. For this reason, the majority of the full-scale projects now under way are of the throwaway type. Full-scale tests of recovery-type processes are also being carried out, however, mainly in the United States and Japan. It is not yet clear which type will be the most economical. The situation should be clarified somewhat in a major process evaluation and cost study being funded by EPA; the study, to be carried out by TVA, will compare those processes in the United States on which full-scale design and operating cost is now available (or soon will be). Three recovery and two throwaway processes will be included.

The ideal waste solid is one that is concentrated in sulfur content, resistant to pile erosion, relatively dense (to reduce disposal volume), and water insoluble. Only three materials meet these qualifications well enough to have received serious consideration--calcium sulfite, calcium sulfate, and elemental sulfur. Of these, sulfur has been considered only in a minor way as a waste solid because it is expected that large quantities can be marketed. There are areas, however, particularly in the Southwest, where the market prospect is so bleak that the waste solid route is being considered. Moreover, if any major portion of the sulfur oxide emitted were recovered as a useful product the resulting market depression could well push elemental sulfur into the waste solid category.

In comparing discard as a waste solid with recovery as a useful product, it can be said as a general observation that recovery does not necessarily avoid the solid waste problem because a large part of the sulfur consumed ends up eventually as a waste, usually in the solid form. Over half of the U.S. sulfur consumption is in the fertilizer industry, where the principal use is in making phosphoric acid. In this process the sulfur is converted to calcium sulfate, a waste solid that is discarded in settling ponds. Some sulfur, much less than in past years, is left in fertilizers such as ordinary superphosphate and ammonium sulfate, and thus ends up on the farmer's fields as a waste solid (since it is either already in the form of calcium sulfate or may become so in calcareous soils) except to the extent that it supplies nutrient calcium and sulfur.

Thus recovering the sulfur in a useful form does not eliminate the waste solid problem but merely diffuses it. It is quite true, however, that recovery reduces the overall quantity of waste solid since otherwise both the fertilizer industry and the power industry would produce a waste.

Waste Sludge from Lime-Limestone Scrubbing

Most of the sulfur dioxide removal systems operating or under construction in the United States are based on CaO-CaCO_3 scrubbing with disposal of the product sludge as a waste. In planning these systems, disposal of the sludge is a major consideration along with cost and reliability of operation. There are still several unsolved problems in these areas but a major effort is under way aimed at solving them. The utilities that have pioneered in CaO-CaCO_3 scrubbing are quite active in this, as well as EPA with its funding of research projects. It is expected that many of the needed answers will be forthcoming from the EPA-TVA-Bechtel test program at TVA's Shawnee station.

Sludge Tonnage

The amount of sludge produced is governed mainly by the excess lime or limestone used, the amount of fly ash collected from the gas in the scrubber, and the degree of sludge dewatering.

Since lime is more reactive than limestone, less excess is normally needed to achieve the same degree of sulfur dioxide removal. The actual excess of each required for good operation, however, is not yet known with any certainty. In the Mitsui Aluminum CaO system in Japan (designed by Chemico), the stoichiometry (mole ratio of CaO to SO_2 in entering streams) apparently has ranged from 0.95 to 1.05 with 80-85% removal. In the TVA limestone slurry pilot plant a stoichiometry of 1.5 has given about the same removal but there is some indication (from the TVA pilot, the EPA pilot at Durham, and the

EPA-TVA operation at Shawnee) that the system might be operated at 1.2, or possibly lower, without much reduction in efficiency. So much depends on type of scrubber, gas velocity, liquor circulation rate, and other factors that no conclusions can be drawn at present regarding the minimum excess of absorbent.

The weights of dry solids obtained under various conditions are shown in Figure 1. The values given are approximate only since in actual operation several factors can vary and change the tonnage to some degree.

The increase in weight of solids resulting from fly ash inclusion can vary over a wide range. When large-scale application of CaO-CaCO_3 scrubbing first began in the United States a few years ago the emphasis was on injecting limestone into the boiler, in which case all the fly ash went with the lime. This approach has now been well nigh abandoned, however, in favor of lime or limestone introduction directly into the scrubber circuit. For such a method of operation, the situation differs between existing plants and those started after the EPA emission regulations came into effect. Since most existing plants have fairly efficient particulate removal systems already, or will have before sulfur dioxide removal equipment is installed, the amount of ash entering the scrubber would be relatively low. (There are exceptions to this, e.g., TVA's limestone scrubbing installation at Widows Creek, where the existing precipitator removes only about 50% of the ash.) For new plants, however, the regulations are such that in most cases scrubbers must be installed initially. In practically all cases so far, dust removal is being combined with sulfur dioxide absorption in either one scrubber or two in series, on the basis that the incremental cost for dust removal is lower than for installing an electrostatic precipitator ahead of the scrubber. There is some difference of opinion as to whether or not this course actually is the most economical but the consensus seems to favor it; much depends on the dust characteristics and on the sulfur dioxide content of the inlet gas, each of which can favor either the precipitator or the scrubber. Another consideration is that some utilities would like to bypass the scrubbers to maintain power production if the scrubber system fails, and consider that this would be more acceptable if the dust could be removed in an independent unit. Some producers also want to retain the option of marketing fly ash and therefore must provide for dry collection.

The type of boiler is also a factor, since the usual types--cyclone, tangentially fired, and front-fired--introduce, in that order, increasing proportions of the coal ash into the stack gas.

Thus the tonnage of ash accompanying the calcium-based solids can vary all the way from an insignificant amount up to as much as 11 tons of ash per ton of calcium solids (for coal containing 20% ash and 0.6% S).

The amount of water remaining in the sludge has an important effect on total tonnage, and is significant mainly when the sludge is to be dewatered and transported to the disposal area as a solid rather than as a slurry. In filtration tests at TVA, vacuum filtration gave a moisture content ranging from about 40 to 45% for various pilot plant samples. Centrifuging at 1000 x gravity gave about 25%.

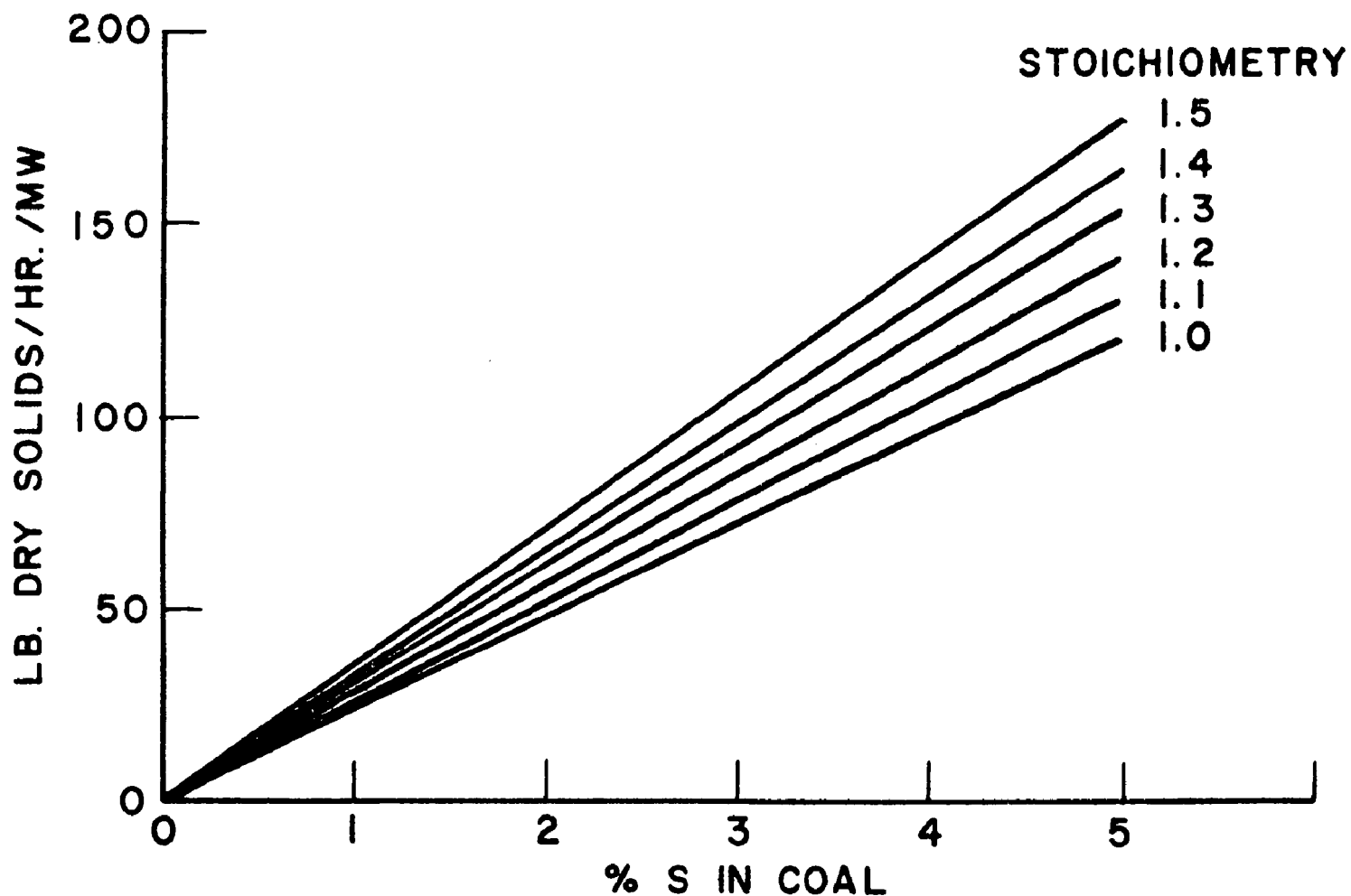


FIGURE I
EFFECT OF SULFUR CONTENT OF COAL ON
AMOUNT OF WASTE MATERIALS PRODUCED

The degree of dewatering depends to a considerable extent on the ratio of calcium sulfate to calcium sulfite, since the normally larger and more blocky nature of the sulfate crystals makes them easier to dewater. For example, in the Chiyoda process (water scrubbing to give sulfurous acid, which is then oxidized to sulfuric acid and reacted with limestone to produce calcium sulfate), centrifuging reduces the water content to 10-15%.

Thus the wet tonnage of dewatered sludge is likely to be 1.3 to 1.8 times the combined dry tonnage of fly ash and calcium solids.

For the TVA Widows Creek installation (550 mw, 4.5% S in coal), which may or may not be typical, the dry tonnage of waste solids is expected to be about 2000 tons per day at full load and 500,000 tons per year at 70% capacity factor. Assuming 40% moisture in filtered solids, this would amount to 3300 tons per day to transport away from the plant each day at full load if a solids handling disposal system were used. Added to this would be the incoming limestone, about 1300 tons per day, or a total solids handling requirement of 4600 tons per day for a 550-mw boiler.

Sludge Volume

In waste solid disposal systems of the type normally operated by utilities and mining operations, the solids are slurried and sluiced to a settling pond from which the sluice water is either overflowed or recycled. Since the pond must be abandoned when it becomes full of settled solids, a key factor in planning is the ultimate pond volume required per ton of solids (dry basis). This varies widely depending on the size, shape, density, and gelling characteristics of the solid particles.

The utility industry is fortunate in regard to fly ash disposal because most ash types settle compactly, requiring only about 20 cubic feet of pond volume per ton of ash (dry basis). Probably one of the worst situations is in the phosphate mining industry, where the clay-laden gangue forms a gel structure in waste ponds and may occupy as much as 125 cubic feet per ton. The situation most analogous to lime-limestone scrubbing is in the phosphoric acid industry, where byproduct calcium sulfate (gypsum) is ponded in large quantities; the pond volume required is about 28 cubic feet per ton.

Unfortunately, the pond volume requirement for $\text{CaO}:\text{CaCO}_3$ scrubber sludge will likely be relatively high since the calcium sulfite tends to crystallize in small, thin platelets that settle to a loose bulky structure and occlude a relatively large amount of water because of their gelling tendency. The crystal form is shown in Figure 2, which is from an electron microscope study by McClellan and Mills (TVA).

In other studies (1), Davenport (TVA) noted three phases in the settling of the slurry--(1) an induction period (slow settling while flocs were forming), (2) free settling, and (3) compression settling. The average



Figure 2. Single and stacked calcium sulfite crystals showing the thickness of some of the crystals.

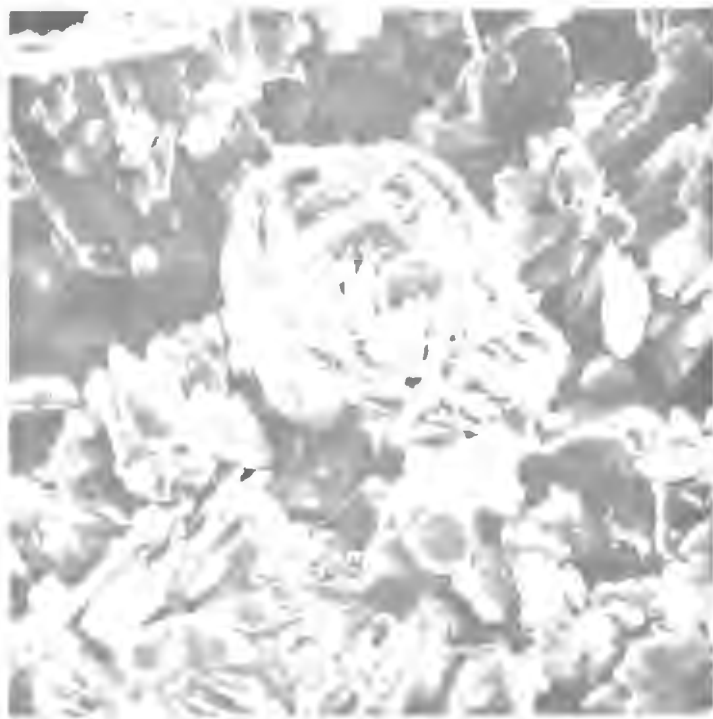


Figure 3. A rosette aggregate of calcium sulfite crystals formed by interpenetration during crystal growth.

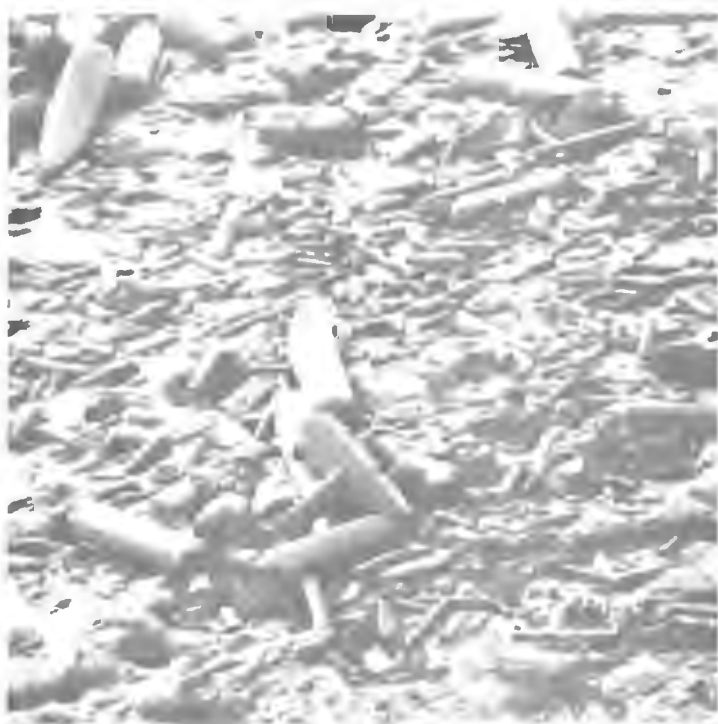


Figure 4. Gypsum from Chiyoda Chemical Engineering & Construction Co., Ltd. (Japan)

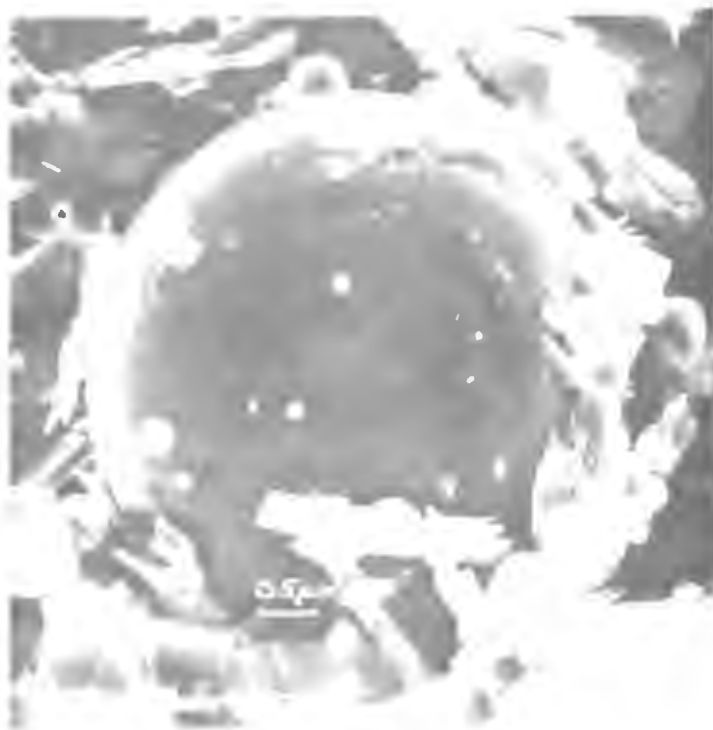


Figure 5. A fly ash particle with calcium sulfite on and next to it.

settling rate over the first two phases was about 5 centimeters per hour. Phase 3 was reached when the flocs began to touch each other, at which point a continuous gel was formed and settling proceeded at a much slower and rapidly decreasing rate. There was very little settling after about 48 hours, even over a period of several months.

Measurements with a torsion wire gelometer showed that a relatively strong gel was gradually formed. A 16% slurry had no gel strength immediately after stirring but developed a strength of 6 g-cm after 30 minutes and >25 g-cm after 18 hours.

Reported values for degree of compaction have varied over a fairly wide range. Many of the data on settling are reported on the basis of water content in the settled sludge, whereas the value needed is weight of the solid phase per unit volume of fully settled sludge; water content is a factor in this but is not necessarily proportional. From calculations and estimates based on the various reports, the packing volume appears to range between 45 and 75 cubic feet per ton of dry solids. This covers a range of roughly 30 to 60% solids in the settled sludge.

The factors affecting degree of compaction have not been identified with any great degree of certainty and very little quantitative information is available. The following considerations are perhaps significant.

1. Hydraulic head. The TVA work mentioned earlier indicated that increasing the height of the slurry column--from 13 centimeters to 100 centimeters--increased compaction by about 15%. Thus a 20-foot head, say, in an actual pond might be quite helpful.
2. Ash content. Since the ash particles are relatively large in comparison with the sulfite, sludges containing a large proportion of ash might settle more compactly. Not much data appear to be available on the point, however, and the high gel strength would indicate that a large proportion of ash would be needed for help in compaction.
3. Degree of oxidation. Since sulfate crystals are normally larger, levels of scrubber operating parameters that increase oxidation might be advantageous. However, both EPA (2) and TVA (3) data indicate that a high degree of oxidation is necessary if compaction is to be increased very much. Presumably the gel structure persists unless the content of sulfite crystals is reduced to a very low level, and thus the situation is analogous to the effect of fly ash content as described in 2.
4. Agglomeration. Agglomeration of sulfite crystals, which presumably should help compaction, has been noted in some tests; a typical agglomerate is shown in Figure 3 /from the work of McClellan and Mills (4)/. However, the scrubber conditions that promote agglomeration have not been identified.

5. Lime versus limestone. There has been some indication that lime scrubbing may produce a more compact settled sludge than does limestone scrubbing. The Chemico-Mitsui Aluminum unit in Japan, for example, apparently produces a settled sludge containing 50 to 60% solids whereas the range for limestone scrubbing has been more on the order of 30 to 50%. There are indications that limestone type and grind may affect settling and filtration characteristics of slurry.
6. Double alkali operation. In the "double alkali" type of operation--scrubbing with a clear water solution of an alkali followed by reaction with lime or limestone to precipitate sulfite and sulfate--the calcium sulfite and sulfate are crystallized under somewhat different conditions as compared with slurry scrubbing and thus might have different settling properties. Exploratory studies indicate that they may be somewhat improved.

In the Chiyoda process oxidation of the sulfurous acid to sulfuric before reaction with limestone produces large crystals of gypsum as the end product (Fig. 4). In Japan this is used in construction products but if the process were used in the United States the sulfate would probably be discarded, in which case the packing volume should be relatively low.

From the planning standpoint, therefore, a relatively large pond volume must be provided for CaO-CaCO_3 scrubber solids unless the situation can be improved or unless some process is used (Chiyoda, for example) that gives low packing volume. For Widows Creek, the pond being provided contains about 100 acres and it is expected that the ultimate depth of the stored sludge will be about 37 feet. The initial storage capacity of the pond is about 4.5 MM cubic yards, with the dikes designed so that they can be increased in height by 10 feet to give an increase in capacity to 5.8 MM cubic yards. The estimated total scrubber effluent ponding requirements over the remaining life of the plant (about 25 years) is 9.3 MM cubic yards based on projected load factors and current knowledge of settling characteristics.

Pond volume requirement is an important factor in overall emission control economics because of the high pond cost. The cost per ton of solids varies widely, of course, with pond size, topography, depth of fill, pond type, and many other factors. The Widows Creek pond, which will accommodate fly ash and sludge in separate sections, is expected to cost on the order of \$0.50-0.75 per cubic yard of capacity.

Methods for Increasing Compaction

The discussion thus far has been concerned with the degree of compaction under normal operation of the CaO-CaCO_3 scrubbing system. There are various special measures that might be taken to get greater compaction.

Slow Stirring: Since the calcium sulfite crystals form a gel, breaking up the gel occasionally by slow stirring allows further settling before the gel reforms. In TVA tests (1) intermittent stirring for short periods was fairly effective. A slurry that had settled to 31% solids was made to settle finally to 48% solids by intermittent stirring (about 1 minute stirring followed by 8 hours or so of settling). Continuous stirring was not effective.

These results indicate that pond capacity might be increased by occasionally removing the supernatant layer completely and stirring the sludge by some method, perhaps by air injection (which might help oxidize sulfite to sulfate) or by towing across the pond a raft equipped with suspended stirring elements. Thickening from 30 to 50% solids, for example, would increase storage capacity by about 80%.

Flocculation: Addition of agents to promote flocculation should improve settling rate but not necessarily the degree of compaction; in earlier TVA work on phosphate slimes (ore washing tailings) flocculation was not effective. In tests of various flocculants added to limestone scrubber slurry (5), settling rate was increased to a major degree but final compaction was not improved. It should be noted that the normal, unassisted settling rate is adequate for providing clear supernatant liquor (for recycle) in a large pond.

Dewatering: If the sludge is dewatered by filtering or centrifuging and transported to the disposal point as a solid, less disposal volume will be required than for settling in a pond. TVA filtration tests have given a packing volume of 39 cubic feet per ton (59% solids by filtration versus 38% by settling). EPA filtration tests on sludge made from another type of limestone gave a solids content of about 70%. Other exploratory tests (TVA) have shown that the "dry" solids do not expand to larger volume when submerged in water or exposed to rainfall.

Disposal as a solid rather than a slurry will be discussed further in a later section.

Increase in Crystal Size: It may be possible to increase the size of the sulfite crystals, or to promote agglomeration, by some technique applied either in the scrubber or in a special vessel through which the slurry would flow on the way to the pond. Apparently no work has been done in this area. It would be necessary, presumably, to increase the size to the extent that gel formation would not occur.

Oxidation: If the sulfite could be oxidized to sulfate at reasonable cost this might be the best answer to the problem. Such oxidation is an established practice in Japan (see paper in this symposium by Jumpei Ando) where the objective is production of gypsum for sale. The method involves blowing air through the slurry after it leaves the scrubber; the main problem is the slow rate of oxidation, which has dictated in many plants the use of special (and expensive) equipment to increase the rate of oxygen absorption.

Extensive work has been done at TVA on oxidizing limestone scrubber slurry (3, 6). The results can be summarized as follows:

1. Air introduction into the scrubber. In one pilot plant test, air was drawn into the scrubber along with the stack gas. Oxidation was increased to 90% and both settling rate and degree of compaction were greatly improved. Similar tests made since did not increase oxidation as much, and compaction was not improved.
2. Oxidation in separate unit. A small grid-packed scrubber (6-inch diameter) in which air was blown through product slurry ($O_2:SO_3^{=}$ mole ratio of 10) was built at the pilot plant. Oxidation was quite slow and the tests were generally unsuccessful.
3. Spinning cup oxidizer. A laboratory-scale "spinning cup" oxidizer such as used in some of the Japanese plants was constructed and tested in the laboratory. Approximately 80% of the sulfite could be oxidized in about 1 hour if the pH were first reduced to about 5 by adding an acid. (The reduced pH is apparently necessary in order to get an adequate supply of sulfite in solution.) Nearly complete oxidation was necessary to achieve any significant improvement in compaction, presumably because this was required to avoid gel formation by residual sulfite. The preferred acid was sulfurous (which perhaps could be obtained by passing part of the stack gas through the product slurry and then into the main scrubber).
4. Use of catalysts. The oxidation could be speeded up, at a given pH, by adding a small amount of catalyst to the slurry. Manganese and iron compounds such as the sulfate and carbonate were the most effective. At a pH of 5.0 and with 0.1% of manganese oxide added, 100% oxidation of a 1% calcium sulfite slurry was attained in 30 minutes.

In general, the work on oxidation to increase compaction has been discouraging. An analysis should be made to compare the cost of pond capacity increase by oxidation as compared with building a larger pond or dewatering.

Pond Management

The way a pond is managed over its lifetime has an important bearing on costs and must be planned in advance. Several questions should be considered.

- Will it be operated as a single unit or divided into sections?
- Will the original depth be the limit or can the walls be built up by using the settled material?

- Shall the pond be partially filled with water before operation begins?
- Can the pond be filled to the top of the dike or must some freeboard be allowed for periods in which rainfall exceeds evaporation?

The usual method of ash pond management is to operate the pond (built by excavating and throwing up a low dike wall of earth) as a single unit with the ash slurry entering at one end, flowing as a stream over settled ash to a low point at the other end where a pool forms, and overflowing supernatant water over a weir or through a standpipe. This is a relatively simple method, feasible only because the ash settles rapidly and compactly. Ash is seldom used to build up the pond wall because the spherical form (Fig. 5) gives it a low angle of repose.

In the phosphate industry, waste gypsum is ponded somewhat differently. The pond is often divided into two or more sections by dikes and operated independently, one filling while the other is drying and hardening. Supernatant liquor is drained from the one being filled by overflow into a standpipe that carries the liquor down through the settled solids and out to a collecting ditch extending around the pond (from which the liquor is recycled to the plant). When the active section is filled with solids almost to the top of the dike wall, the slurry flow is transferred to another section. After a time the solids dry and harden to the extent that excavating equipment can be used to build the wall up a few feet higher with excavated solids. The cycle is then repeated, resulting in some gypsum piles as much as 100 feet high.

Whether this system can be used to reduce the acreage requirement for lime-limestone scrubber slurry ponds remains to be seen. Small-scale tests indicate that under some climatic conditions the sludge might harden adequately for such a technique and that the angle of repose and stability of the wall should be acceptable.

The necessity for recycling may make it desirable to start with some water in the pond to provide recycle until the supernatant overflow can take over. Otherwise the water balance and pumping situation at the scrubber could be a problem. This will affect the composition of any seepage, as discussed later.

In most areas evaporation and seepage from the pond should exceed the rainfall collected but the local situation should be evaluated in planning. Seasonal variations in the balance could make it necessary to keep some surge capacity for supernatant liquor in the pond, in which case the effective pond volume would be reduced.

In some situations it may be feasible to use a mined-out area as the pond, as is done in some phosphate plants in Florida. The important considerations are distance from the main plant and suitability of the area for retaining liquid.

In other cases it may be possible to use existing waste ponds for the calcium solids--for example, ash ponds in power plants, tailing ponds at smelters, and gypsum ponds at phosphoric acid plants. The last of these would be especially appropriate because liquor-recycling facilities will already be available in most cases. A complication, however, is that the calcium sulfite (produced by absorbing sulfur dioxide from the sulfuric acid plant tail gas) could decompose and give off sulfur dioxide if mixed with the acidic supernatant liquor in the phosphogypsum pond.

Landfill Disposal

Since waste ponds are expensive and sometimes infeasible because real estate is not available, the possibility of landfill disposal must be considered. The term "landfill" as used here includes both (1) dumping into suitable excavated areas (mines, quarries) or natural depressions, and (2) piling solids at some suitable point near the main plant. All require dewatering the sludge and getting the material in suitable physical form for transport as a solid. The discarded solids may or may not be covered with earth later, depending on the situation.

The attainment of suitable handling characteristics depends in the first place on the degree of dewatering. As noted earlier, about 25-40% water is typical for filtration and centrifuging tests carried out so far. With some sludges, there are indications that this degree of dewatering would result in acceptable handling properties, but this no doubt depends on factors such as proportion of fly ash, CaO versus CaCO_3 , degree of oxidation, crystal size, and type of limestone. At any rate there is some question at present whether simple dewatering will be adequate. Some of the utilities, Commonwealth Edison, for example (7), plan to add dry materials to the sludge to improve its properties. Dry fly ash is an obvious possibility since it acts somewhat like a cement.

The cost of dewatering, plus any treatment to improve handling properties, is likely to be quite high. Filtration rate has been fairly good in TVA tests, typically 50-55 gal/hr/ft². Exploratory centrifuging tests have indicated that lower moisture content can be obtained as compared with filtering, and if satisfactory centrifuging techniques and rates can be developed, this method of dewatering might be utilized if solids are to be transported without reslurrying. The optimum type of filter or centrifuge has not been established.

For operation in which a relatively low solids content is carried in the scrubber slurry, it may be economical to operate a thickener before the final dewatering device. Use of a thickener as the sole dewatering unit would not seem indicated, however, since the relatively low degree of dewatering would increase the amount of dry material necessary to give a manageable solid.

A further possibility is to "thicken" the water in the sludge. Relatively small amounts of certain commercially available materials thicken water to a solid or semisolid and thus could convert a soupy sludge to a form more easily handled.

Again, oxidation to sulfate should give a product with good handling properties directly from the filter or centrifuge. The Japanese processes, both sulfurous acid oxidation (Chiyoda) and calcium sulfite oxidation (Mitsubishi, Bahco, Ishikawajima-Harima Heavy Industries Company, Ltd.) produce a relatively dry solid by centrifuging or filtering and very likely could do so by thickener settling.

Assuming production of a solid with good handling properties, the next problem is planning the transport system--truck, rail, barge, belt, overhead cableway, or other. The cost of any of these systems will normally be much higher than for sluicing to a waste pond, which is the reason that phosphogypsum disposal seldom involves dry transport; in only two or three of the world's phosphoric acid plants, located in Europe, are the waste solids transported in the solid state (by truck or conveyor belt).

If the dewatered sludge can be piled satisfactorily, it may be attractive to transport to a suitable area near the plant and there build a mound something like the coal pile. The saving in pond construction cost and liquor recycle should be considerable. For the relatively short distance involved, it might be feasible to pump the dewatered sludge with a positive-displacement pump.

From the long-range standpoint, a good case probably can be made for returning the sludge to the limestone quarry or the coal mine--thus returning the nonusable constituents of the original raw material back to the place from which they came. There are obvious problems but the very large tonnages may make such a course imperative.

For both landfill and ponding, wind and water erosion of the exposed sludge surfaces could become a problem. If so, covering with earth may be an acceptable solution but an expensive one. Or established practices for stabilizing the surface of waste piles may be applicable.

One consideration in landfill is whether the dumped solids will bear the weight of people or animals. As noted earlier, ponded phosphogypsum will eventually bear the weight of even excavating equipment. From preliminary tests it appears that some CaO-CaCO_3 scrubbing solids may eventually behave similarly. It should be noted, however, that differing process conditions produce waste solids of different characteristics. Type of limestone seems to have an effect, some producing waste solids much more thixotropic than others.

Water Pollution

Although calcium sulfite and sulfate are relatively insoluble compounds, small amounts dissolve in the liquid phase of the scrubber slurry; moreover, magnesium in the limestone produces soluble salts and soluble materials such as chlorides and nitrates are introduced with the gas. Also, in double alkali processes some of the alkali will usually be left in the sludge, dissolved in the liquid phase.

The nature of the water pollution problem resulting from these dissolved impurities depends mainly on whether the system is open or closed loop in regard to water. By closed loop is meant operation without any purging or "blowdown" of liquor other than that remaining in the discarded solids. In contrast, full open loop is similar to current ash pond practice in which all the sluice water is overflowed to a watercourse.

In open-loop operation, fresh water must be added to the scrubber loop at a rate sufficient to maintain the desired solids concentration in the slurry to the pond. Since this is usually 5-15% (unless a thickener is used), a large amount of water must be introduced--which, incidentally, makes scrubber operation much easier. As a result, the chlorides and other impurities are purged rapidly and the concentration of these constituents remains at a low level. Sulfite and sulfate concentrations are not affected as much because the solution is in contact with excess crystals all the time and thus can become saturated. The concentration is still below that for closed-loop operation, however, because eliminating the recycle from the pond prevents supersaturation from building up to the high levels encountered in closed-loop systems.

Thus open-loop operation produces a relatively low concentration in the overflow, low enough to meet many water pollution regulations. A typical liquid phase analysis for open-loop operation, taken from runs in the TVA pilot plant, is given in Table I. For comparison, the overflowing sluice water from a fly ash pond (TVA at Widows Creek) contains about 250 mg/l of dissolved solids.

The situation in regard to water pollution regulations is quite complex, making it quite difficult to predict the degree to which open-loop operation can be tolerated. In some cases the regulations are based on the degree to which the impurity concentration in the receiving watercourse is increased, which depends, of course, on the ratio of watercourse flow to effluent flow, the impurity concentration already in the watercourse, and the amount of pollutants introduced by the effluent. Thus each situation must be evaluated separately in regard to open-loop acceptability.

As an example of the complexity, the Illinois regulation applicable to the Commonwealth Edison's limestone scrubbing system originally was such as to limit the dissolved solids in the effluent to 750 ppm (7). This was changed recently to read that "total dissolved solids shall not be increased more than 750 mg/l above background concentration unless caused by recycling or other pollution abatement practices, and in no event shall exceed 3500 mg/l at any time." The latter is much more lenient and reportedly would allow open-loop operation.

TABLE I

Composition of Pond Liquor (Open-Loop Operation)

<u>Constituent</u>	<u>Concentration, mg/l</u>
Calcium	815
Magnesium	85
Sulfate	1450
Sulfite	70
Chloride	675
Sodium plus potassium	59
Iron	0.17
Barium	0.15
Cyanide	<0.01
Zinc	0.04
Mercury	0.0003
Nickel	0.22
Copper	0.035
Chromium	0.07
Cadmium	0.004
Phosphate	0.1
Total dissolved solids	4500

Even if open loop should be allowable, the general trend is toward tighter regulations on liquid outflow and for this reason the industry has aimed generally at closed-loop operation. This has caused major problems in operating the scrubber system, to the extent that it is not yet clear whether or not a completely closed loop is practicable. The end result may be a partially open loop.

The TVA situation at Widows Creek (planned installation of a 550-mw limestone scrubbing system) is of interest in this respect (8). If the system were operated open loop, the pond water flowing into the Tennessee River would increase the dissolved solids content of the river water by only 0.43 mg/l average or 1.43 mg/l maximum above the usual level of 70 to 140 mg/l, whereas the Alabama Water Quality standards allow 500 mg/l of dissolved solids. The hardness would be increased from the natural level of 80 mg/l (maximum observed) to 80.77 mg/l

Sulfite oxidation, with consequent oxygen demand, also would not be expected to be a problem. The sulfite concentration is low and oxidation has been shown to be slow.

The heavy metal concentrations (see Table I) are also low, well within the Alabama regulations.

From the above discussion it might be concluded that open-loop operation would not pose any major water pollution problems except in special

situations and that closed-loop operation would unquestionably eliminate any concern. This is not necessarily true, however, because regulatory attitudes differ so much that, although in some areas full pond outflow is allowed, in others there is concern even about seepage from the pond. The latter has become so much in question, in fact, that major research programs are being mounted to determine the magnitude of the problem, if any, and possible means for solving it.

In closed-loop operation, all constituents build up in the liquid phase until the purge afforded by the liquor remaining with the solids (which must be replaced with fresh water) brings the concentration to a steady-state level. Thus the final liquor content of the fully settled solids will determine the actual steady-state concentration, low residual liquor in the solids giving high dissolved solids concentration in the liquor. If any water is placed in the pond before startup (because of the pumping arrangement, as discussed earlier), this also will affect liquor composition, making it less concentrated in the beginning of the pond operation and more concentrated toward the end.

Liquor composition will also vary widely with the composition of both the limestone and the coal (or the oil, the ore, or other source of sulfur dioxide). The best situation is in scrubbing tail gas from a sulfuric acid plant, for which the impurities come only from the limestone. The coal and limestone compositions expected for TVA's Widows Creek operation are given in Table II. Under closed-loop operation, it is expected that the composition of the pond liquid phase will approximate that given in Table III. Although the concentrations of some of the major constituents are higher than for open-loop operation, the increase is not enough to cause a significant effect on river water quality even if major seepage occurred.

TABLE II

Expected Composition of Coal and Limestone
for TVA's Widows Creek Operation

<u>Limestone, % by wt</u>								
<u>CaO</u>	<u>MgO</u>	<u>Na₂O</u>	<u>K₂O</u>	<u>Cl₂O₃</u>	<u>Fe₂O₃</u>	<u>S</u>	<u>CO₂</u>	<u>Acid insoluble</u>
51.1	2.1	0.01	0.17	0.66	0.40	0.04	40.8	4.0

<u>Coal, as fired</u>				
<u>% by wt</u>			<u>Heating value, Btu/lb</u>	
<u>Sulfur</u>	<u>Ash</u>	<u>Moisture</u>		
4.5	25	5	10,000	

TABLE III

Composition of Pond Liquor (Closed-Loop Operation)

<u>Constituent</u>	<u>Concentration, mg/l</u>
Calcium	830
Magnesium	230
Sulfate	1400
Sulfite	145
Chloride	1200
Sodium plus potassium	50
Iron	0.07
Barium	0.2
Cyanide	<0.01
Zinc	0.02
Mercury	<0.0002
Nickel	<0.05
Copper	0.03
Chromium	0.11
Cadmium	0.001
Phosphate	0.1
Total dissolved solids	5700

It seems likely that there will be little seepage from ponds in any event. Well-constructed ponds are designed to avoid leaks and seepage, by proper selection of fill material and control of its water content. Clay can also be used to seal the surface if unusual conditions are encountered. Moreover, it is expected that small ash and calcium sulfite particles will soon blind the surfaces and make them impervious. Tests by STEAG (Steinkohlen-Elektrizitat Aktiengesellschaft) in West Germany have indicated little or no seepage from test ponds (9).

The TVA situation described above may be more favorable than others that may be encountered, for the following reasons.

1. Limestones in other areas may be higher in magnesium, which will increase the magnesium sulfate content of the liquor.
2. If a double alkali process is used, the liquor will contain sodium or ammonium salts unless a solids washing or repulping step is included between the scrubber and the pond.
3. Some coals will contain larger amounts of metal impurities.
4. The Tennessee River is a relatively large watercourse, with a high dilution factor, and any seepage from the Widows Creek operation would tend to flow into the river. In other situations, any seepage might flow to wells.

5. In some areas, sandy soil conditions might make an impervious pond difficult to construct. (However, a lining of clay or other impervious material could be used.)

It should be noted that there are many large waste ponds over the world that in some instances contain liquors much more impure than that from lime-limestone scrubbing. The liquor in phosphogypsum ponds, for example, has low pH and a high concentration of fluoride. Seepage from such ponds does not appear to be a problem.

For landfill the situation is somewhat different since the disposal area would not ordinarily be prepared as carefully as a pond. A primary consideration would be protection against erosion of solids. Dissolution in rain water, however, would not appear to be a problem. If it should prove to be, the methods described earlier for improving the handling properties by a cementing or water thickening action should also reduce any leaching in landfill disposal.

Waste Calcium Sulfate from Acid Neutralization

There are at least two situations that might arise in which sulfuric acid made in the process of reducing sulfur dioxide emission could be justifiably neutralized with limestone to make waste calcium sulfate. One is the situation in many smelters, where the stack gas is rich enough in sulfur dioxide to make acid production by the standard method the most appropriate way for reducing emission. However, in some areas, particularly in the western part of the United States, there is little or no market for acid beyond that already being produced and therefore the acid would have to be neutralized. The second is the situation in which a system has been installed for acid recovery and sale but the market fails or becomes inadequate, in which case the acid must either be stored or neutralized. Since acid storage is expensive (requiring 17.6 cubic feet per ton), neutralization would appear to be more economical. Thus it may be desirable to install neutralization facilities even though sale of the acid is the principal method of disposal.

Work is under way on determining the best method of neutralization. The preferred method, if feasible, is to react strong acid (such as produced in a standard plant) directly with limestone to make a solid product, thus avoiding the need for a solids separation step. The problem is similar to that in making "ordinary superphosphate" in the fertilizer industry, where phosphate ore (mainly calcium phosphate) is reacted with strong sulfuric acid. The product slurry sets up in a short time to a solid that can be handled and piled, but several weeks are required before complete reaction of the acid is attained. In the fertilizer industry, the "curing" is done in a covered building. For the sulfur dioxide removal situation, transfer of the solid to a landfill disposal area could pose an "acid leach" problem until reaction was completed.

Another approach is to dilute the acid, react with limestone, and separate the solid. Complete reaction can be attained in the dilute system, and the solids can be washed, if desired, to remove occluded acid. Research is also being carried out on this method.

Elemental Sulfur as a Waste Material

At the moment it seems unlikely that production of elemental sulfur as a waste material will become significant. However, it is conceivable that, with further development, such a system would be more economical in some situations than production of calcium sulfite-sulfate or calcium sulfate as the waste product.

The closest analogy would appear to be the current situation in western Canada, where large quantities of sulfur have been produced from sour natural gas and stockpiled because of marketing problems. The problems are the cost of reclaiming if the sulfur is ever marketed and also the emission of hydrogen sulfide from the pile. Sulfur produced from sour natural gas by the Claus process may contain up to about 0.01% hydrogen sulfide which causes an odor but is not considered very hazardous in outside storage; hydrogen sulfide evolution could present a problem in inside storage and the odor in outside storage would be quite objectionable.

There is also the possibility of wind and water erosion, plus oxidation that would produce acid constituents subject to leaching. It appears that these problems have not been adequately evaluated for the situation in which sulfur is discarded permanently in the vicinity of plants in populated areas.

Assuming that these problems can be handled satisfactorily and that the economics are acceptable, sulfur as a waste material has some attractive features. The volume requirement is only about 23 cubic feet per ton, and since there are no diluting constituents the waste storage volume required is only about 10% of that for lime-limestone scrubber sludge. The potential (long term) value of the material is also important; even if discarded, it should remain available for use at relatively low reclaiming expense, if at some future time the demand were such as to make marketing attractive.

Use of Lime-Limestone Scrubber Sludge

Although the sludge from lime-limestone scrubbing is a somewhat unattractive material--wet, impure, and containing unreacted limestone--there has been a considerable amount of research on finding a use for it. Companies such as Combustion Engineering, G. and W. H. Corson, Dravo, and others are involved in this, and EPA has funded work by West Virginia University and by the Aerospace Corporation.

The main approach has been to find bulk uses for the material that require very little processing. One such use is as a soil amendment, analogous to use of waste gypsum from the phosphate industry as "land plaster" in the Far West. The main value for such use, however, is to improve the physical properties of alkali soils, a problem that is of little significance in the areas where most of the sludge is likely to be produced. Farmers would have little incentive to accept the material, and even if they did the net result would appear to be a relatively expensive type of landfill operation. And the leaching problem would be magnified.

Other efforts have been aimed toward converting the sludge to a material suitable for use as a highway base material. It has been demonstrated that some quantity of sludge can be sold for such use but it seems highly unlikely that a market could be developed for any significant proportion of the potential sludge tonnage. Special treatment would be necessary since gypsum used as such has been known to dissolve slowly and collapse under weight.

Other uses, such as for structural products, mineral wool production, and beneficiation to produce minerals, would appear to be almost hopeless. The situation can be compared with that of fly ash, which is an excellent additive to cement--used in large quantities (10,000 tons in 1972) by TVA in power plant foundations and in dam construction. Notwithstanding an intense promotional effort, TVA has been able to move less than 1% of the annual fly ash production. The situation would thus appear quite difficult for moving scrubber sludge, which is much less useful and economical than fly ash.

Gypsum for Construction Use

The usefulness of lime-limestone scrubber product solids can be improved if fly ash is kept out, unreacted calcium oxide or calcium carbonate is eliminated, and calcium sulfite is oxidized to sulfate. The result is a fairly clean grade of gypsum, suitable for use in making wallboard or as an additive to cement.

The only use of this approach has been in Japan, where the general use of oil as fuel eliminates the fly ash problem, acid is added to react with any excess absorbent, and the sulfite is oxidized in special equipment to sulfate. One of the papers in this symposium describes this practice in detail.

Sulfite oxidation equipment is also being installed at the Mitsui Aluminum plant in Japan, where coal is used as boiler fuel. However, the plant is equipped with very efficient electrostatic precipitators that keep the ash content of the sludge at a minimum.

It should be noted that even with oil firing there is some residual soot that darkens the product gypsum. Moreover, the cost of oxidizing and of drying the product solid is not insignificant. In the United States, where there are large natural deposits of dry, relatively pure gypsum, costs of oxidizing and drying scrubber sludge would appear to be unacceptable. Moreover, the dark color (in coal-burning plants, from fly ash and other impurities)--as compared with the white color of wallboard made of natural gypsum--could be a major obstacle to marketing.

For the Chiyoda and Hitachi processes, the gypsum is made from sulfuric acid and therefore the expensive oxidation step is not required. This would improve the economics.

Sulfuric Acid

Several of the proposed recovery methods give sulfuric acid as the end product. Catalytic oxidation (Monsanto) and some of the carbon processes (Lurgi, Hitachi) are restricted to acid as the product, and the magnesia methods (Chemico-Basic, Grillo, United Engineers), plus some of the carbon processes (Reinluft, Bergbau-Forschung, Sumitomo), are better suited to acid than to elemental sulfur. Others, such as copper oxide (Shell, Esso-B & W), sodium scrub (Wellman-Lord, Ionics-S & W), and ammonia scrub (EPA-TVA), usually give an essentially pure stream of sulfur dioxide that can be converted either to acid or elemental sulfur as the situation dictates.

Acid production methods can be said to be farther along than sulfur processes, on the basis that acid production from sulfur dioxide is a well-established technology whereas sulfur dioxide reduction to sulfur has been operated commercially in only one plant. The main problem with acid, other than operability of the gathering processes for producing the sulfur dioxide (or of the Monsanto and the carbon methods that produce acid in situ in the main gas stream), is marketing of the product.

One problem is that the acid from some processes (Monsanto, Hitachi, Lurgi) is not commercial grade, either because of lower concentration than normal or because of impurities. There would be more difficulty in selling such acid than for the standard 92-98% water-white product.

Even if the acid produced is high grade, however, the very large tonnage, the high cost of storage and shipping, and the vagaries of the acid market are major problems.

This is particularly true in the Southwest and Mountain areas, where the large sulfur dioxide emission from smelters and power plants, the limited acid consumption in these areas, and the long distance to an adequate market combine to make acid production for sale a very dubious proposition.

In a study made by the Arthur G. McKee Company for EPA (10), it was estimated that only about 60-65% of the sulfur dioxide emitted from western smelters could be sold as acid (5.0-5.3 million tons per year) and that this could be done only if the acid were priced at \$4 per ton. This leaves the remainder of the smelter acid capacity and all of that from the power plants and other sources as essentially unsalable.

Probably the best situation for acid production is that in which a process for using the acid is operated contiguous to the power plant, thus avoiding the cost of shipping and marketing the acid. A phosphate fertilizer plant is the most likely prospect because most of the sulfur consumption is in the fertilizer industry. Phosphoric acid, triple superphosphate, and ammonium phosphate are the logical end products.

An appropriate location for such a joinder of processes is the upper Midwest, where over half of the phosphate fertilizer produced in the United States is consumed and where many of the power plants burning high-sulfur coal are located. It should be noted, however, that there are many drawbacks to such an arrangement, the main one being that the sulfuric acid must be used as it is produced (unless expensive surge storage is installed) and thus the fertilizer facility would have to be operated even at times when otherwise it would not be economical to do so.

The overall problem of marketing sulfuric acid is quite complicated, too much so for any full treatment here. EPA is funding a market study at TVA which should be useful in evaluating the situation; the TVA power system will be used as an example and an analysis made of the potential quantity of acid, shipping cost to various points, and the amount of acid that could be produced and marketed for various levels of netback (including zero and minus levels). The study is in the beginning stages.

Elemental Sulfur

Sulfur has several advantages over acid as a product for marketing, including lower cost of storage, higher concentration for shipping, better marketing flexibility, and broader spectrum of use. It seems likely, however, that costs will be higher because of the need for a reducing agent. Moreover, the basic economics are questionable since the sulfur is in the oxidized form in the stack gas and this is the form (as sulfuric acid) in which most of it is used. It does not seem reasonable to back and fill by oxidizing the sulfur compounds in the fuel during combustion, reducing the resulting sulfur dioxide back to sulfur, and then oxidizing it again to acid before use--unless, of course, storage and shipping costs are overriding considerations. It is for these reasons that installing an acid-using facility at the power plant seems economically desirable.

The future of sulfur versus acid as a recovery product is uncertain at this time. Much will depend on the process economics as they finally develop--plus, of course, local considerations that may favor one product over another.

Some of the processes /Westvaco (carbon), Institut Francaise du Petrole (ammonia scrub), U.S. Bureau of Mines (sodium citrate scrub)/ produce sulfur only. Others, as noted above, can convert the gathered sulfur dioxide either to sulfur or to acid.

Fertilizer Products

Some processes produce a fertilizer material directly without sulfuric acid or sulfur being involved as an intermediate. An example is ammonium sulfate, which is made in Japan either by ammonia scrubbing (with ammonium sulfite oxidation) or by the Mitsubishi manganese absorption process (reaction of manganese sulfate with ammonia to give ammonium sulfate). Bufete Industrial, an engineering and construction firm in Mexico, also has a process in which ammonia scrubbing is followed by ammonium sulfite crystallization and oxidation of the sulfite to sulfate in the dry state.

There is some question as to the marketability of ammonium sulfate in large quantities. Even in Japan, where ammonium sulfate has been a more important fertilizer than in the United States, the material is losing ground. The relatively low nitrogen content, as compared with fertilizers such as ammonium nitrate and urea, is a major handicap. It is considered, however, that if ammonium sulfate were made in power plants located on the Mississippi River system, barge transportation could be used effectively to reduce the adverse effect of low concentration on shipping cost. By pricing the material below the present level, fairly large tonnages probably could be moved.

One factor offsetting the low nitrogen content of ammonium sulfate is that sulfur is also a plant nutrient. In the past the natural supply of sulfur compounds in the soil, plus that supplied incidentally in fertilizers, made primary application unnecessary. This situation is changing because of soil depletion and general use of fertilizers containing little sulfate. Thus the sulfur in byproduct ammonium sulfate is likely to have increasing value as soils become further depleted.

Other fertilizers, including some nitrogen-phosphate combinations, can be made in scrubbing processes that do not involve intermediate production and shipping of sulfuric acid. These have been evaluated in a TVA study carried out for EPA (11). It was concluded that a fair tonnage of such products could be sold even in direct competition (same netback) with present commercial fertilizers.

Future Market for Sulfur Products

Whether sulfur products will be recovered and marketed in large quantities depends on the cost of recovery processes versus the throwaway type of operation (see earlier discussion of forthcoming EPA-TVA study). This in turn depends, in part at least, on whether the recovered products can be marketed and what netback they will provide.

A major question in this is how well the demand for sulfur-based products will keep up with the supply from byproduct sources. This is a complicated question, covered in a recent study for EPA by Esso Research and Engineering and summarized by a paper in this symposium. Up until a few years ago, the main production was from natural deposits and the supply could therefore be adjusted more or less to comply with the demand. With the growing production from desulfurization of sour gas and now perhaps from fuel and stack gas cleaning, the supply from byproduct sources is beginning to outstrip the primary production. As a result, the market situation has become more complex, more difficult to analyze, and more discouraging to those who need a reasonably stable market prospect if they are to invest billions of dollars in stack gas cleaning installations.

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STUDY OF DISPOSAL AND UTILIZATION
OF BY-PRODUCTS FROM THROWAWAY
DESULFURIZATION PROCESSES

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ABSTRACT

This paper summarizes an on-going Aerospace Corporation study for the Environmental Protection Agency concerning the ecologically sound disposal of sludges produced by the limestone scrubbing of coal-fired utility boiler flue gases. Related utility disposal problems concerning lime-coal and limestone-oil sludges are also considered. In addition, the usage of sludge in commercial products is briefly summarized. A review of critical factors which affect disposal requirements and techniques is given. These include items such as the chemical characteristics of process materials and sludges, sludge physical properties, water quality criteria, trace element constituents, and liquor recirculation. Disposal methods described include ponding and landfill-type operations. The impact of input parameters on disposal methods is briefly discussed, as well as features of ponding and landfill requirements.

1. Introduction

With the expanding use of coal by the electric power utilities, and the incorporation of lime or limestone scrubbers to desulfurize the flue gases, the disposition of and resultant effects of the sludges produced by these processes has become a major concern. The concern for the disposition of the sludges is based on two principal factors: (1) the sludges contain soluble salts and some compounds containing trace elements -- all or part of which may leach or drain from ponds, landfills or other usage areas to ground or surface waters and produce problems of water pollution, and (2) many lime/limestone/sulfur sludges are highly water retentive and are therefore not structurally acceptable in their natural form as landfill materials. At this time, little is known of the potential effects, if any, that may result from these sludges; however, there has been considerable effort expended in the determination of technology to support the utilization of the sludges and to condition them for use as a landfill material. Since the sulfur scrubbing technology is just emerging from its pilot plant stage, representative power plant operational disposal data are not abundant. Additionally, current water quality standards are not directly applicable in many cases, or are very difficult to apply to the leaching of sludges. Therefore, adequate data do not exist to verify whether the sludges can or will be used or disposed of in any ecologically sound manner.

The EPA Control Systems Laboratory, Research Triangle Park, North Carolina, has designed a program to establish a valid understanding as to whether the sludges pose a water quality problem, to assess solutions or approaches to solutions in the event the sludges do pose a problem, and to assess the industrial status of sludge usage and disposal in light of this analysis. As part of this program, a contract has been let to The Aerospace Corporation to perform analyses and bench scale tests of limestone-coal sludges to study the potential effects just mentioned, and to assess the status of industrial usage and disposal technology. Background for this study is fully described in an EPA position paper (Ref. 1).

The Aerospace study is now in the early stages of a program directed toward an understanding of limestone sludges from power plants burning eastern coal and western coal. That program* is the subject of this paper

* A potential expansion of the program to include additional samplings from other power plants so that a broader data base can be obtained, and to include a more detailed study of material conditioned for usage or disposal is being planned by the EPA (Ref. 1).

which is a status report that essentially summarizes the program's objectives and progress to date.

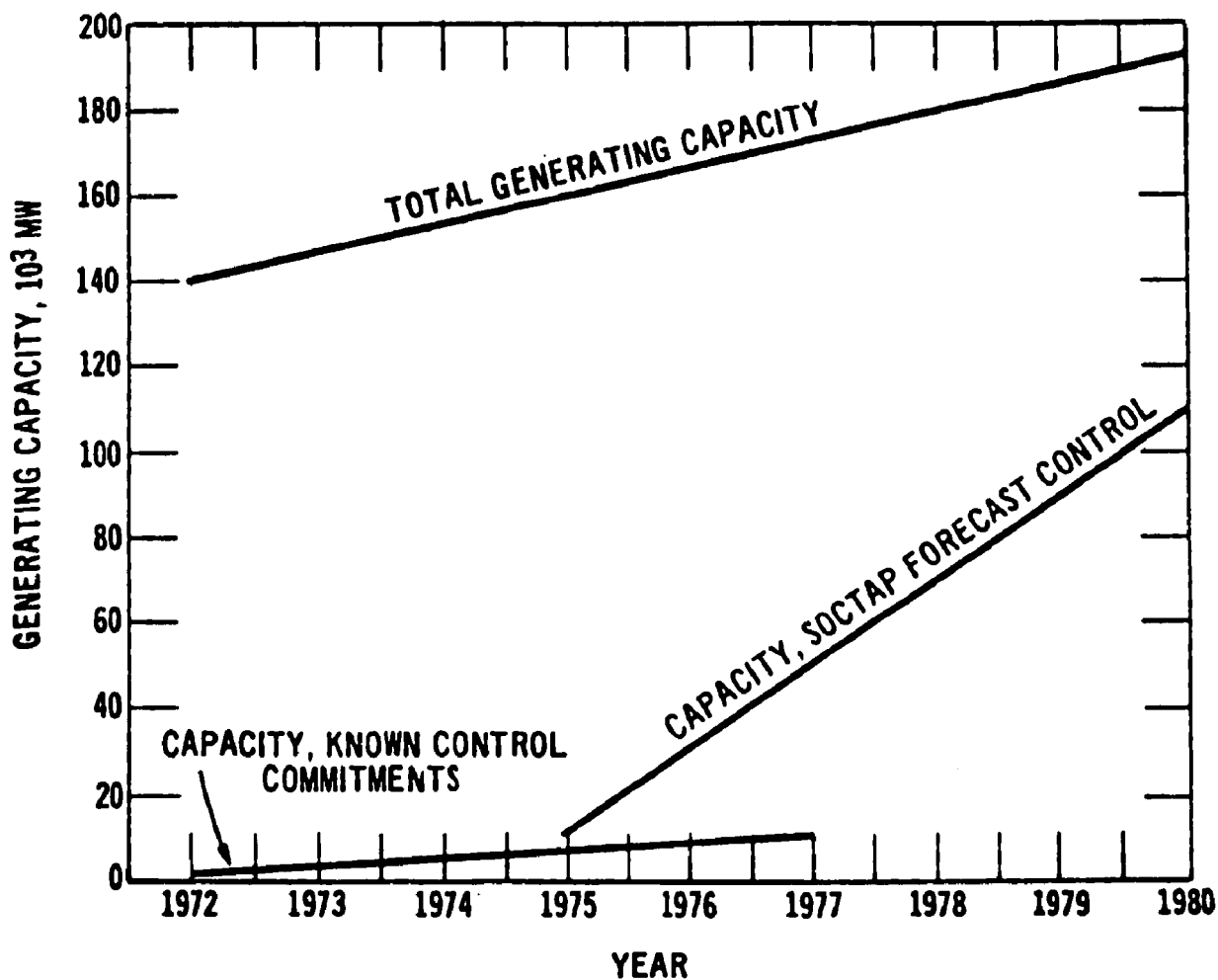
2. Rationale

Much has been written about the projected abundance of sulfurous sludges and the technical feasibility of their use as a constituent of commercial products or as a landfill material. For example, in Reference 2, Brackett presents data taken in a 1971 survey of the electric utilities industry which estimates a sludge plus bottom and fly ash production of 117 million tons in 1976. And, in Reference 1, it is noted that a government interagency Sulfur Oxide Control Technology Panel has made a preliminary lime/limestone sludge (50% solids) production forecast of 86-112 million tons annually by 1980. That value is based on 75% of coal burning power plants using a desulfurization system, 75% of which will be lime or limestone scrubbers (see Figure 1).

Although these values are necessarily "soft," they highlight an acute by-product disposition problem. It is significant to note that the plants committed to lime or limestone scrubbers are located in widely spaced areas such as Pennsylvania and Nevada as well as in the North, Mid-West and the South. Thus it is evident that disposition is not a matter of local concern, but definitely one of national interest.

The concern for potential toxicity problems is emphasized by some trace element data presented by Aerospace in Reference 3. These data, produced for the EPA by the Shell Development Company and the Oak Ridge National Laboratories, were taken from samples of ash modified by the dry injection of limestone into the boiler. The elements of concern show little tendency to be concentrated in any size fractions, five of which ranged from an average diameter of 28.7 μm to 1.5 μm . In all size fractions, however, heavy metals were reported at levels high enough to cause concern, e.g., As: 50 to 200 ppm; Ba 200 ppm; Pb: 200 to 500 ppm; V: 200 ppm. If these elements are combined such that they are chemically inert, there would be little concern over their reaching ground or surface waters. However, application of wet lime/limestone scrubbing of flue gases from coal-fired boilers is just emerging and the possibility of producing toxic water-soluble compounds has not been determined. The most often considered methods of sludge disposal are ponding and landfilling

Figure 1
COMPARISON OF ESTIMATED ELECTRIC
UTILITY COAL GENERATION CAPACITY WITH CURRENT
AND FORECAST CONTROL BY LIME/LIMESTONE SCRUBBING



Courtesy of EPA Control
Systems Laboratory
(See Reference 1)

and, for commercial applications, as an additive in road base construction among other technically feasible products (Refs. 8 through 12). Sludges used in these applications, whether treated or not, can possibly leach or drain toxic trace elements (as well as other contaminants) to ground or surface waters. It is on this basis that a determination is considered necessary as to whether the sludges pose an ecological problem.

3. Aerospace Study Plan

The plan on which the Aerospace study is based was derived from information such as that previously mentioned (Ref. 1). Supporting data regarding the production of lime/limestone sludges are given in an EPA paper "Control of Sulfur Oxide Pollution from Power Plants" (Ref. 4), an article, "Removing SO₂ from Stack Gases," (Ref. 5), and a previous Aerospace study, "Technical and Economic Factors Associated with Fly Ash Utilization," (Ref. 3). From these and other data, the EPA Control Systems Laboratory defined a one-year program, "Limestone-Coal Sludge Characterization and Toxicity Study," which The Aerospace Corporation is now conducting. This study is currently limited to analyses of limestone-coal sludges from one plant burning eastern coal and one burning western coal; however, surveys of disposal techniques and utilization effects are not restricted to these two plants. An EPA plan for the potential expansion of this effort to other plants including some which use lime as the absorbent material for eastern and western coal-burning plants, and limestone scrubbing at an oil-burning plant is given in Reference 1. This potential expansion is designed to produce a reasonably broad data base such that adequate results can be obtained to apply generally to lime/limestone scrubbers.

Following is a listing of the program objectives of the current Aerospace study and descriptions of each phase:

- a. Chemical Characterization - chemical characterization (including trace element identifications) and crystalline phase determinations are being made of sludge, process liquors, coal, limestone, make-up water, and regular fly ash. Special emphasis will be placed on the chemical and physical state of toxic elements. These chemical analyses will determine possible elemental losses that occur in the combustion or collection processes; they will determine the possible toxic hazards associated with fresh materials that have been dewatered and with materials that have experienced subsequent treatment and they will identify

soluble components and sublimation components. At this time, samples are being analyzed from the Prototype Turbulent Contact Absorber (TCA) scrubber at TVA Shawnee Unit #10 in Paducah, Kentucky (Ref. 6) and the pilot TCA scrubber at the Mohave Station Unit #1 in Nevada (Ref. 7).

- b. **Potential Toxicity Determination** - A literature study is being conducted to determine any potentially toxic effects of the compounds identified in the chemical analyses. This will include a determination of the means of inhalation or ingestion in humans, and an assessment of the potential intake of toxic elements in plants and animals.
- c. **Physical Properties** - Physical property studies are being conducted on sludges that have experienced aging, i. e., drying, leaching, exposure to sunlight, to assess permeability, compressive strength, pozzolanic properties, and other factors which may have an effect on the use of the sludge as a landfill material.
- d. **Detoxification** - An assessment of the potential for detoxification of the sludge will be made. This will include schemes such as oxidation, fixation, and heating. Positive indications will result in process definitions, estimated costs, and the potential impact on handling and disposal or usage.
- e. **Disposal Methods** - In light of any potentially toxic effects identified, evaluations will be made as to the feasibility of various types of disposal such as ponding, landfilling, and mine filling. Also, a limited bench scale program is being conducted to define the properties that will affect the economics of transporting the sludge to disposal sites. This includes corrosive properties, abrasion, adhesion, thixotropic properties, viscosities of suspension, and bulk densities as a function of water content.
- f. **Disposal Costs** - An engineering study will be conducted to define the relative costs for the ecologically sound disposal of the sludge as a function of variables such as transport type and distance, treatment processes, receiving site preparation, operations, and maintenance.

- g. Water Quality and Solid Waste Disposal Criteria Review - A review of federal and state solid waste disposal and water quality criteria is being made. The findings of this program will be incorporated and a reasonable interpretation will be made as to the impact of the disposal of sludges on the existing or proposed criteria.

The potential EPA expansion of this program will include additional sampling sources representing a broader cross-section of disposal and treatment processes as well as other sorbent/fuel classes. Particular emphasis will be given to the assessment and evaluation of both on-going and developing treatment processes now being employed by industry and government agencies.

4. Water Quality and Solid Waste Disposal Criteria

In conformance with the requirements of the Water Quality Act of 1965 which amended the Federal Water Pollution Control Act of 1965, all of the states, the District of Columbia, and the territories of Guam, Puerto Rico and Virgin Islands established or are establishing water quality standards* for interstate (including coastal) waters. In December 1970, the responsibility for administering the Water Quality Act of 1965 was transferred from the Secretary of the Interior to the Administrator of the EPA. Most of the state standards have now been written, and accepted by the EPA. The state standards are therefore the major sources of criteria by which the power plant scrubber effluents are to be judged at this time and they deal with the quality of the receiving surface waters only. Further, the state standards when citing criteria for domestic water supplies or for food processing, generally repeat or refer to the Public Health Service Drinking Water Standards (Ref. 18) which apply to water distribution systems.

Other legislation, e. g., the Federal Water Pollution Control Act Amendments of 1972 (PL92-500) which applies to both surface and ground waters, establishes a goal of zero pollution discharge by 1985. While calling for interim guidelines and standards to regulate pollution discharges, it establishes the applicability of two definitions of particular interest to future consideration in sludge studies. They are:

* Significant background information for the state standards can be found in "California Water Quality Criteria," McKee and Wolfe (Ref. 16); "Federal Water Quality Criteria," FWPCA, Dept. of the Interior, (Ref. 17); and "Public Health Drinking Water Standards," PHS Publication 956 (Ref. 18).

- a. "The term 'navigable waters' means the waters of the United States including the territorial seas."
- b. "It is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited."

Summarizing regulations, we find the following:

- a. Current standards are established by the states which specify water quality criteria for interstate (including coastal) waters.
- b. Future standards will regulate pollution discharges to all waters of the United States including ground waters. And the discharge of toxic elements in non-toxic amounts may be allowed.

The route by which potential pollutants can reach various water systems is either by direct discharge or runoff, or by leaching through the soil to ground waters or surface waters. Because of the high concentration of dissolved solids (generally sulfates, carbonates, sulfites and chlorides) regardless of other possible pollutants, the process liquors generally cannot be discharged without additional treatment and are therefore recycled. Disposal sites can be constructed to prevent drainage. This leaves leaching as the only other route (barring accidents) to potential pollution.

The effect of a leachate from a disposal pond or landfill on the quality of a receiving body of water is generally a variable factor depending on local weather, soil conditions, topography, the chemical and physical characteristics of the leachate, and the flow and quality of the ground and surface receiving waters. Because this effect is so difficult to determine, regulatory bodies ordinarily will prohibit the earth disposal of an untreated sludge if it contains heavy metals considered toxic in concentrations exceeding the safe limits set for drinking water. This of course assumes that the toxic element(s) exists in a soluble compound within the sludge and that after leaching through the soil it will appear in the receiving water in toxic concentrations. Such an approach is undoubtedly safe, but the knowledge of when, where and under what conditions these precautions are necessary is not known.

It can be argued that the concern for toxicity in the sludges may not be critical since it will be necessary to treat the material to cause a fixation condition which will eliminate the formation of a bog. This would permit the landfill site to be reclaimed for some useful purpose and it may effectively encapsulate the undesirable constituents of the sludge. This is no doubt true in some instances; however, a fixation treatment isn't necessarily required for all sludges and furthermore, it is not known what the impact of the leaching

of a conditioned sludge will be. If it is considered harmful, then a problem is defined. If it is not considered harmful, then the conditions which are acceptable should be identified so that those who have both the problems of disposal and regulation can satisfy their requirements.

Although the foregoing applies specifically to water quality, a few comments regarding solid waste disposal are in order. The EPA Office of Solid Waste Management Programs is in the process of issuing guidelines for land disposal and thermal processing operations. This is in response to the Resource Recovery Act of 1970 (PL91-513) which amended the Solid Waste Disposal Act of 1965 (PL89-272). The presently proposed guidelines do not apply to hazardous materials because of a lack of sufficient information; however, hazardous wastes and sludges containing free moisture are considered special wastes which under certain circumstances may be accepted for disposal at a disposal site but under the authority of the responsible agency. Most state standards for solid waste disposal which may be applicable to sludges are similar, i. e., special permission is required of the responsible office, and finite criteria are not given.

In light of the foregoing, the current Aerospace study effort has focused on determining the potential toxic hazard posed by the sludge as a consequence of the variations that arise in alternative disposal schemes and selected processing variables. A potential toxic hazard from a pond or disposal site may exist in the leachate, the run-off, a purge flow, from vapors arising from a dry pond, or fine dust particles blown from a dry pond surface, or from anaerobic attack from the bacteria in the containment soils. Toxicity in any of these cases is defined by existing state and federal standards but is subject to the chemical considerations discussed in the following section.

5. Toxicity

The determination of the toxicity of a sludge is dependent upon the factors relating to what kinds of elements it contains, how much are present, and in what form they exist. Many elements and substances that are acceptable or even essential to the body can be toxic when consumed in large doses. The question of what constitutes a large dose is often never well defined in physiological terms but is instead the consequence of arbitrarily defined factors. In a few cases, such as mercury, arsenic, lead and cadmium, where the metal

serves no known biological function, a toxic dose and threshold has been defined from physiological experience. In most other cases, the concentration threshold is less well definable and "safe" dosage levels tend to be defined by standards. In this study an attempt will be made to correlate toxicity with specific physiological effects when possible and also with existing state or federal standards.

An additional factor that determines the toxicity of a specific element besides its concentration, is the chemical form in which it is found. Even the most toxic material can be non-toxic when it is in a form that is unavailable to the body. However, caution must be taken to ascertain that it does not exist in a form that could be assimilated by plant or animal life and thereby become available to humans. Thus, a determination of a chemical analysis, in itself, can not define toxicity but instead defines only concentration. In addition to chemical analyses, this study will determine the chemical state of each potentially toxic element and its subsequent availability to humans.

The study will start with a precise determination of the chemical analysis of the sludge and its liquor, and the coal, limestone and process waters constituting the raw materials in the process. A composite listing of sampling points is given in Figure 2. In Table I is an analysis of a composite sample of western coal (Ref. 19) and an analysis of a specific sample of an eastern coal from Aerospace experimental data. Only those elements that could be potentially toxic were selected. Also in Table I is a specific analysis of fly ash and bottom ash from a western coal (Ref. 19).

A comparison of the coal samples analyses reveals specific differences. Such differences can be found between coal samples within the same region and do not necessarily indicate specific differences between eastern and western coal. In general, the western coals are associated with more basic minerals; the eastern coals with more acidic minerals. The western coals tend to contain a broader spectrum of rare earth elements. The trace elements are found usually as contaminants in minerals codeposited with the coal or in the organic matter from which the coals originated. In this regard, general statements referring to relative toxicity between the two types is not possible.

The coal for which the fly ash and bottom ash were derived contained approximately 10% ash. As a consequence, the ash samples could be expected

Figure 2

COMPOSITE SAMPLING OF TCA SCRUBBER SYSTEMS

1. LIMESTONE
2. COAL
3. FLUE GAS PARTICULATES AT SCRUBBER INLET
4. FLUE GAS PARTICULATES AT SCRUBBER OUTLET
5. BOTTOM ASH
6. SLUDGE AT SCRUBBER EXIT
7. CLARIFIER UNDERFLOW
8. RECYCLE LIQUOR
9. CENTRIFUGE PRECIPITATE

Table 1. Selected Elements in Coals and Ash (ppm)

<u>Element</u>	<u>Eastern Coal Aerospace Data</u>	<u>Western Coal Composite Sample (Ref. 19)</u>	<u>Fly Ash (Ref. 19)</u>	<u>Bottom Ash (Ref. 19)</u>
Arsenic	N. D.	3	15	3
Mercury	<0. 01	0. 05	0. 03	<0. 01
Antimony	<0. 05	0. 17	2. 1	0. 26
Selenium	N. D.	1. 6	18	1
Cadmium	N. D.	<0. 5	<0. 5	<0. 5
Zinc	180	0. 56	70	25
Manganese	350	15	150	150
Boron	46	15	300	70
Barium	1800	400	5000	1500
Beryllium	<0. 01	N. D.	3	<2
Nickel	N. D.	25	70	15
Chromium	310	5	150	70
Lead	30	4	30	20
Vanadium	180	9	150	70

N. D. - Not detected

to have a concentration of a specific element 10 times that of the coal sample. (Since the western coal analysis was from a composite sample a direct comparison between the coal data and ash data is not valid in this case). Comparing the fly ash and bottom ash reveals a major difference in heavy metal concentrations. Relative to the fly ash, the bottom ash is low in refractory metals and metals having high vapor pressures at combustion temperatures. In contrast, those base elements that easily slag, are more predominant in the bottom ash.

In Table 2 is an analysis of sludge water that may be typically found in an ash pond (Ref. 20) and an analysis of a scrubber liquor from Aerospace data. The analysis represents the solubility of some of the elements specifically found in a boiler ash and a sludge. Whereas only one of these elements (manganese) poses a health hazard at the given levels in those cases, they may not represent the actual case. In addition, factors existing in the sludge processing technology may serve to concentrate other elements thereby posing additional hazards.

As an example of the concentration effect, the case of fixation technology will be used. In general, this technology requires the introduction of additives to the sludge which react with the dissolved sulfates to form a new crystalline phase. If toxic elements are accepted within this new phase, they become eliminated from solution and no longer become available as a contaminant in leaching or run-off waters. On the other hand, if they are rejected by the new phase, they could become concentrated within the remaining water and thereby pose a health hazard. Details of the specific chemistry of each potentially toxic element have not yet been determined and the toxic hazard of sludges in the various forms they may be found has not yet been assessed.

6. Disposal

Of the many million tons of sludge that will be produced each year, the possibility of economic utilization exists for only a small portion of the total. The major quantities of sludge produced will require disposal in an ecologically sound manner. Presently, the alternatives being considered are ponding and landfilling; both disposal operations will require the establishment of procedures that avoid hazards related to health and safety or land use.

Table 2. Selected Elements in Solution (ppm)

<u>Element</u>	<u>Ash Pond (Ref. 20)</u>	<u>Scrubber Liquor Aerospace Data</u>	<u>PHS Drinking Water Standards</u>
Lead	.01	<.01	.05
Antimony	.015	N. D.	-
Barium	.07	<.05	1.
Manganese	.075	1.6	.05
Mercury	<.001	N. D.	-
Beryllium	.002	N. D.	-
Boron	.5	11	-
Nickel	.015	.05	-
Cadmium	.01	N. D.	.01
Selenium	.035	N. D.	.01
Zinc	.03	N. D.	5.
Arsenic	.01	N. D.	.05

N. D. - Not detected

The requirements for disposal will be strongly dependent upon whether or not the sludges are found to be toxic. If the sludges are found not to be toxic, the problem of disposal is simplified, but the problem of safety and land use must still be addressed. An untreated sludge will retain a considerable quantity of water. Laboratory tests on a limestone sludge containing a relatively high sulfate content will settle only to 45% solids content if underdrainage is not provided, but if drainage to sub soil is allowed, the settled sludge will reach a content of 50% solids. A maximum particle packing equivalent to a value of about 70% solids content is reached upon air drying. When a dried sludge is re-wetted, the sludge will bloat and decrease its bulk density depending upon the quantity of water absorbed by the sludge. When a sludge contains a high sulfite content, the sludge will settle to a value of about 35% solids whether underdrainage is provided or not. A sulfite sludge does not dry as readily or settle as much during drying as a sulfate sludge.

A sulfate sludge for which underdrainage is provided will produce savings relative to one with no such provision because the higher packing density allows for the disposal of about 20% more sludge in the same ponding volume. However, if the sub-soil is the only means of underdrainage, the possibility for soil plugging exists especially in the case of sulfate sludges containing high concentrations of dissolved solids. Depending upon soil type, salts will precipitate within the soil, filling pores and preventing further water passage. Thus, the advantage of underdrainage would be lost. The more reliable system is one in which underdrainage is provided. Although in the case considered the sludge is assumed not to be toxic, it is very likely that the leachate would not be of a quality to be acceptable for discharge to a water course.

Ponding can be used not only for the final disposal of the sludge, but also as an interim measure to allow settling before removing the material to a landfill site. The most fundamental problem in the ecologically sound disposal of the sludge arises when the hazard exists for leaching toxic elements or soluble salts to ground or surface waters, or drainage to surface waters. The immediate solution to this potential problem may require dewatering and/or fixation of the sludge and storing it in a clay lined pond so that permeation to the sub-soil is minimized. Overdrainage and underdrainage

must return waters to the scrubber system thereby eliminating direct discharge to surface waters. Such a pond can serve as a final disposal site, but in most cases because of the large volumes of sludge and water to be handled, the pond can serve as primary settling basin from which the sludge can be periodically removed and placed in a landfill. A fixation treatment applied to the sludge prior to placing it in the pond is an alternative technique generally applicable only if the sludge is to be removed to a landfill after curing. This treatment has a dual purpose, one, the removal of water and increasing compaction qualities and, two, the minimization of leaching by decreasing the permeability of the material.

If a sulfate sludge is found to be toxic, it may be adequate to store it untreated in a pond having an impervious base. The use of underdrainage and overdrainage would be required to prevent the formation of a bog and the possibility of overflow, especially in areas where rainfall exceeds evaporation. This, of course, requires the lining of a large area pond, monitoring, and maintenance as necessary. A further problem would be faced when a point in time is reached where the generating plant can no longer accept all drainage originating from rainfall from all its disposal ponds, and direct discharge to streams would not be allowed, or where the plant is to be abandoned. Under either of those conditions, encapsulation by covering with an impervious material may be the best solution.

Numerous alternatives for ponding with or without pond lining or sludge conditioning may be possible. A cursory survey of the industry has shown that many of these alternatives are presently being considered and employed. Alternatives, such as treatment processes mentioned earlier, produce a high solids content sludge material having acceptable structural qualities for a landfill usage; a process for producing aggregate has been developed. The details of these processes will be discussed by the various process developers. Future concern by Aerospace for processes of this sort will be in the assessment of alternative disposal systems regarding potential ecological problems.

Some very rough approximations of costs for interim pond and fixation disposal have been put at about \$7 to \$10 per ton of dry sludge, (Refs. 15, 21) which includes labor, trucking, additives, supervision, and fixation processing. The cost of lining a pond varies considerably. For ponds in the 5 to 10

acre size, estimates have been put at \$5,000 to \$20,000 per acre for clay linings and stabilized pozzolan base linings, respectively, without piping - the clay lining will undoubtedly require maintenance to repair damage when the "dried" sludge is removed. A soil covered plastic lining complete with all drainage can cost \$25,000 to \$30,000 per acre. At this stage of our study, these values, though only approximate, underline the need for the determination of whether lined ponds with their attendant maintenance and monitoring (equipment) are necessary and where they should be located.

7. Utilization

The utilization of sludges will be discussed by several speakers at this symposium, therefore it is mentioned here only in terms of what the ecological implications may be and how that relates to the Aerospace study. Numerous programs directed toward sludge utilization have been conducted through government sponsorship and by industry alone (see Table 3). Some of the more significant of these are: 1) the successful development of the technology for autoclaved calcium silicate products, mineral wool and soil amendments at the Coal Research Bureau, West Virginia University under EPA contract (Refs. 10, 12); parking lot construction, Federal Highway Administration (Ref. 8) and I. U. C. S. (Ref. 11); landfill, road bases, aggregate, and structural shapes, I. U. C. S. (Refs. 9, 11); characterization and multiple use investigations at Combustion Engineering; and landfill and sludge properties by the Dravo Corporation (Ref. 13).

A review of the many possible utilization schemes indicates the following significant factors regarding their potential impact on ecologically sound disposal or utilization:

1. Applications to be considered for potential pollution effects are:
 - a. Fixation treatments for landfill
 - b. Aggregate for either landfill storage for future use, or construction usage in road building
 - c. Road base construction
 - d. Soil amendment

The applications listed above are all subject to various degrees of leaching. For item 1. a above, permeability values ranging from 2×10^{-5} cm/sec to 10^{-7} cm/sec have been reported. In some industrial tests of the treatment of acid waste sludges, it has been claimed that the permeability has been reduced from 10^{-5} to 10^{-7} cm/sec and the concentration of trace elements in the leachate was additionally reduced by about two orders of magnitude.

TABLE 3
POTENTIAL UTILIZATION OF SLUDGE

<u>Technology</u>	<u>Research Organization</u>	<u>Reference</u>
Calcium-silicate Products; Mineral Wool; Soil Amendments	Coal Research Bureau, West Virginia University, Under EPA Contract	10, 12
Parking Lot Construction	Federal Highway Administration, Wash. D. C.	8
Research Review	Coal Research Bureau West Virginia University	14
793 Sanitary Structural Land Reclamation; Compacted Road Base; Binder for Stabilized Road Base; Aggregate; Structural Shapes	I. U. Conversion Systems, Inc. Plymouth Meeting, Pa.	9, 11
Utilization Survey	The Aerospace Corporation El Segundo, California	3
Sludge Properties	Dravo Corp., Pittsburgh, Pa.	13
Characterization, Multiple Utilization	Combustion Engineering, Windsor, Conn.	-
Lightweight Aggregate	Michigan Institute of Technology	-

Thus, as a consequence of chemically combining trace elements into new crystalline phases and the reduction in leaching ratio, soluble salts or toxic contaminants that may be available to ground or surface waters are reduced by about 10,000 times over sludge that is not treated.

2. Aside from using the sludge as a landfill, the commercial applications listed in item 1 above constitute a potential outlet for the usage of vast tonnages of power plant sludges. A survey of the potential fly ash market by The Aerospace Corporation (Ref. 3) in 1970-71 indicated that the maximum potential marketability of fly ash in the near term was approximately 25 percent of the supply. Major inhibitions identified were transportation economics coupled with competition from other materials and the lack of control of fly ash quality and supply. A growing market for bottom ash in road construction brightens the total ash utilization picture somewhat (Ref. 2). However, with the flue gas scrubbing which increases the by-product tonnage by a factor between two and three, a simple deduction identifies "disposal" as the major outlet for the sludge, particularly in the near term.

A summary of potential utilization schemes for the sulfate sludges (other than sulfur or sulfur products), the researchers, and related literature is given in Table 3. Sulfur and sulfur product recovery are considered in other presentations at this symposium.

8. Summary

The laboratory results presented herein represent only the initial phase of experimentation. Since these data were derived from the analyses of samples taken from one plant on a given day, they should in no way be considered necessarily representative or typical. They do serve as a base point, however, to which other experimental and analytical data will be added so that a reasonable interpretation will be made of the potential impact of the disposal of scrubber sludges on water quality and solid waste disposal standards.

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EXPERIENCE IN THE DISPOSAL AND UTILIZATION
OF SLUDGE FROM LIME-LIMESTONE SCRUBBING PROCESSES

by

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INTRODUCTION

The C-E waste disposal program was initiated in 1969 with the primary objective of providing ecologically safe methods for the disposal of solid and liquid waste materials discharged from the C-E air pollution control system. A second objective was to investigate and develop beneficiation methods capable of producing useful products that would offset the disposal cost.

The program was formulated after considering a number of factors relating to the feasibility of beneficiation processes and its effect on the smooth operation of the power plant. One of the major factors considered was the industry experience in promoting the utilization of fly ash. Although fuel ash was first used as an admixture to concrete in 1936 with favorable results, its utilization in 1971 amounted to only about 20% of that produced. This low utilization persists despite the formation of a national organization with the single objective of promoting the use of ash from utility boilers. This is in contrast to the relatively high utilization in other industrialized countries, for example, Germany -- 80%, France -- 65%, United Kingdom -- 55%, etc. Another consideration was the desire of the utilities that any utilization or disposal scheme could not interfere with their primary role of producing power. A third consideration was the requirement that waste material from the APCS would have to be disposed of within the ecological limits set by the Federal Environmental Protection Agency as well as local control agencies.

Using the above factors as major criteria, a program was formulated to develop ecologically safe and economically sound disposal and/or utilization methods for APCS sludge. The program was divided into five phases and are discussed below.

PHASE 1, THE ENVIRONMENTAL SURVEY

The Procedure

The addition of a limestone wet scrubbing air pollution control system to a coal-fired steam generating unit more than doubles the amount of solids (modified ash) to be disposed of by the utility. In order to approximate this effect on the ash handling and disposal capabilities presently used and to gather other pertinent environmental data, a survey of the present practices was made in September 1970. The survey also gathered available data concerning pollution control limits of local regulatory agencies which were more strict than Federal regulations.

Forty-two utilities covering the continental U. S. were reviewed and from these 22 were selected to be surveyed. The companies were chosen on the basis of:

- a. Geographic location
- b. Population center
- c. System capacity
- d. Type of coal

These companies account for about 30% of the electricity generated by coal in continental U. S. A. Questionnaires were delivered to the utilities by C-E sales personnel at which time

an appointment was made for future discussions between C-E's engineers and the utility's environmental engineer. During this latter visit, the questionnaire was discussed and filled out.

Data Analyses

General plant site data -- About 25% of the stations had multiple means of fuel delivery. The data showed that railroads were used 67.5%, barge 39.6%, trucks 14%, and conveyor 7% for the transportation of coal. Railroad delivery was not further defined as to unit train or regular rail transportation.

Furnace type data were reported on 215 units which represented 83.2% of the units surveyed. Balanced draft units represented 71.7% and pressurized furnaces represented 10.7%.

Firing method data were improperly stated on 29 of the units. The data indicated the following for the firing methods reported:

Tangential	40.5%
Stoker	15.8%
Horizontal	8.4%
Vertical	1.9%
Cyclone	4.7%
Improper response	
Pulverized coal	28.8%

Air data -- Air pollutant data (stack, wind, and emission rates) were requested to permit determination of ground level concentration. However, insufficient emission data were obtained to determine concentration by calculations. It may

have been more fruitful to request ground level concentrations directly as well as emission rates. (One of the stations did report ground level concentrations when emission rates were requested.) It is significant to note that only a very few stations reported NO_x emission rates. This indicates that very few stations were determining NO_x stack emission levels at the time of the survey. (The regulations on NO_x emissions had not yet been promulgated and may explain this minimal response.)

The waste solids were transported from the dust collector hopper to the disposal area by sluicing through pipes by 74% or by trucking by 28%, respectively, for the stations reporting. Approximately 24% of the stations were planning future improvements in their equipment for control of atmospheric emissions.

Land Waste Disposal Data Plant waste solids disposal rates varied from 80 to 440 tons per day. The average solid waste disposal rate of the 41 reporting plants was 800 tons per day. Fourteen plants reported sales of waste solids of from 1 to 74% of the ash produced. Actual sales tonnage based on all 41 reporting plants was 1200 tons per day of 33,000 tons produced. This represents the sale of less than 4% of the ash produced. Maximum daily sales for any plant was 400 tons per day.

Nearly 16% of the ash sales were made by stations using plant acres for disposal. Over 84% of the sales were made by plants using off-site disposal areas. Since plant site solid waste disposal is used by 79% of the plants in the survey it appeared that the economic pressure, cost of the off

site disposal, may be a major factor in the need for developing sales outlets for solid wastes.

Solid waste disposal costs were reported by 81% of the plants in the survey. The cost varied from \$0.03 to \$1.10 per ton for sluicing compared to \$0.11 to \$1.33 per ton for trucking the solid waste to an off-site disposal area. The average sluicing rate cost for 25 plants was \$0.45 per ton while the average trucking rate for 10 plants was \$0.51 per ton.

Water Waste Data -- The boiler blowdown and demineralizer waste disposal data obtained were not amenable to specific statistical analysis. This was also true for cooling tower and ash sluicing water data.

Once-through condenser cooling water temperature rise data were obtained from 58% of the reporting power plants. The average temperature rise was 16 F for cooling water flow rates varying from 0.5 to 7 million gallons per day.

More than one-half of the utilities did not report the composition of the waste water streams from their stations. This type of data had not been obtained, in most cases, at the time of the survey.

Conclusions

The electric power industry's response to the C-E environmental survey was very good with 86% of the canvassed companies completing the questionnaire. The high rate of response is a direct indication of utility interest and concern with environmental problems. As a result of the survey, a greater appreciation for the complexity and diversity of problems associated with

waste disposal was acquired by both C-E and the cooperating utilities.

PHASE 2, THE CHARACTERIZATION OF APCS SLUDGE

Methods of Study

Since there was very little information available on the physical, chemical, and engineering properties of the modified ash produced by the APCS, it was decided that this should be one of the first areas to be investigated. Hence, the second phase of the program was designed to completely characterize the APCS sludge. The laboratory program initially concentrated on the solids APCS discharge which was to be followed by a study of the treatment methods for any waste water stream associated with the system.

Properties relating to the permeability, solubility, compactibility, drying, etc. of sludge are important considerations in the direct disposal of this material. Thermal properties such as melting points, decomposition temperatures, sinterability, etc. are important in many areas where utilization as building products are considered.

In order to supplement the classical analytical methods and the X-ray fluorescence and diffraction spectrometers used in the characterization of the sludge, a thermal analyzer was obtained. The equipment shown in Fig. 1 is capable of performing simultaneously thermogravimetric analysis (TGD), differential thermal analysis (DTA), and differential thermogravimetric analysis (DTG). Some of the engineering and rheological studies

that require specialized equipment were contracted to laboratories specializing in establishing these properties.

Analytical Procedure

Initially, four sludges were selected as standards for the characterization studies. The sludges were selected to represent the material that would be produced by the different types of air pollution control systems using the lime or limestone scrubbing method. This number was eventually increased to ten standard samples when the variations in the scrubbing processes increased. The chemical composition of these ten standards, identified in Table I, are listed in Table II. X-ray analyses were also performed on these ten standards and the results are listed in Table III. Each of the samples, which weighed about 50 lbs., were dried to a constant weight at 100 F and stored for future analysis. Instructions were also given to the contracting laboratories to treat the sludges that they received in the same manner so that interlaboratory data pertaining to a particular sludge could be compared. Table IV gives the range of the specific gravity of the as they varied with the water content. A summary of the leaching studies using water at two pH levels is given in Table V.

Thermal Analysis

In order to accurately characterize the changes that occur when the sludges are heated to various temperatures, an extensive program of thermal analysis was set up. The program started with the determination of the thermal properties of some pure compounds found in the APCS sludges. This was followed by a study of the effect of fly ash on these

thermal properties. The study was then extended to synthetic mixtures of compounds formulated to simulate APCS sludge. TGA curves of the known materials were used to identify and analyze these components in the actual sludges. A summary of the work on pure compounds and with fly ash added is shown in Tables VI and VII and represented in Fig. 2, while Table VIII compares the analytical results obtained with the differential thermal analyzer to those found using wet chemistry. Figure 3 shows thermogravimetric curve of some synthetic sludge samples formulated in the laboratory, while Fig. 4 shows a differential thermalanalysis curve of a representative sludge.

PHASE 3, DIRECT DISPOSAL METHODS

Based on the assumption that most utilities would prefer the minimum modification of their present waste handling practices, this program investigated methods of direct disposal immediately after the characterization step had been completed. Since direct disposal could take the form of either ponding or recoverable land fill operations, C-E's study investigated both of these.

Ponding Studies

The ponding studies began by investigating the permeability of settled and compacted sludge to determine its ability to act as its own sealant. This was followed up by a field study that is currently in progress. Two consultant hydrologists were interviewed and one was selected to draw up a test program to determine the effect of a sludge pond on the surrounding ground water.

After preparation of the pond site and before the introduction of the sludge, a series of 14 wells were placed around the perimeter of a new APCS installation. Weekly samples were taken from wells for two months prior to the introduction of sludge and analyzed to establish the initial quality of the water. Sampling will continue for at least one year and any change and rate of change in the quality of the water will be tabulated and analyzed. A diagram of the ponding site and wells is shown in Fig. 5. A description of the wells is contained in Table IX.

Land Fill Studies

Laboratory studies have indicated that in order to produce a stable land fill, an air pollution control system sludge would have to be dewatered to about 70% solids. Studies have also indicated that conventional vacuum filters probably will not dewater the sludge to that extent and other equipment or procedures will have to be used. These other procedures may involve the mixing of the sludge with dry fly ash if enough of it is available to reduce the moisture content to the required level. Other equipment under consideration includes a press type filter, various drying equipment, and mixing apparatus. An extensive program involving laboratory characterization, pilot plant testing, and full-scale field demonstration of processes that would produce a solid suitable for land fill application is planned. Figure 6 shows one such scheme.

Road Construction

In addition to the work with stable land fill material, an extensive program dealing with the formulation and testing of sulfate sludge for use in road construction is being carried out. During these studies, APCS sludges were dried and compacted into test cylinders that have reached compressive strengths of 5,000 psia after 28 days of curing. Other sludges, however, have exhibited compressive strengths of only 250 psi.

Another phase of the study on the use of APCS sludge as a highway construction material was C-E's participation in a project at Dulles Airport in Washington D. C. This project is described in a later section.

PHASE 4, BENEFICIATION METHODS FOR SLUDGE UTILIZATION

Procedure

Consideration was given to the possibility that in some metropolitan areas a combination of high disposal costs and a shortage of raw material for which APCS sludge could be substituted might lead to a situation where it would be economical to develop some beneficiation process that would lead to the development of products. We believe that due to the volume of the sludge involved, any by-product utilization schemes would be similar to those with the normal fly ash. Further, it was believed advantageous to the disposal and/or utilization of both the modified and unmodified ash if a systematic investigation was made of where the APCS sludge could be substituted for fly ash and where the use of sludge would be detrimental

to areas where fly ash is being used. In this study, data collected by other organizations, such as the Bureau of Mines and the West Virginia Coal Research Bureau, were considered. Table X is a partial list of the areas where investigations in varying degrees were made for the utilization of the APCS sludge.

The Most Promising Schemes

A number of the more promising utilization methods were investigated either in our Kreisinger Development Laboratory or by laboratories already working with fly ash in these areas. Figure 7 and 8 show some of these processes. A number of products made from the fly ash involve sintering. Since laboratory studies have shown that with APCS sludge sintering is accompanied by the decomposition of the calcium sulfate and subsequent release of SO_2 , a study of the economics of the joint process involving the sintered product and sulfur recovery was made by two sulfur-producing companies. One of these companies developed processes for the production of sulfur from Gypsum. Even while the study was in progress, the price of sulfur changed from about \$40 per ton to about \$10 per ton making any process depending on the sale of this material uneconomical at this time.

LARGE SCALE DEMONSTRATION STUDIES

C-E participated in a project with the Research and Development Division of the Federal Highway Department to study the use of sludge as a highway construction material. The program was part of the U. S. Governments' International Transportation Exposition (Transpo '72) that was held from

May 24 to June 4, 1972 at the Dulles Airport in Washington, D. C.

In order to accommodate the 50,000 automobiles and 600 buses expected daily at the exposition, a 120-acre parking lot was constructed. The Research and Development Division of the Federal Highway Administration used this opportunity to demonstrate the recycling of waste products as highway construction materials. The major portion of the parking lot was paved with a mixture of fly ash and sulfate sludge from an acid plant. Other portions of the parking lot were paved with waste products such as air pollution control system sludge and acid mine drainage sludge.

Combustion Engineering transported 75 tons of sludge from Lawrence, Kansas to the Dulles site - a distance of about 1300 miles. Since this was the first time that APCS sludge had been transported by any vehicle, the project was designed to obtain the maximum amount of information on possible materials handling problems. The sludge was dredged from a pond at Kansas Power and Light where it had been stored for 6 months. It was allowed to drain for 24 hours and loaded on flat and round-bottom trucks for the non-stop trip. Two C-E engineers monitored the sludge during the entire trip taking measurements and samples for laboratory analyses at various intervals.

In general, there was no problem of sludge leaking from the trucks while they were on the road. Excess water did leak from the track tailgate during the trip. At Dulles, the sludge was removed from the truck.

It was considerably easier to unload the round bottom trailers than it was those with square beds. All of the sludge slid out readily from the former while the latter required manipulation with the backhoe to complete removal of the sludge.

The APCS sludge was slurried with water, mixed with fly ash and lime, and placed in a test section of the parking lot. Evaluation of the suitability of APCS sludge as a highway construction and repair material is continuing. In a recent report to the third International ash association, the highway administration indicated that so far the performance of the material was satisfactory. An analysis of the densities of the sludges at the bottom of the truck is given in Table XI. Figure 9 shows the loading, hauling, and unloading of the sludge material.

CURRENT STATUS

At present, C-E is applying its efforts to the area of direct disposal. Beneficiation methods and studies are limited to those that are necessary to dewater the slurry from 10% solids to the 70% for land fill operation. To support this study, APCS sludge in 200-gallon lots has been shipped to the laboratories of manufacturers of commercial drying equipment for tests. One spray drying test has proved to be very satisfactory.

The more we get involved in the study of waste disposal the more we learn the enormity of the problem and the effort that must be applied before a solution is reached. A portion of the waste disposal dilemma is a result of our attempt to supply the nation with energy without an adverse effect on our environment. C-E is not in the waste disposal business and has nothing to gain from the sale of any products produced from the sludge or from the various contracts for the sludge handling that the utility may enter. Utilities, suppliers, and the federal government should share the expense of waste disposal utilization studies.

TABLE I

IDENTIFICATION OF APCS SLUDGE STANDARDS

STD I	--	Flyash from Connecticut Light and Power Company's Devon Station
STD II	--	C-E sludge - CaCO_3 , 150% stoichiometry, 2000 ppm SO_2
STD III	--	Kansas Power and Light sludge
STD IV	--	C-E sludge - Ca(OH)_2 , 38% to 50% stoichiometry, 50 to 60% SO_2 removal, slurry feed 220 gpm, recycle 165 gpm with 55 gpm blowdown
STD V	--	Union Electric sludge
STD VI	--	C-E sludge - CaCO_3 , 150% stoichiometry, 45 to 55% removal, no recycle
STD VIA	--	STD VI plus 50% STD I (flyash)
STD VII	--	C-E sludge - 300 to 325% stoichiometry, 64% SO_2 removal, 300 lb/hr flyash, 550 lb/hr CaCO_3
STD VIII	--	C-E sludge - 120 to 130% stoichiometry Ca(OH)_2 , 90.8% removal, 120 gpm Ca(OH)_2 slurry underbed, inlet SO_2 860 to 840 ppm, outlet SO_2 80 ppm, 145 lb/hr Ca(OH)_2 , no flyash addition
STD IX	--	C-E sludge - 220 gpm H_2O spray, 275 lb/hr lime feed, 300 F reaction temperature

TABLE II

WET CHEMICAL ANALYSIS OF SLUDGE STANDARDS

	<u>STD I</u>	<u>STD II</u>	<u>STD III</u>	<u>STD IV</u>	<u>STD V</u>	<u>STD VI</u>	<u>STD VIA</u>	<u>STD VII</u>	<u>STD VIII</u>	<u>STD IX</u>
SiO ₂	46.7	1.5	30.7	0.79	19.4	1.1	27.7	4.6	1.2	2.0
Al ₂ O ₃	23.2	0.32	6.6	0.05	6.8	0.01	14.7	2.3	0.48	0.45
Fe ₂ O ₃	13.7	0.27	8.6	0.18	5.4	0.09	8.3	1.6	0.72	0.72
CaO	4.7	49.6	22.7	42.5	27.6	52.5	24.2	40.1	42.5	46.2
MgO	0.9	0.54	1.5	0.10	3.2	0.52	0.70	0.20	0.90	0.40
Na ₂ O	0.3	0.04	0.50	0.03	0.08	0.02	0.16	0.05	0.05	0.04
815 K ₂ O	2.6	0.17	1.1	0.05	0.24	0.14	1.2	0.29	0.07	0.21
TiO ₂	1.5	<0.02	0.26	<0.02	0.32	<0.02	0.79	0.11	<0.02	<0.02
P ₂ O ₅	0.3	0.05	0.11	0.06	0.08	0.13	0.19	0.08	0.06	0.07
CO ₂	2.6	29.2	5.3	3.7	7.2	36.6	15.3	13.6	11.5	24.4
SO ₂		11.7	5.8	38.8	2.2	6.3	3.4	5.4	24.1	13.7
SO ₃	0.8	3.5	6.5	3.3	12.3	0.5	<0.1	24.9	8.4	4.4
CaCO ₃	5.9	65.7	12.0	8.4	16.3	80.6	34.7	30.9	26.1	55.4

TABLE III
X-RAY ANALYSES OF APCS SLUDGES

Standard	Major	Minor	Trace
I	SiO ₂ 3Al ₂ O ₃ ·2SiO ₂	Fe ₂ O ₃	CaCO ₃ Fe ₃ O ₄ CaSO ₄
III	SiO ₂	Fe ₃ O ₄ CaCO ₃ 2CaSO ₃ ·H ₂ O	3Al ₂ O ₃ ·SiO ₂ Ca(OH) ₂ CaSO ₄ MgO
IV	2CaSO ₃ ·H ₂ O		SiO ₂
V	SiO ₂ CaCO ₃	CaSO ₄ ·2H ₂ O	Ca(OH) ₂ 2CaSO ₃ ·H ₂ O Fe ₃ O ₄ 3Al ₂ O ₃ ·2SiO ₂
IV	CaCO ₃	2CaSO ₃ H ₂ O	CaSO ₄ SiO ₂
VIA	CaCO ₃	SiO ₂ 2Al ₂ O ₃ ·2SiO ₂	2CaSO ₃ ·H ₂ O CaSO ₄ Fe ₂ O ₃
VII	2CaSO ₃ ·H ₂ O	CaCO ₃	2CaSO ₃ ·H ₂ O CaSO ₄ ·2H ₂ O SiO ₂
VIII	2CaSO ₃ ·H ₂ O	CaCO ₃	Ca(OH) ₂ SiO ₂
IX	CaCO ₃		2CaSO ₃ ·H ₂ O SiO ₂ CaSO ₄ ·2H ₂ O Fe ₂ O ₃ Ca(OH) ₂

TABLE IV

THE VARIATION OF THE SPECIFIC GRAVITIES OF STANDARD SLUDGE WITH WATER CONTENT

% H ₂ O	<u>STANDARD</u>									
	I	II	III	IV	V	VI	VIA	VII	VIII	IX
0	2.28	2.64	2.18	2.48	2.18	2.62	2.33	2.62	2.34	2.19
5	2.10	2.27	2.16	2.00	1.86	2.41	2.21	2.42	2.20	2.19
10	2.06	2.09	2.06	1.91	1.80	2.27	2.09	2.22	1.98	2.01
20	1.83	1.91	1.92	1.72	1.81	2.00	1.92	1.94	1.86	1.84
30	1.62	1.70	1.58	1.51	1.62	1.78	1.66	1.84	1.70	1.65
40	1.50	1.54	1.47	1.44	1.44	1.57	1.54	1.56	1.57	1.48
50	1.38	1.43	1.40	1.34	1.38	1.43	1.43	1.42	1.37	1.40
60	1.29	1.32	1.28	1.25	1.28	1.32	1.30	1.31	1.31	1.30
70	1.21	1.22	1.21	1.18	1.18	1.22	1.21	1.25	1.20	1.21
80	1.13	1.14	1.12	1.13	1.13	1.14	1.12	1.12	1.14	1.13
90	1.06	1.07	1.06	1.07	1.06	1.06	1.07	1.07	1.06	1.07

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STD	pH 5.90				pH 4.15			
	Wt. Loss, g	% Wt. Loss	Volume, ml	Loss, g/ml	Wt. Loss, g	% Wt. Loss	Volume, ml	Loss, g/ml
I	0.8178	2.64	6400	0.127×10^{-3}	0.2525	1.06	6495	0.038×10^{-3}
II	0.5515	2.94	6250	0.088×10^{-3}	0.5821	3.71	6750	0.086×10^{-3}
III	3.2688	16.21	5825	0.561×10^{-3}	1.8784	10.54	6885	0.272×10^{-3}
IV	0.6599	6.53	6810	0.097×10^{-3}	0.8218	8.68	5175	0.158×10^{-3}
V	4.6063	33.60	8915	0.516×10^{-3}	3.1613	27.92	6625	0.477×10^{-3}
VI	0.5258	2.95	6870	0.077×10^{-3}	0.6936	3.64	7295	0.095×10^{-3}
VIA	0.5491	2.36	6650	0.083×10^{-3}	0.3009	1.59	5095	0.059×10^{-3}
VII	4.3096	23.77	6890	0.625×10^{-3}	4.1662	30.01	6315	0.659×10^{-3}
VIII	1.9332	11.91	8330	0.232×10^{-3}	1.3071	9.90	7285	0.179×10^{-3}
IX	0.9464	6.55	6655	0.142×10^{-3}	1.1391	7.93	7155	0.159×10^{-3}

*Air dried uncompactd materials

TABLE VI

THERMAL ANALYSIS OF SOME PURE COMPOUNDS FOUND IN APCS SLUDGE

Temperature and Events <hr/> Compounds	0-500 C Dehydrations, %H ₂ O		500-700 C Oxidation of CaSO ₃ , % Weight Gain		700-900 C Decomposition of Limestone, % CO ₂		1200-1400 C Decomposition of Calcium Sulfate, % SO ₃	
	Lit.	Exper.	Lit.	Exper.	Lit.	Exper.	Lit.	Exper.
CaSO ₄ · 2H ₂ O	20.9	18.7					46.5	46.7
CaSO ₄ · 1/2H ₂ O	6.2	3.5					55.2	48.2
CaSO ₄							58.8	
CaSO ₃ · 1/2H ₂ O	7.0	6.8	13.3	5.0			62.0	64.2
CaCO ₃					44.0	43.5		
Ca(OH) ₂	24.3	22.5						

TABLE VII

DECOMPOSITION TEMPERATURE OF COMPOUNDS WITH AND WITHOUT FLY ASH

COMPOUND	Decomposition Temperature, C		
	Literature	Without Fly Ash Experimental	With Fly Ash Experimental
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	128	130	130
$\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$	162	145	145
CaSO_4	1200	1400	1200
$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$	400	400	400
CaCO_3	825	730	730
Ca(OH)_2	580	460	460

TABLE VIII

ANALYTICAL RESULTS OBTAINED BY WET CHEMISTRY AND THERMAL ANALYSIS

		Total SO ₃		Equivalent Calcium Sulfate		CO ₂		Equivalent Calcium Carbonate	
		Chemical	Thermal	Chemical	Thermal	Chemical	Thermal	Chemical	Thermal
Standard I		0.8	1.9	1.4	2.9	---	2.6	---	5.9
821	III	12.5	14.5	21.1	27.0	---	4.1	---	9.1
	V	13.5	14.7	22.8	27.5	---	4.7	---	10.7
	VI	5.1	6.5	8.6	10.2	34.6	34.9	79.5	80.0
	VII	32.3	34.4	55.0	58.4	13.5	11.3	30.8	25.8
	VIII	39.7	* 29.3	65.7	* 49.3	8.8	6.2	---	14.2
	IX	24.2	22.8	41.2	38.7	23.8	21.9	54.3	49.82

* Did not reach maximum temperature during the thermal analysis

TABLE IX

SAMPLING WELLS AT THE FULL SCALE PONDING STUDY SITE

Well Number	Depth* (Feet)	Water Level* (Feet)
1	28	23
2	32	23.2
3	29	24.8
4	34	24
5	23	20
6	29	20
7	27	23.4
8	31	23
9	27	22
10	30	19.8
11	28	23
12	32	23
13	28	25
14	32	24.5

* These values include 2 feet of pipe above the ground level

TABLE X
UTILIZATION AREAS FOR FLY ASH AND MODIFIED ASH

1. Airport pavement mixture
2. Asphaltic filler and wear-course aggregate
3. Cement manufacture
4. Concrete admixture for construction
5. Grouting agent in wells
6. Filler for glass
7. Filler for fertilizer
8. Filler for paint
9. Filler for plastic
10. Filler for rubber
11. Fill material for land recovery
12. Fill material in abandoned mines for fire control
13. Fill material in abandoned mines for subsidence control
14. Neutralization of acid mine drainage
15. Manufacture of sinter bricks
16. Manufacture of autoclaved bricks
17. Manufacture of light weight aggregate
18. Manufacture of mineral aggregate
19. Production of cenosphere
20. Soil amendment
21. Soil stabilizer for road base, dam, embankments, etc.
22. Recovery of gypsum
23. Recovery of sulfur
24. Sealant in sanitary land fill operation
25. Sludge dewatering
26. Reclamation of polluted lakes
27. Sand blasting
28. Production of mineral wool
29. Recovery of magnesium oxide
30. Recovery of calcium oxide

TABLE XI
DENSITY MEASUREMENT MADE ON THE SLUDGE IN TRANSPORT

	<u>Miles</u>	<u>Dike</u>	<u>Truck 1</u>	<u>Truck 2</u>	<u>Truck 3</u>	% Solids [All readings for bottom of bed except as noted]
0		51.5				
5-1/2	(Weigh Station)					54.3 top 56.8 bottom
11	(KPL-Weigh Station Round Trip)		54.6			
35	(Kansas Tpke Toll Station)		54.2	57.1	53.6	
103	(Between K.C. & Mexico, Mo.)		54.2 54.2	48.4 top 53.1 bottom		
214	(Mexico, Mo.)		55.4	55.8		
431	(Effingham, Ill.)		56.2	56.7		
657	(Richmond, Ind.)		47.8	55.4		
931	(Wheeling, W. Va.)		42.7			
1375	(Dullas Airport)		64.2		60.9	

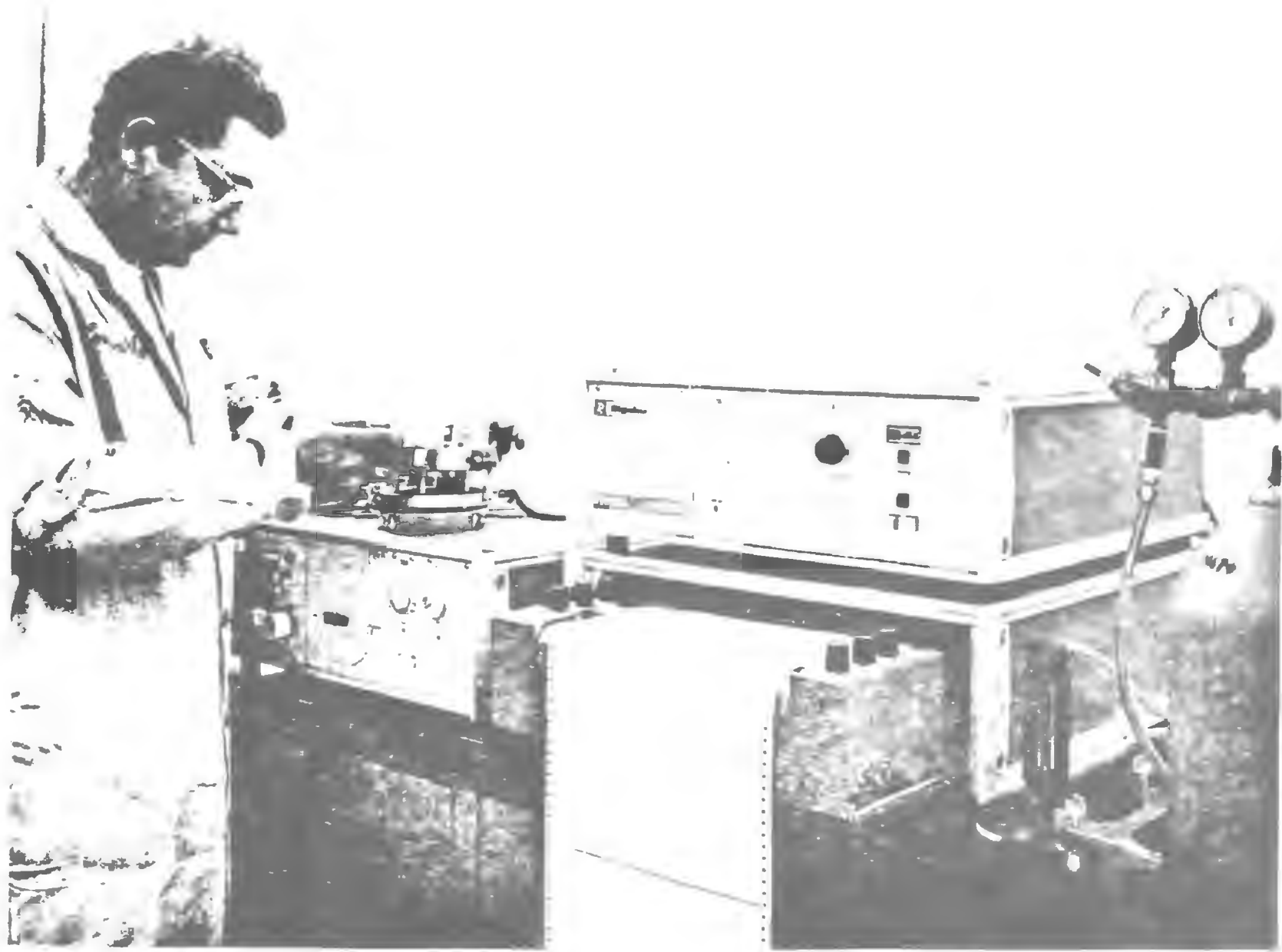


Fig. 1: Simultaneous analyses equipment

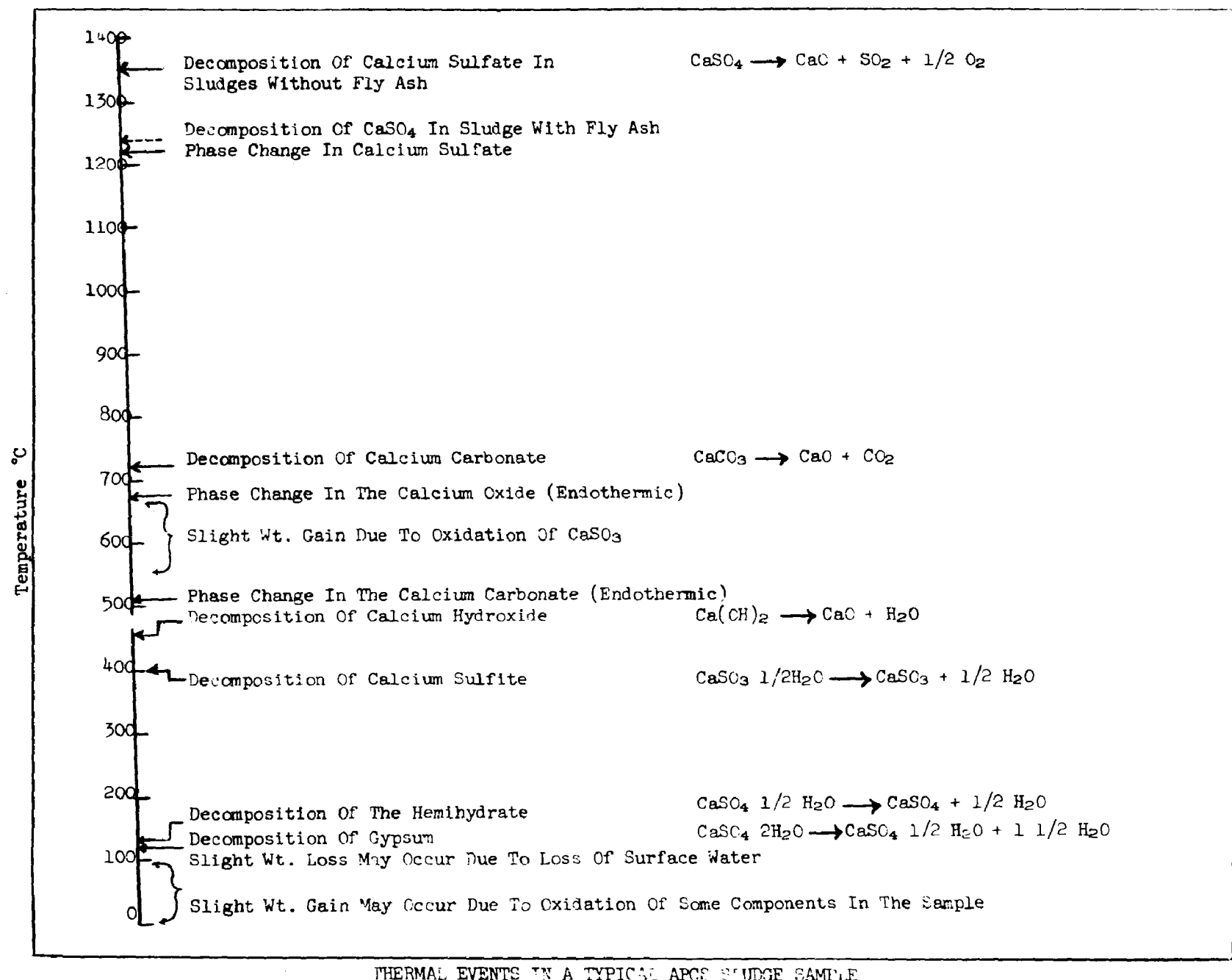


Fig. 2: Summary of the work on pure compounds with fly ash added

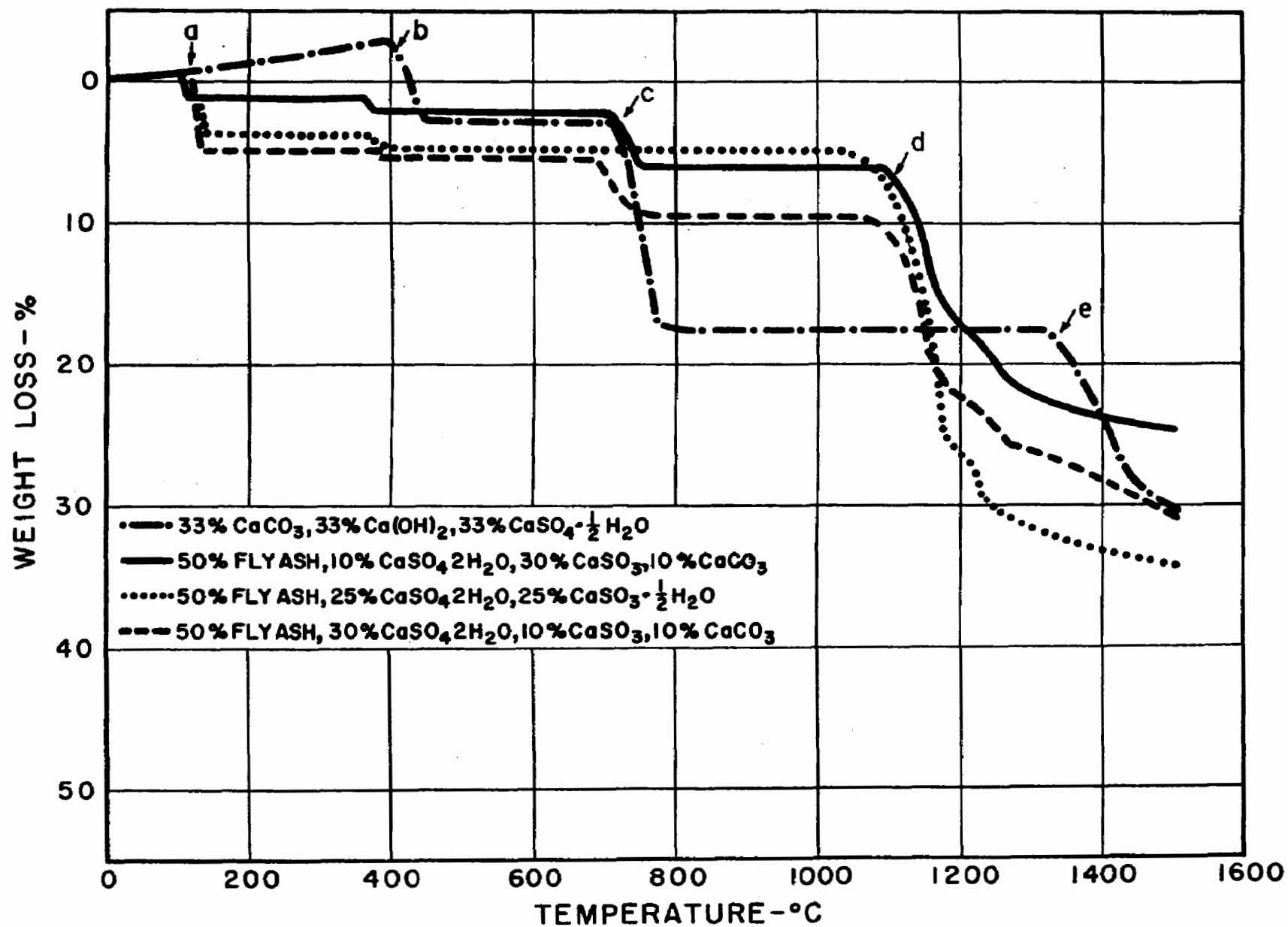


Fig. 3: Thermogravimetric curve of some synthetic sludge samples

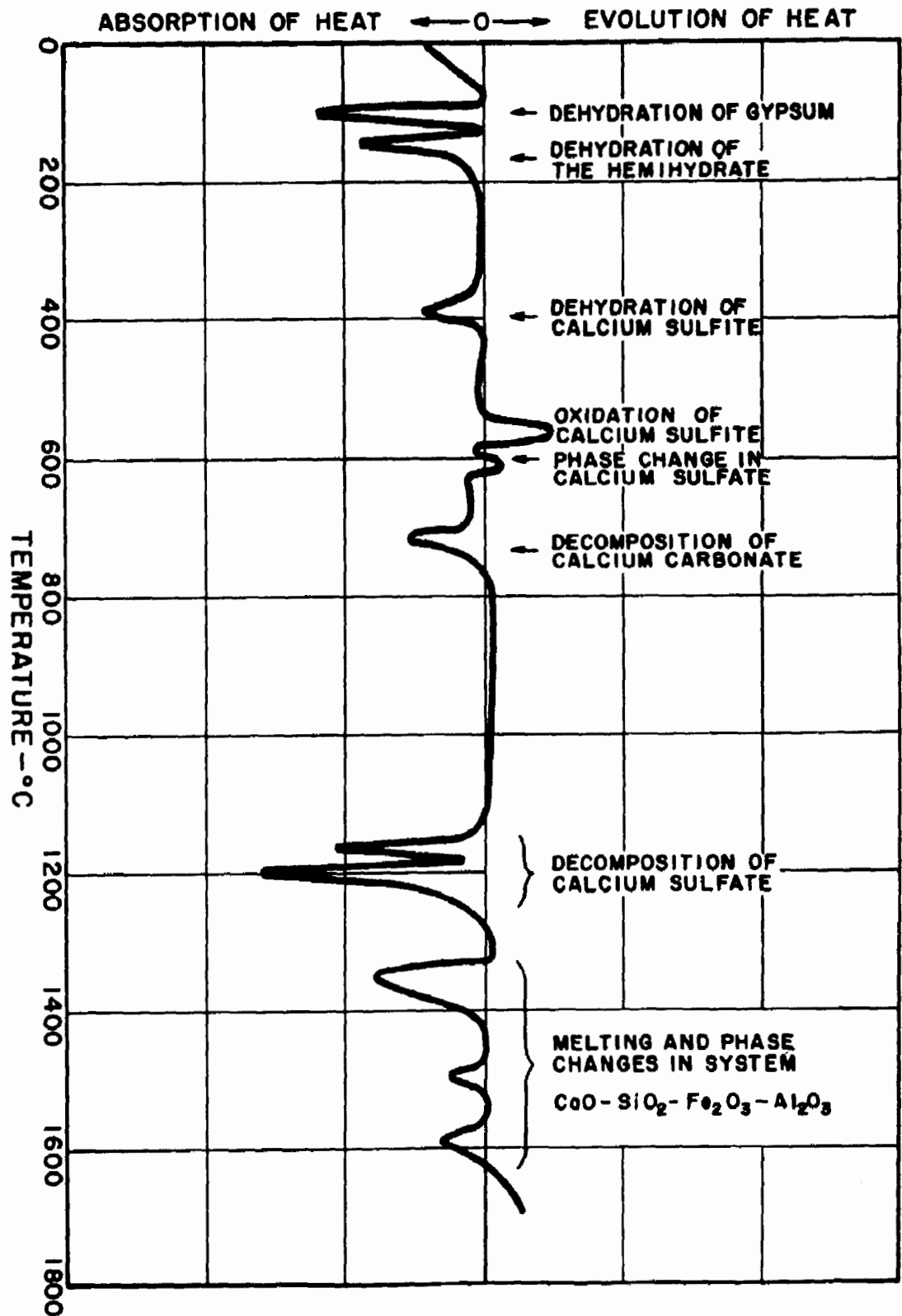
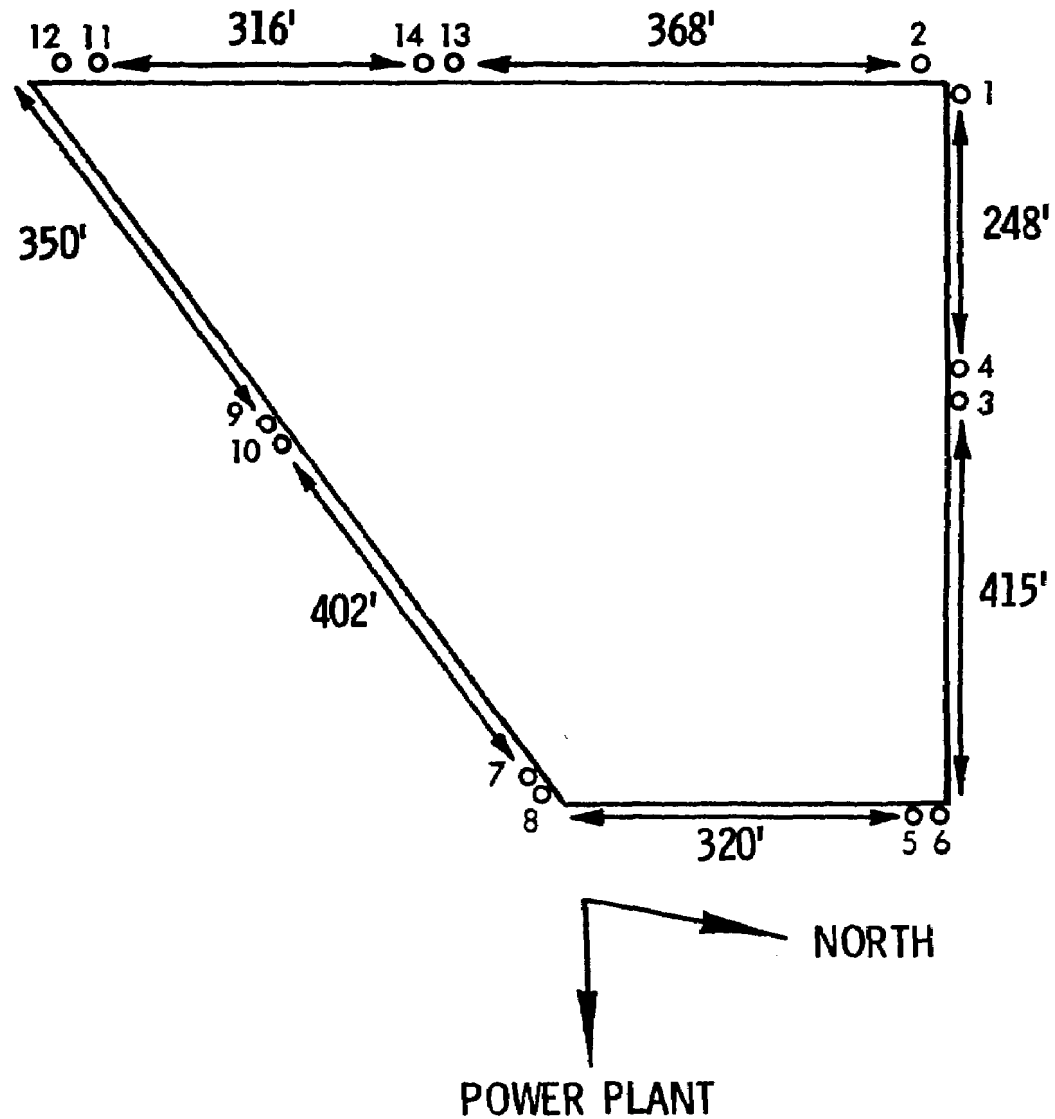


Fig. 4: Differential thermalanalysis curve of representative sludge

EVEN NUMBERED WELLS ARE DEEP, ODD NUMBERED WELLS ARE SHALLOW
 DISTANCES ARE APPROXIMATE IN FEET



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Fig 5: Ponding site and wells diagram

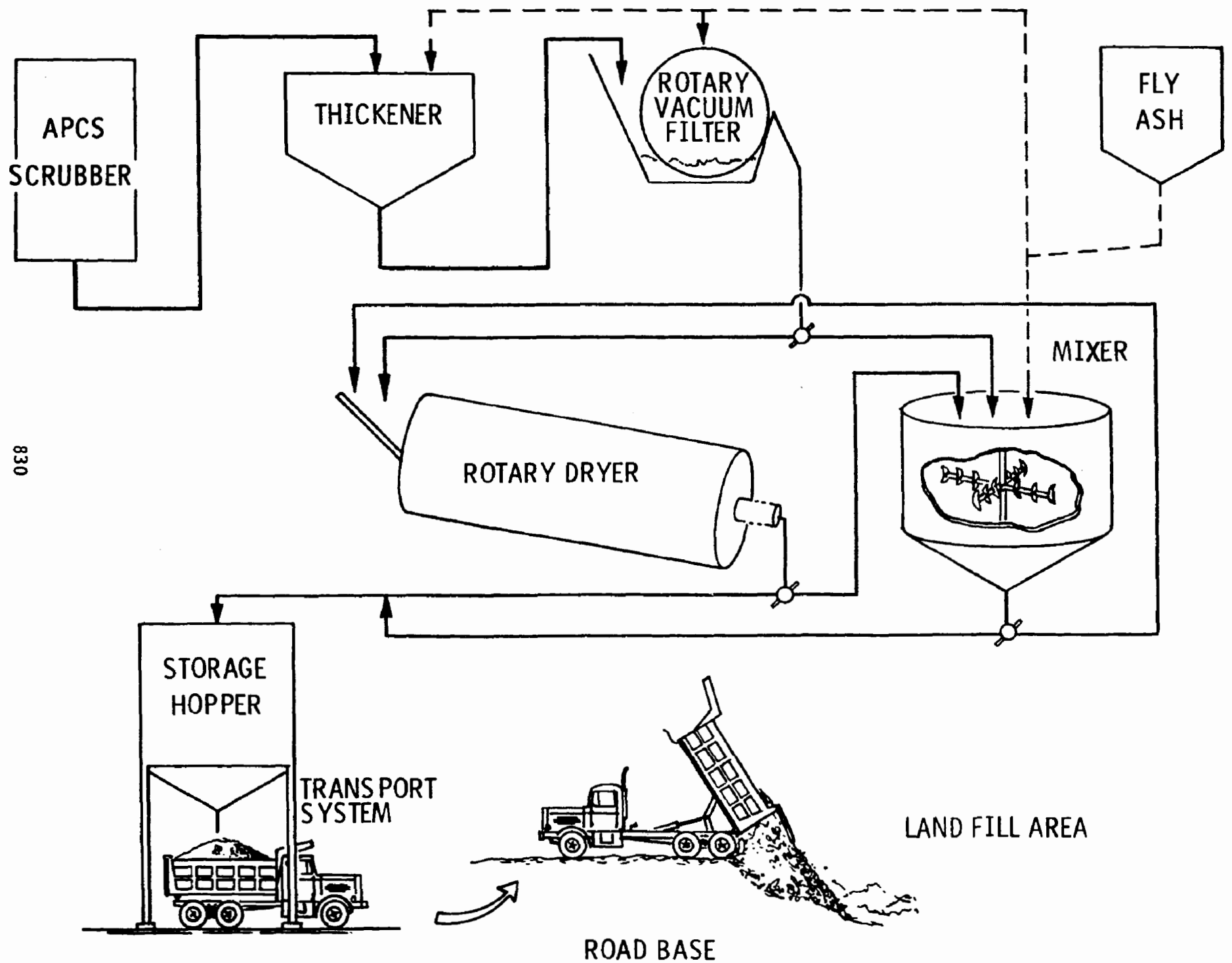


Fig. 6: Scheme for producing suitable land fill

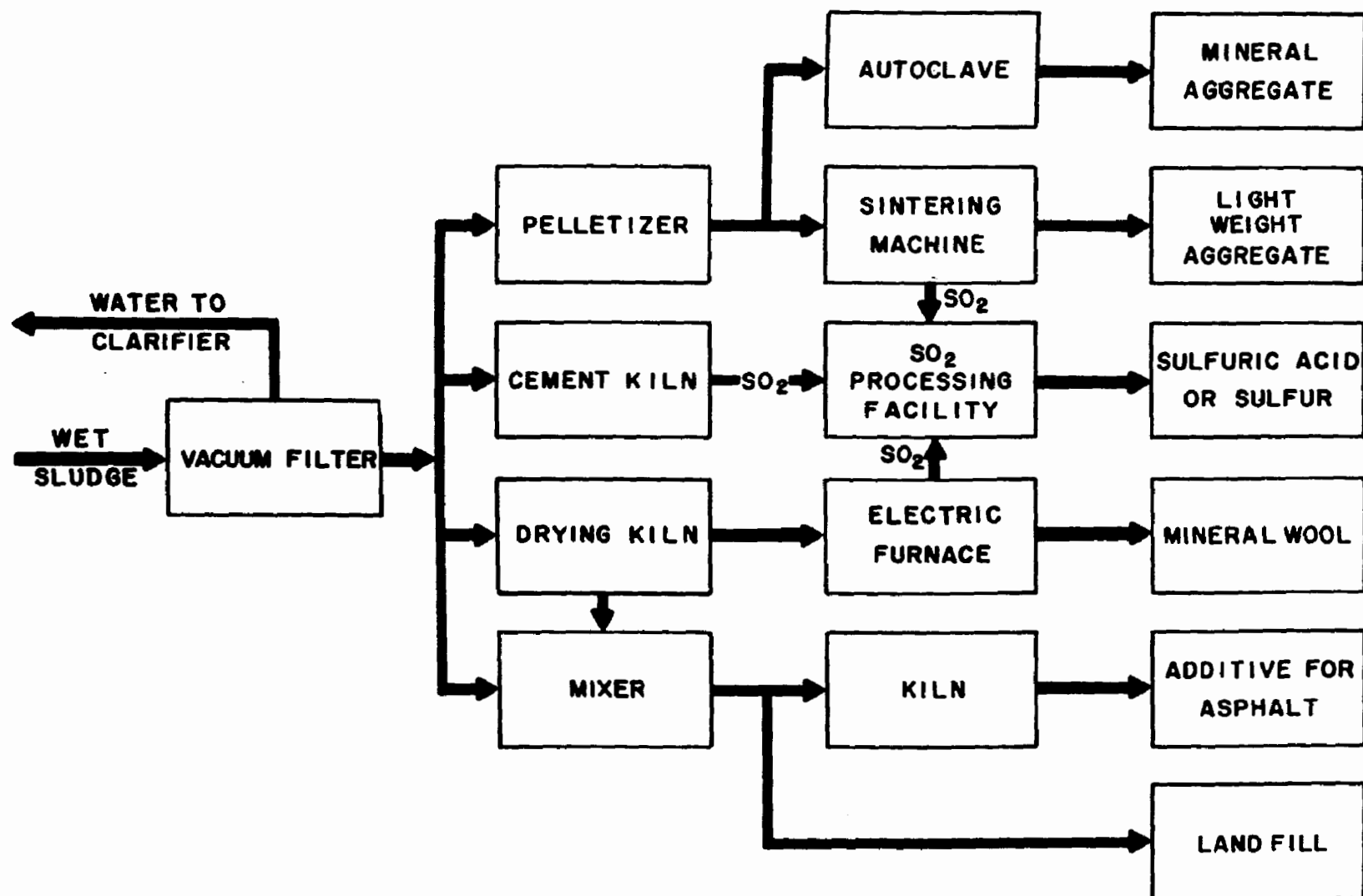


Fig. 7: Sludge disposal schemes for a single scrubber system

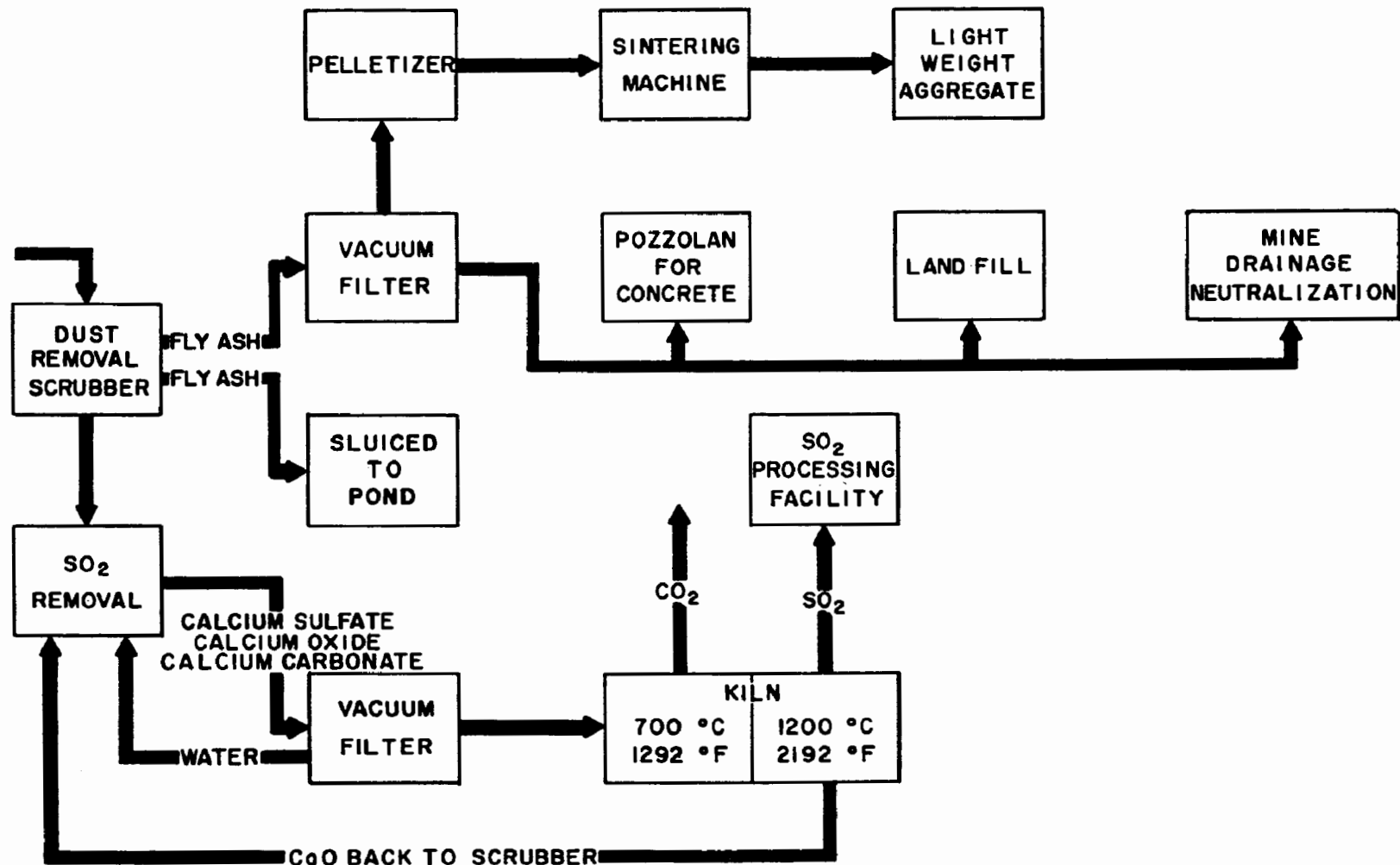
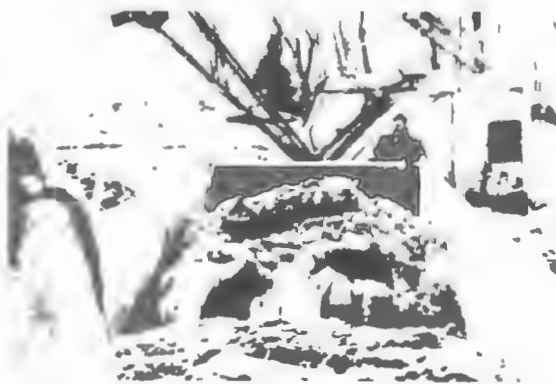


Fig. 8: Sludge disposal schemes for a dual scrubber system



(a)



(b)



(d)



(c)



(e)

FIXATION AND DISPOSAL OF FLUE GAS
WASTE PRODUCTS:
TECHNICAL AND ECONOMIC ASSESSMENT

by

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FIXATION AND DISPOSAL OF FLUE GAS
WASTE PRODUCTS -
TECHNICAL AND ECONOMIC ASSESSMENT

L. John Minnick^{1/}

The three primary by-products produced in the burning of coal in modern power plants consist of fly ash, bottom ash, and sulfur oxides. Over the years considerable technology has emerged with respect to the disposal and utilization of fly ash and bottom ash, and a number of commercially viable processes are available. Unfortunately, however, the large tonnages require that the major portion of these ash constituents must be sent to dumps, which presents a disposal problem to the power industry. As the industry complies with the regulations relating to control of sulfur oxide emissions, a similar situation will exist if an attempt is made to reclaim large tonnages of sulfur. Opportunities for utilization will, of course, be available: some sulfuric acid can be produced and sold, and some elemental sulfur or liquid SO₂ may find a market, but the majority of the sulfur will unquestionably be faced with a lack of marketing opportunities and therefore may have to be discharged as waste to disposal sites.

The lime and limestone scrubbing processes which are

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receiving considerable attention at the present time result in a by-product slurry or sludge and because of the lack of any commercial market for this material, it is necessary to transport this waste to disposal sites. Therefore these scrubber operations are currently referred to as "throwaway" systems.

The prime purpose of this paper is to outline the opportunities that are available to convert power plant waste materials through suitable processing steps to stabilized structural fill material or, if desired, to usable manufactured by-products. This concept converts the "throwaway" waste into products that can be placed or used and recycled in an ecologically acceptable manner.

The main concept of the system is based on modifications of existing technology dealing with the stabilization or beneficiation of fly ash. To some degree fly ash is being used in the construction industry as an additive to portland cement, lime, and asphaltic compositions. Millions of tons have also been used throughout the world in the construction of structural embankments, reservoirs, dams, road base materials and the like. Large scale utilization programs have been carried out by governmental agencies in England, France, and by a number of organizations in the United States; for example, National Ash Association, University of West Virginia, and

by private companies such as Chicago Fly Ash Company and G. & W. H. Corson, Inc.

Several years ago the Corson company discovered that the addition of sulfur oxide salts beneficially improved the structural properties of stabilized fly ash. While the original work was done with waste sulfate sludges from the chemical and coal industry (from the neutralization of acid mine drainage), it was also determined that the underflow sludges from lime and limestone desulfurization scrubbers worked equally well. The net effect of this activity has been to provide the coal burning plants with a practical and economical tail end conversion process which includes the sulfur oxide sludges as an important and integral part of stabilized structural materials.

DESCRIPTION OF THE CONVERSION SYSTEM

Basically the tail end process is a modification of Poz-O-Pac®, which has been used for many years in structural applications such as road bases, reservoirs, dams, and embankments. The basic chemistry involved in Poz-O-Pac® is a combination of (1) the pozzolanic reaction that occurs between the silica content of the fly ash and hydrated lime, which is added in small amounts (2 to 3% by weight), to form cementitious hydrated calcium silicate compounds; (2) the more rapid reactions that occur between the soluble salts present in fly ash with lime and the alumina that is found in the fly ash

glass; and (3) the mechanical support derived from the addition of various aggregate materials which serve as bulk fillers in the fly ash-lime matrix. Of considerable importance in the design of Poz-O-Pac® is the water content of the mixture. In fact, whenever fly ash is used as a structural composition, it is essential that optimum moisture contents be utilized and, in addition, it is important to specify adequate compaction when the material is placed.

In contrast to Poz-O-Pac®, the stabilization of fly ash using sulfur oxide sludge - commercially referred to as the Poz-O-Tec* process - is based on additions of large quantities of calcium and/or magnesium sulfite, calcium sulfate, and, in certain instances, magnesium oxide which results when dolomitic lime is used in the treatment of the sulfur oxide acids or waste gases. The presence of the sulfites and sulfates are beneficial to the cementitious reactions and, in addition, allow the reactions to proceed at a much more rapid rate. The engineering properties of the end products are improved to the point where it is possible to place the stabilized fill compositions without the addition of aggregate. This does not mean that aggregate cannot be used; in fact, Poz-O-Tec* mixtures have been produced with various types of aggregate including bottom ash from coal burning power plants, by-product slags,

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culm, or mine refuse materials, as well as conventional construction aggregates. Work has also been carried out with these mixtures to encapsulate potentially toxic materials such as crushed storage battery cases.

Much of the chemistry involved in the Poz-O-Tec* process can be compared with reactions which have been described many times in the literature by investigators dealing with portland cement. Calcium sulfate reacts preferentially with calcium aluminates to form hydrated calcium sulfoaluminates. Hydrated calcium sulfoferrites, analogues of the sulfoaluminates, perform equally well in the cementing process. The Poz-O-Tec* process involves a special and inventive application of these established chemical concepts used by the portland cement industry, although the conditions under which these reactions proceed and the ultimate performance criteria are different.

Of considerable interest to the utilities is the effect of sulfite ions in the mixtures since calcium sulfite is produced in large quantities in the scrubber slurries. The presence of sulfite provides several advantages in the conversion process, an important example being the acceleration of the cementitious reactions. Figure 1 shows scanning electron micrographs which illustrate visually the characteristic of a fly ash sulfur oxide sludge mixture as freshly prepared and a similar composition after processing and aging for a period

of 6 months. The original platelets that are made up primarily of calcium sulfite (or sulfate) are substantially depleted after curing. The crystalline material which is formed assists in the hardening or cementation process. Figure 2 shows X-ray diffraction profiles and demonstrates the rapid rate with which available lime is used up in these compositions during the aging process.

Figure 3 shows a series of patterns developed using an electron probe scan of a fly ash-calcium sulfite-lime mixture which has been cured at room temperature for 10 days. The presence of aluminum in the scan indicates early formation of calcium sulfoaluminate crystals which are developing within the calcium sulfite platelets.

Figure 4 is a transmission electron micrograph showing the hydrated calcium silicate structures (tobermorite-like material) that results in both Poz-O-Pac® and Poz-O-Tec* compositions. This cementitious product contributes substantially to the ultimate strength and durability of the structure.

Figure 5 is a flow diagram of the tail end conversion process. In the processing of the fly ash and sulfur oxide sludge, it is usually necessary to modify the water content of the discharge from the power plant which in some cases can be a fairly major operation. As indicated in the sche-

matic drawing, the fly ash may be added into the primary dewatering vessel as a wet slurry or, if the fly ash is discharged from an electrostatic precipitator, it can be added in a dry or damp state, thereby assisting in the dewatering process. Depending on the type of scrubber that is used, and the particular discharge system which is adopted, dewatering may or may not require a secondary state (usually a vacuum filtering step). Dewatering devices of this type have been used conventionally in many large scale applications related to the coal and steel industries.

The mixing and conditioning step is basically a modification of a conventional Poz-O-Pac® plant. Figure 6 shows one of these plants of recent design. This plant has a production capacity of 600 tons per hour. After applying minor changes to a plant of this type, the fly ash and sulfur oxide sludge can be supplied to the mixer and adjusted in composition with make-up additives which may include additional lime, limestone, fly ash, bottom ash, other sulfur oxide salts, and, if desired, aggregate or other waste products.

As indicated in the flow sheet, Sulf-O-Poz®, suitable for placement as a stabilized fill material, is discharged from the mixing and conditioning device.

Although Sulf-O-Poz® is primarily a disposal material, it has certain minimal structural qualities which would allow its

application in some cases as structural embankments, land reclamation projects, liners for reservoirs, etc.

As also shown in the flow sheet, Sulf-O-Poz® can be further processed to produce other compositions such as synthetic aggregate which are suitable for use in producing structural shapes, portland cement or asphaltic concrete, or may be supplied directly for use as a high strength monolithic road base composition equivalent to stabilized road base required in "primary" highways, airport runways, trucking terminals, and the like. This supplementary processing is of interest since it offers opportunity to convert the power plant waste material from a "throwaway" to a "layaway" disposal system. In this connection aggregate can be stockpiled and made available for commercial projects as they develop in the future. It has been well publicized that shortages of aggregates are already of serious concern in many areas of the country. Poz-O-Tec* aggregate is therefore one approach to solving this critical problem.

PROPERTIES OF THE CONVERSION PRODUCTS

The two areas in establishing criteria for products produced in the conversion process consist of, first, the ecological, and, secondly, the engineering properties of the materials. Both of these properties relate to the mix design and are involved with the ratios of fly ash to sulfur oxide sludge, concentrations of lime and water, and also to the

basic chemical properties of the fly ash and lime. For example, fly ash made from lignite coal which contains high CaO works quite differently than fly ash produced from bituminous coal. Underflows from limestone scrubbers present substantially different design requirements than underflows from hydrated lime systems.

Ecological Properties

The evaluation of the various compositions as related to effect on the environment is dependent primarily on measurements of permeability and leachability, whether the compositions are simply placed as a stabilized fill or used as a construction material. Where massive quantities of Sulf-O-Poz® are placed as a stabilized fill, land improvement, or road base construction project, the specific ecological concern is with permeability measurements and possibly with surface runoff.

Table 1 includes some results of permeability tests made on compositions associated with the recent Transpo 72 project at Dulles International Airport using standard falling head permeability procedures. Figure 7 is a graph that shows the reduction in permeability in sulfur oxide containing mixtures when compared with those that have been previously made with standard Poz-O-Pac® compositions. Permeability values of freshly prepared compositions usually run in the range of 10^{-5} cm/sec, which quickly changes during the hardening process to values

ranging from 10^{-6} to 10^{-7} cm/sec. Obviously a road base or embankment with this low permeability provides excellent protection against leaching of deleterious materials through the mass.

From the standpoint of making leaching measurements, while no "standard" tests are available, it is recognized that all materials can be subjected to special laboratory procedures that will exhibit the presence of small quantities of soluble salts. Accelerated tests run on specimens weighing 500 grams which were placed in plastic containers covered with two liters of distilled water then shaken continuously for 48 hours are given in Table 2. The table includes limits for potable water as described in U. S. Health Service, HEW Bulletin No. 956 on Drinking Water Standards. Figure 8 is a photograph of the equipment used in the shaking test. For the sake of comparison, materials other than stabilized fly ash compositions are included in this table. It will be noted that raw, loose materials are subject to substantially higher quantities of leachate in a test of this type. This observation is a further indication of the beneficial effect of forming a monolythic structural Sulf-O-Poz® mass.

The question of leaching of heavy metals from surface runoff is one that has been studied extensively by the United States Potters Association and the International Lead Zinc Research

Organization, Inc. The object of these studies was to evaluate the effect of temperature, time, and pH on the amount of heavy metal that could be leached from ceramic surfaces. Recent studies at Rutgers University School of Ceramics using a scanning electron probe has shown the pattern of lead concentration across the surface of the ceramic ware. Figure 9 is an example of this type of investigation. Careful examination of the lead profile shows that leaching has occurred to a depth of approximately 1/2 micron. Techniques of this type may be of interest for stabilized fly ash materials since this affords a good method of determining the total impact of consolidated masses on the environment. It is evident from laboratory leaching tests of the type described that stabilized structures can provide virtually non-significant quantities of leachable ions to the environment.

Runoff tests have also been carried out by preparing slabs of the fly ash-sulfur oxide compositions. Two liters of distilled water were poured over the surface of the specimens to provide a runoff that could be tested by atomic absorption techniques. Table 3 shows some of the results of these tests. Figure 10 illustrates the technique that has been used.

It is beyond the scope of this paper to make detailed recommendations as to the most appropriate method of test for these stabilized compositions or to suggest absolute limits

that might be acceptable from an environmental standpoint. However, the values that have been obtained fall well within limits that have been established by a number of governmental organizations which have addressed themselves to this type of situation.

The Poz-O-Tec* compositions that have been studied not only meet rigorous environmental requirements, but due to the high pH of these compositions they, in fact, can serve to "protect" the environment from attack. It has been noted, for example, that when spoil bank materials which contain pyrites are encapsulated within Poz-O-Tec* mixtures that leaching of sulfuric acid is avoided and the attack on vegetation in the spoil bank area is therefore eliminated. This type of chemical encapsulation is a phenomenon analogous to studies that have been made in portland cement compositions. The technical literature provides numerous references which describe the method by which soluble components migrate into the lattice complexes of a cement structure becoming chemically bound, thus preventing the leaching of soluble ions. A well known example of this is the lime-alkali-silica complex resulting from the solid state diffusion of soluble NaOH or KOH into the lime hydrous silica complex. When in this form, the Na^+ and K^+ ions are chemically entrapped thus preventing potentially harmful leaching.

Engineering Properties

The most important engineering factor which must be evaluated is the strength of the reacted mixtures. A correlation exists between the formation of cementitious compounds of the types described above and the development of strength and other engineering properties in fly ash-sulfur oxide mixtures.

Figure 11 shows the effect of aging on the strength of a Sulf-O-Poz® composition. The method of measuring penetration resistance is based on a modified vicat procedure, the penetration needle having a cross section area of one-fortieth of a square inch. The measured penetration resistance represents the pressure that must be applied in pounds per square inch to cause a penetration of one inch.

Figure 12 provides information on a similar composition when cast into 2 x 2 x 2" cubes and tested for unconfined compressive strength and Figure 13 presents California Bearing Ratio values. Based on results of this type, it is possible to design compositions with strength properties commensurate with intended applications.

Table 1 presents compressive strength tests that were made for design purposes at Transpo 72. Table 4 shows results that were obtained from a field project and is based on cores that were removed after periods of 4 and 6 weeks.

The major criteria which relate to the ultimate strength

of these mixtures are composition, moisture content, and compacted density. Where a Sulf-O-Poz® fill or a land rehabilitation project is contemplated, strengths may not be required to exceed those that are conventionally developed in embankments, earthwork dams, and the like. However, where the product is to be used under heavy loads such as for foundations of bridges or for road base, strengths must not only be higher but should be required to reach specified values at earlier ages. The moisture contents which can be used may range from 20% to 50%, depending on the end use which is contemplated and on other factors. In certain applications additives may be used to accelerate the early strength.

In addition to strength, a second factor that is of considerable importance from an engineering standpoint is structural integrity. Procedures that have been used to evaluate this characteristic are usually of two types; first, laboratory measurements of dimensional stability, and, secondly, field performance. Data from a few of the mixtures that have been evaluated in the laboratory are given in Figure 14. These measurements were made on moist cured bars (1 x 1 x 10") cured at 73°F. In each case slight expansion is developed at early ages, although the degree of expansion reaches a constant value after several weeks and does not change significantly from that point on. It is believed that this type of expansion

is beneficial particularly where the material is used in mass applications since it helps to control shrinkage cracks (a concept that is used when expansive portland cements are used in mass structures).

The structural integrity of the sulfur oxide-fly ash mixtures as observed in field applications to date has indicated that these mixtures perform quite well. By making comparisons with early Poz-O-Pac® evaluation programs, it is indicated that mass structures such as have been placed in reservoirs and dams can perform for many years with little detectable deterioration. Poz-O-Tec* mixtures which have been used for road base work have proven to be superior to the Poz-O-Pac® compositions, although like Poz-O-Pac® they should be covered with an adequate wearing course, as the stabilized mixtures per se are not capable of withstanding the action of excessive traffic.

ECONOMIC CONSIDERATIONS

The costs of converting the by-product wastes of a power plant depend on whether or not the end product is produced in a marketable form. The least conversion costs result when Sulf-O-Poz® is produced since this product may simply be disposed of as stabilized fill which is designed to meet full ecological, but only minimum structural and engineering criteria. In many cases, depending on factors to be elaborated below, Sulf-O-Poz® can be economically competitive with ponding and

ecologically unsound disposal methods.

In certain markets, it may be economical to produce and sell or stockpile for future sale a usable end product such as Poz-O-Tec* road base or aggregate. Revenues from the sale of these products might appropriately be credited to the additional costs of converting the waste by-products to stabilized structural materials.

Since both the nonmarketable and the marketable approaches result in an ecologically sound material, the decision as to which approach to take is primarily an economic one.

A second area of importance in developing cost estimates is related to the nature of the installation, thus if the conversion process is added on to an existing plant, the capital costs and operating costs may be quite different than would be realized in the case of a completely new installation. In an operating plant, fly ash may already be recovered in electrostatic precipitators and this would obviously affect the capital cost of the tail end system.

The major factors which influence the cost of the conversion may be summarized as follows:

- Annual tonnages to be handled by the conversion process.
- New boiler installation versus existing facilities.
- The type of equipment selected for fly ash removal
-- for example, electrostatic precipitators versus wet scrubbers.

- The chemical analysis of coal -- sulfur, CaO, and ash contents.
- Location of plant -- on site versus off site.
- Transportation costs -- to and from conversion plant.
- Redundancy factor -- duplication of equipment versus emergency holding basins, etc.
- Type of scrubber -- limestone versus lime.
- Acquisition and cost of land.
- Type of end product selected.

In view of the fact that each of these items considered alone or grouped together can cause major variations in both the capital and operating costs, it should be recognized that specific estimates cannot be given unless each situation is reviewed on an individual basis. On the other hand, IU Conversion Systems, Inc. has had an opportunity to make numerous cost evaluations based on the programs which are currently underway, and it is at least possible at this time to suggest a few examples which may be helpful to the utilities in evaluating the conversion system approach in individual cases.

In several installations in which lime scrubbers have been specified for new plants in the general size range of 1000 to 2000 megawatts, the cost of conversion to Sulf-O-Poz® fill material will range between about \$1.50 per ton to \$2.50 per ton, the variation depending in large measure on items such as listed previously. Converting this to a basis

of cost per million Btu for coal of approximately 3 to 4% sulfur and 10 to 15% ash represents a range of about 2 to 3-1/3 cents per million Btu. Adding the necessary equipment and operating staff to convert from a simple Sulf-O-Poz® stabilized fill process to one in which commercial products are fabricated would increase these costs by approximately 20 to 50% before allowing for any offsetting credits from the sale of commercial products.

IU Conversion Systems, Inc. can provide the power plant with the necessary hardware on a turnkey basis and will undertake to operate the conversion plant on the basis of a long-term contract. In general, the power industry prefers to contract with an outside organization to take care of the disposal of its waste materials since it is not normally geared up to operate this type of plant. What the industry requires then is a reliable process which will give them the assurances of low-cost disposal with adequate warranties and guarantees. It is also essential that the conversion system shall not interfere with the operation of the power plant.

At the present time the cost estimates given above appear to be quite attractive since they are, in fact, competitive in many instances to what the power plant pays simply to hire a trucking organization to haul the waste material to a dump or lagoon. In view of the concern of the environmentalists

and the difficulty in obtaining permits for disposal of the waste material, it is clearly indicated that a system which converts the waste to ecologically safe compositions is to the advantage of a power plant operation.

SUMMARY

The extension of existing technology dealing with the stabilization of fly ash into the area where waste sulfur oxide sludges can be utilized provides a practical solution to the question of fixation and disposal of flue gas waste products. The real effectiveness of the fixation process depends on the concept of converting the waste materials into compositions that comply with ecological and engineering criteria that allow for the disposal or utilization of the product in a manner which is beneficial or at least not deleterious to the environment.

The performance of the stabilized mixtures as demonstrated in laboratory tests and field evaluation programs has been quite favorable. The ratios of ash to sulfur oxide sludges that are produced in the average coal-burning operation fall within the ranges that can be utilized for the manufacture of the various compositions.

The conversion system is adaptable to power plants as a retrofit application or to new installations. Since the process depends on the availability of fly ash, it is not appli-

cable to oil fired operations unless such operations are carried out in the vicinity of stockpiled waste fly ash.

Cost evaluations which have been made to date indicate that for full sized plants the conversion system is usually competitive with costs that would be incurred simply by transporting the waste material to dumps or lined lagoons. In specific cases commercial opportunities may be available which would allow the utilization and sale of products produced in the process.

Based on the findings to date, it is indicated that a realistic solution to the disposal of sulfur oxide sludges from lime and limestone scrubbers can be attained.

TABLE 1

**RESULTS OF TESTS OF SELECTED STABILIZED ROAD BASE MIXTURES
PREPARED AT DULLES AIRPORT TRANSP0 72 PROJECT**

Moisture Content (%)	Dry Density (pcf)	Falling Head Permeabilities (cm/sec)	Compressive Strength at 100°F (psi)		
		7 Days	2 Days	14 Days	28 Days
19.5	98.8	2.4×10^{-6}	301	732	881
19.4	98.1	N.D.*	267	586	622
20.0	98.3	2.9×10^{-6}	369	630	889
19.8	98.2	6.5×10^{-6}	196	458	490
19.7	100.6	5.7×10^{-6}	333	772	861
20.0	98.8	1.0×10^{-6}	290	761	789
19.1	100.4	N.D.	200	868	1091

*N.D. - Not Determined

TABLE 2

ATOMIC ABSORPTION TESTS FOR LEACHABLE IONS ON SELECTED
SPECIMENS SUBJECTED TO 48 HOUR SHAKING TEST

	pH*	Total Dissolved Solids	Sulfate	Cl	Al	Total Iron	Mn	Cu	Zn	Cd	Cr ⁺³	As	Hg	Pb	Sn
FEDERAL SPECIFICATIONS-MAX.	10.6	500	250	250	None	.3	.05	1.0	5.0	.01	.05	.01	.001	.05	None
<u>Individual Solid Specimen</u>															
Dulles Cylinder (13 Days)	9.5	840	100	8	.38	.08	.18	.08	.02	<.01	.02	.02	<.001	.08	.10
Dulles Cylinder (22 Days)	9.5	620	120	12	.37	.08	.16	.08	<.01	<.01	<.01	.02	<.001	.09	.10
Poz-O-Tec* Test Road Core	6.7	90	16	14	.03	.06	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Poz-O-Tec* Test Road Cylinder	9.2	250	136	16	.05	.10	.10	.08	<.01	<.01	<.01	.01	<.001	.01	<.01
Poz-O-Pac® Cylinder	9.3	150	44	26	.10	.25	<.05	.08	<.01	<.01	<.01	.01	<.001	.02	<.01
Fly Ash Concrete	10.7	440	170	46	.22	.01	<.05	.04	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Cinder Block	8.2	410	60	6	.01	.04	<.05	<.01	<.01	<.01	<.01	<.01	<.001	.02	<.01
Clay Brick	7.3	110	28	12	.03	.10	<.05	.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Asphalt Roofing Shingle	7.1	150	46	22	.01	.12	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
<u>Aggregate</u>															
Argillite	6.9	120	28	22	.07	.06	<.05	.08	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Dolomitic Limestone	9.75	96	8	18	.02	.36	<.05	<.01	.02	<.01	<.01	<.01	<.001	.07	<.5
Calclitic Limestone	8.4	180	8	-	.02	1.8	<.05	<.01	.04	<.01	<.01	<.01	<.001	.03	<.5
Steel Slag Aggregate	10.8	840	16	28	.05	.15	<.05	<.01	.02	.01	<.01	<.01	<.001	.01	<.05
Pumice	7.1	120	< 1	10	.06	2.2	<.05	<.01	.03	<.01	<.01	<.01	<.001	.06	<.05
Fly Ash-Sludge Aggregate	11.7	700	< 1	16	.03	.26	<.05	<.01	.02	<.01	<.01	<.01	<.001	.06	.5
Cement Mortar Balls	9.0	530	27	8	.04	.17	<.05	<.01	.01	<.01	<.01	<.01	<.001	.03	<.01
Mine Tailings	3.95	130	6	2	.05	.15	<.05	.16	.02	<.01	<.01	<.01	<.001	.07	<.05
<u>Loose Powdered Materials</u>															
Fly Ash	9.8	2900	1500	8	.11	.26	<.05	<.01	.01	<.01	<.01	<.01	<.001	.06	<.5
Portland Cement	12.0	3700	200	20	.05	.44	<.05	<.01	<.01	<.01	<.01	<.01	<.001	.04	<.5
<u>Water Samples</u>															
Tap Water	7.5	180	36	76	.02	<.01	<.05	.08	.05	<.01	<.01	<.01	<.001	.04	<.01
Snow Sample from Pittsburgh	6.45	40	< 1	6	.06	.46	<.05	<.01	<.01	<.01	<.01	<.01	<.001	.02	<.01
Water Supply (Peggs Creek)	7.25	316	-	-	-	2.9	<.05	.05	.02	<.01	<.01	<.01	<.001	.02	<.01

*With the exception of pH, all values are reported in parts per million.

TABLE 3
ATOMIC ABSORPTION TESTS MADE ON SURFACE RUNOFF OF A
STABILIZED FLY ASH-SLUDGE MIXTURE

	pH*	Total Dissolved Solids	Sulfate	Cl	Al	Total Iron	Mn	Cu	Zn	Cd	Cr ⁺³	As	Hg	Pb	Sn
Dulles Cylinder (13 Days)	7.0	100	26	12	.10	.22	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Dulles Cylinder (23 Days)	6.9	96	32	18	.15	.06	<.05	<.01	<.01	<.01	<.01	<.01	<.001	<.01	<.01
Sulfite Beam	7.2	85	8	18	.13	.06	.60	.12	<.01	<.01	<.01	<.01	<.001	.03	<.01

*With the exception of pH, all values are reported in parts per million.

TABLE 4
RESULTS OF FIELD TESTS SHOWING COMPARISON
OF POZ-O-PAC® AND POZ-O-TEC* FORMULATIONS

Description	Dry Density (pcf)	Compressive Strength at 100°F (psi)		Strength of Cores from Road ¹ (psi)	
		2 Days	7 Days	4 Weeks	6 Weeks
Standard Fly Ash Mix	121.2	66	770	NCP ²	NCP
Fly Ash-Sludge Blend A	121.4	348	729	NCP	1034
Fly Ash-Sludge Blend B	120.8	318	746	756	1089

¹Average temperature during curing period was 50°F.

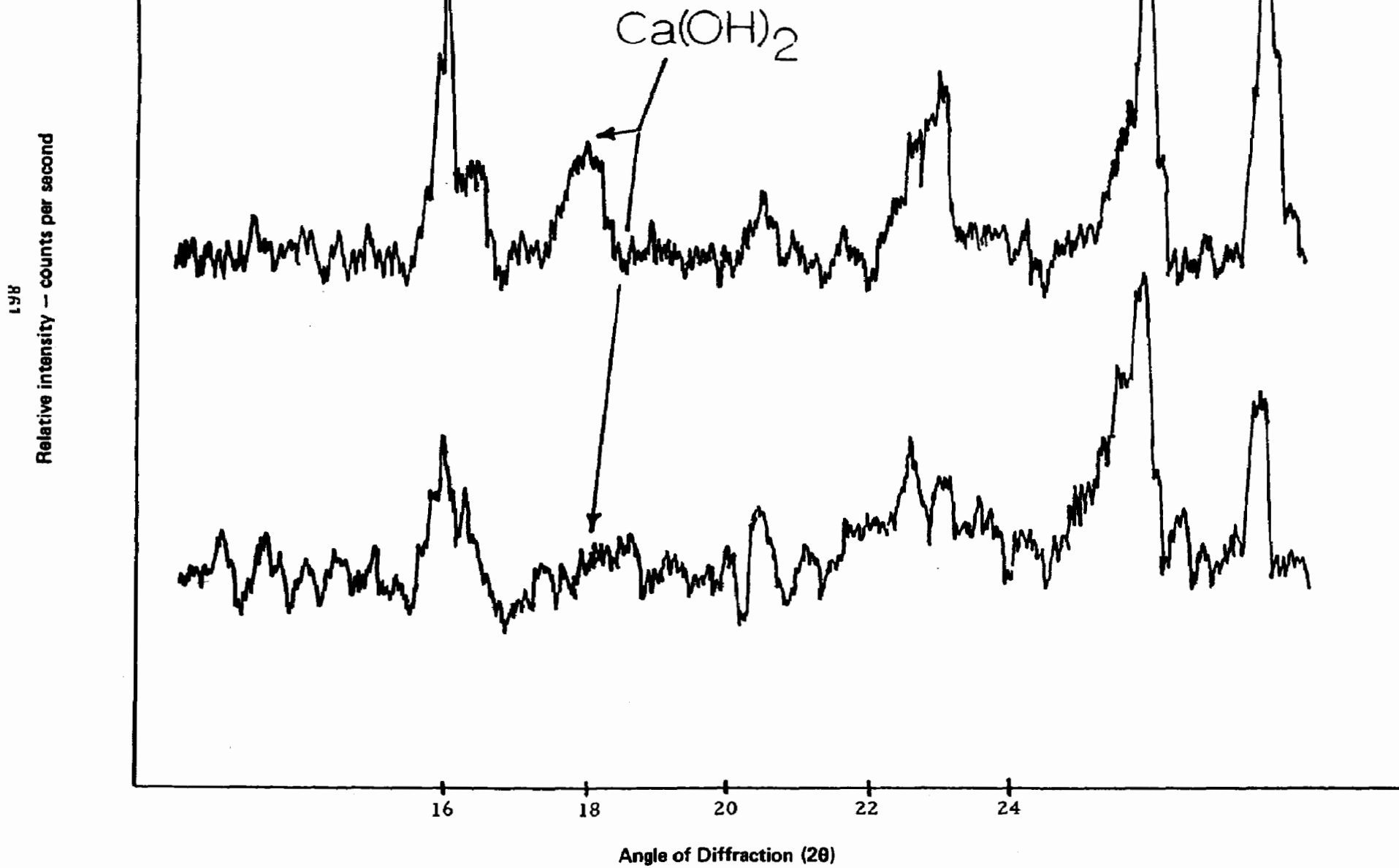
²NCP - No core possible due to insufficient strength.

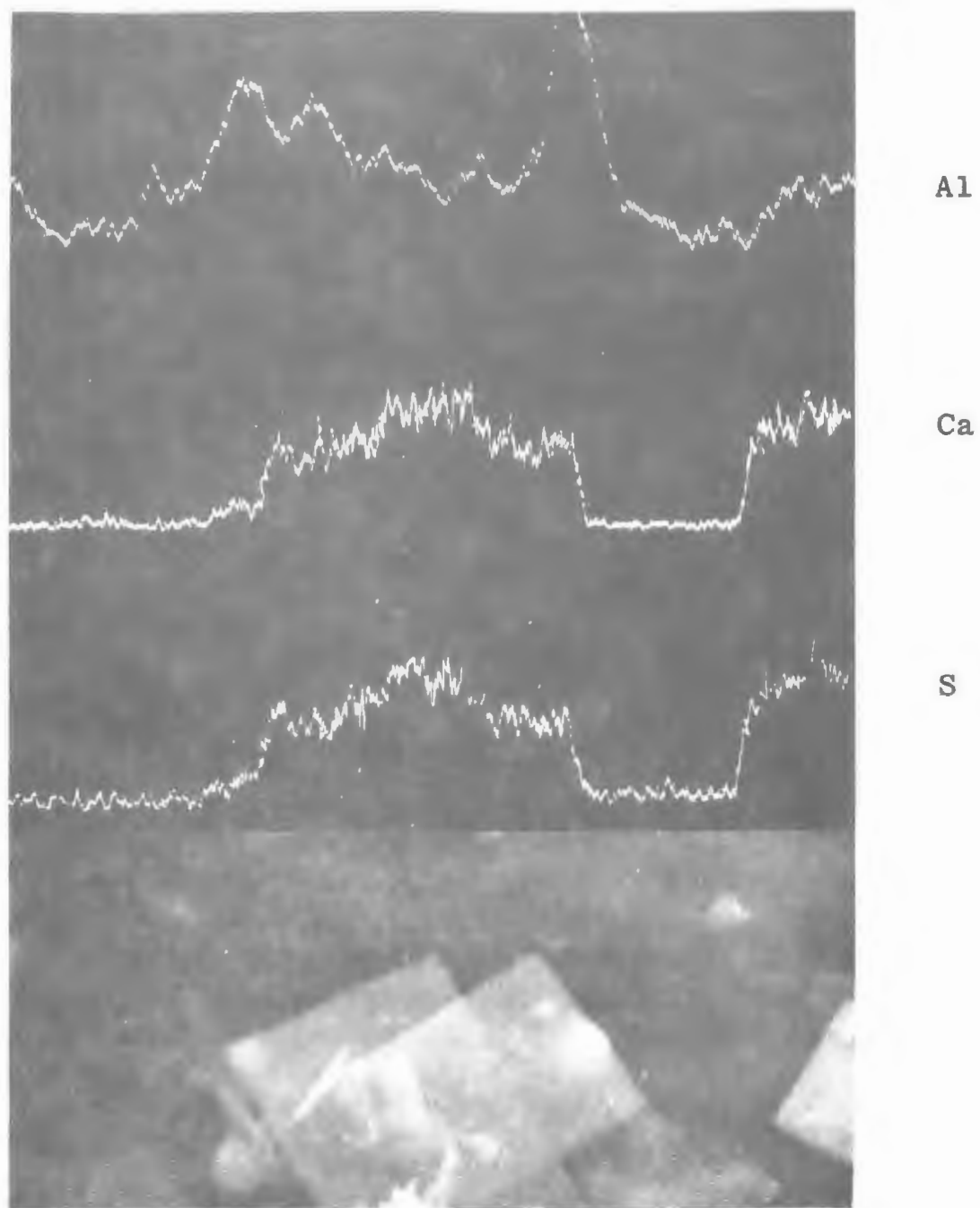


FIGURE 1 — Freshly prepared mixture of fly ash, sulfur oxide and sludge (Left View).

**Ettringite crystals formed after aging
(Right View).**

FIGURE 2 — Comparison of fly ash-calcium sulfite-lime mixture showing depletion of free Ca(OH)_2 after aging. Upper profile — unaged. Lower profile — aged 2 weeks.





2000X

FIGURE 3 — Electron probe patterns showing early reaction involving Al_2O_3 and calcium sulfite.



FIGURE 4 — Tobermorite crystals resulting from reaction between SiO_2 in fly ash with lime.

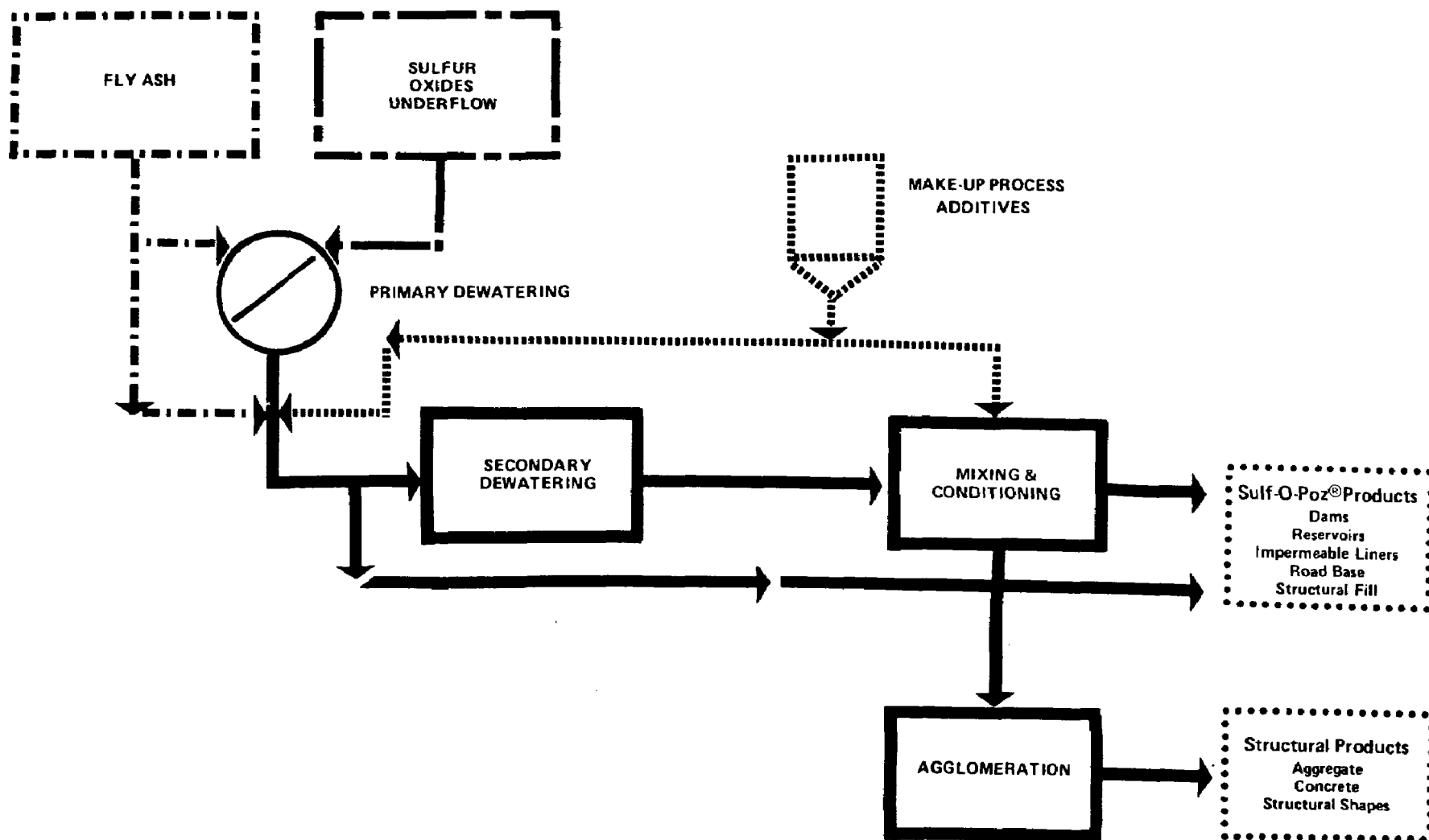


FIGURE 5 – Schematic diagram of Poz-O-Tec® process.



FIGURE 6 — Fly Ash stabilization (Poz-O-Pac®) plant.

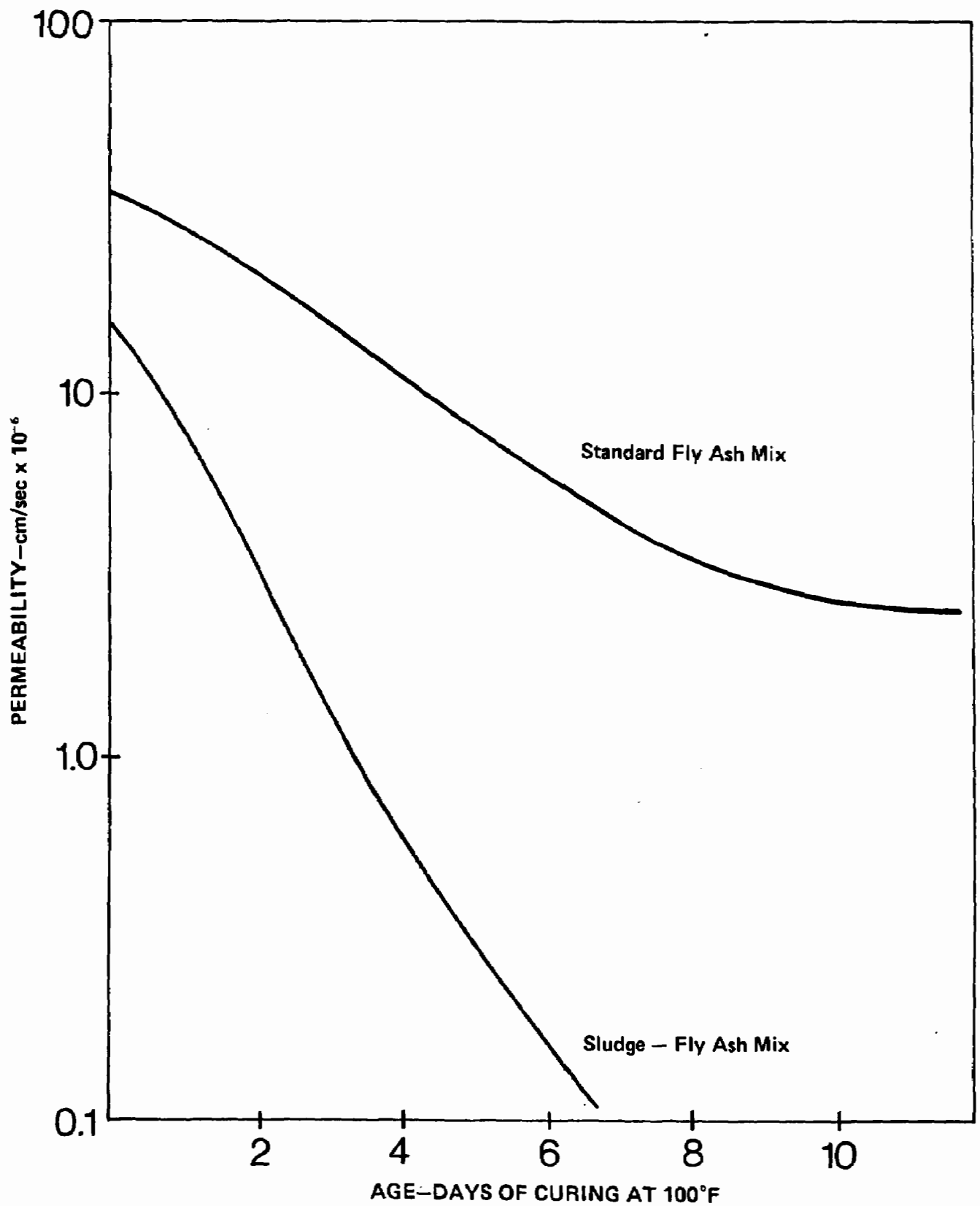


FIGURE 7 — Comparison of Poz-O-Pac® and Poz-O-Tec* permeability values.



FIGURE 8 — Shaking apparatus used for laboratory shaking test.

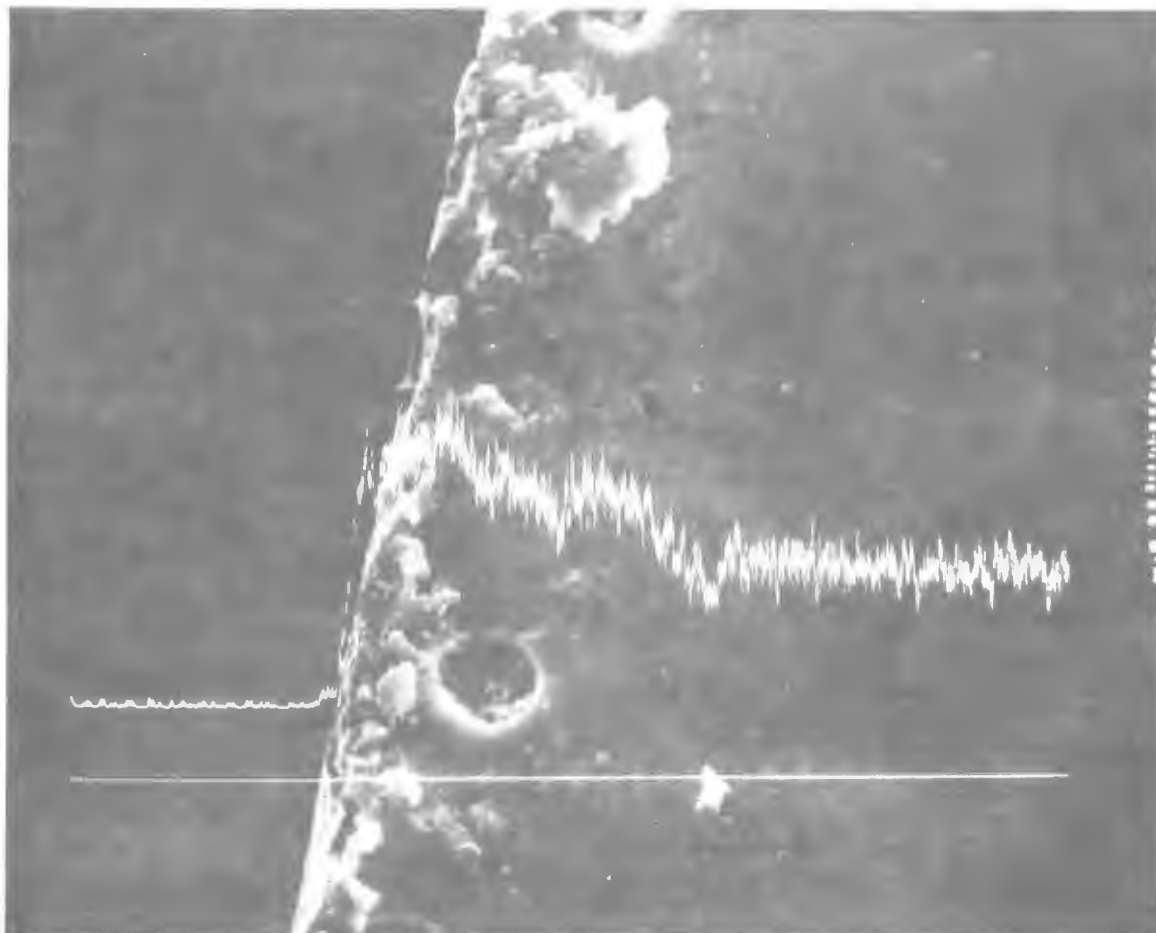


FIGURE 9 — Electron probe scan showing lead profile in ceramic ware subjected to long time outside exposure.



FIGURE 10 — Runoff test as conducted on sulfite stabilized fly ash specimens.

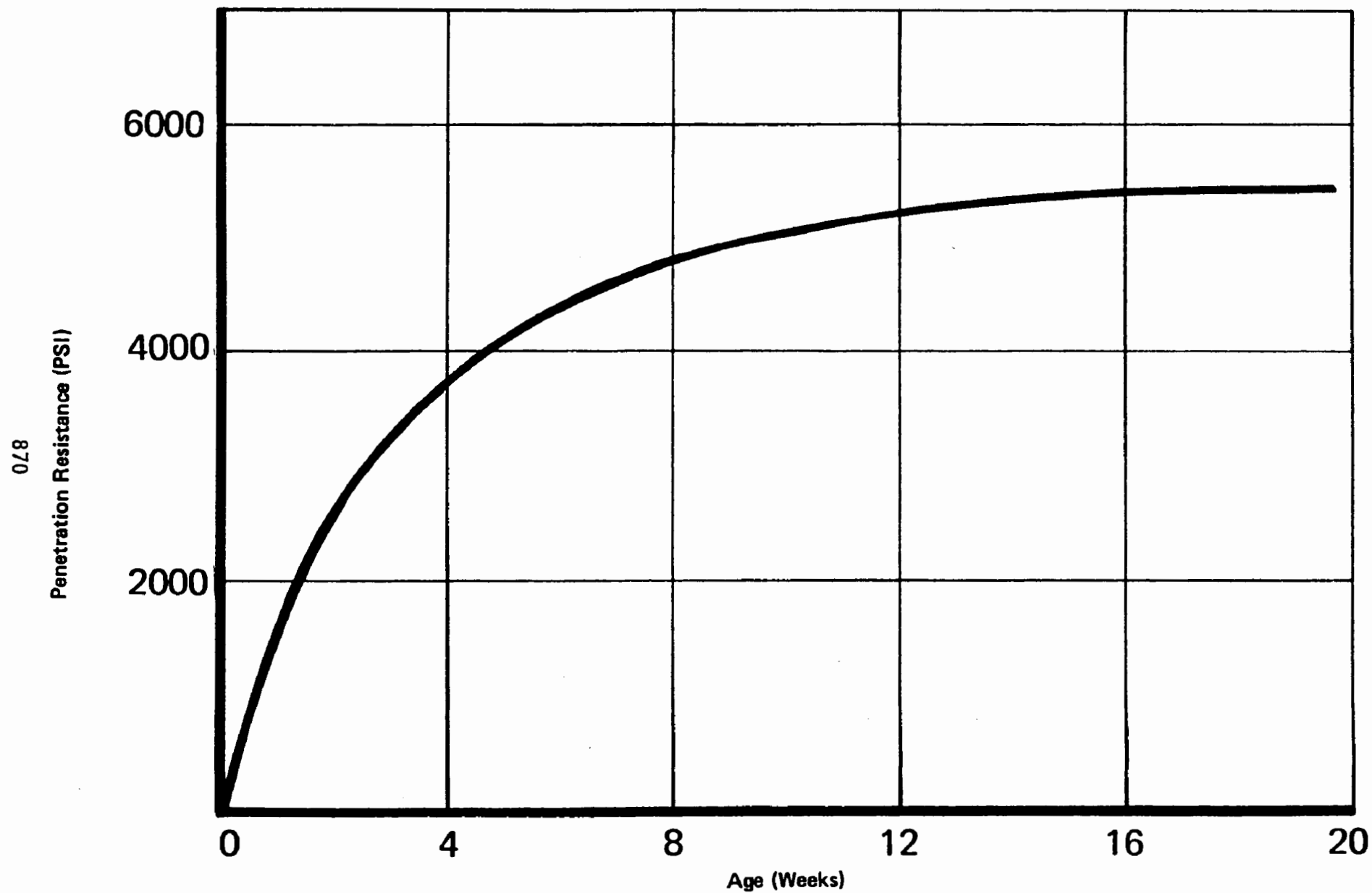


FIGURE 11 – Penetration resistance for a typical fly ash-calcium sulfate-lime mixture.

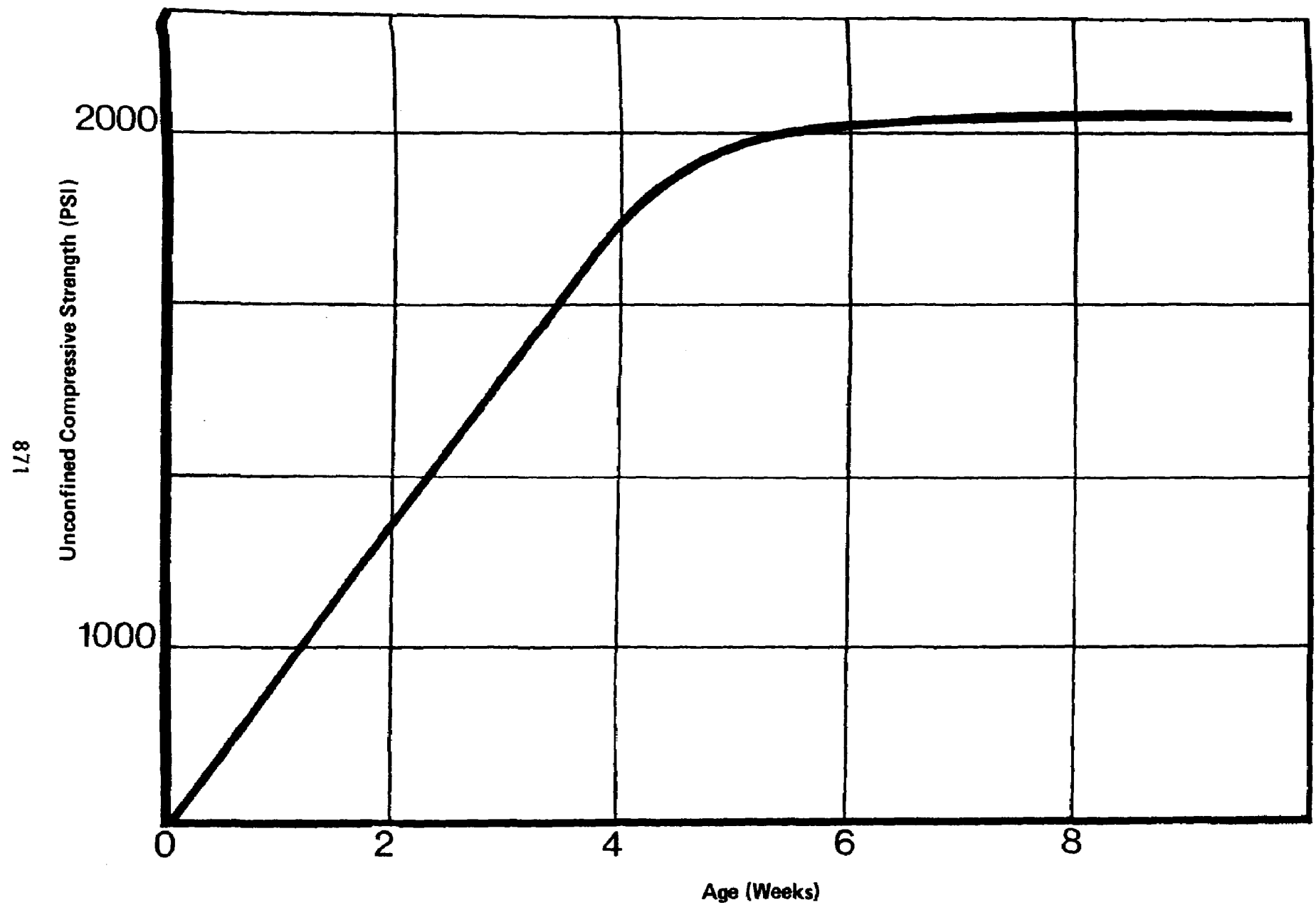


FIGURE 12 — Compressive strength for a composition similar to that given in Figure 11. Moisture content of composition is 35%.

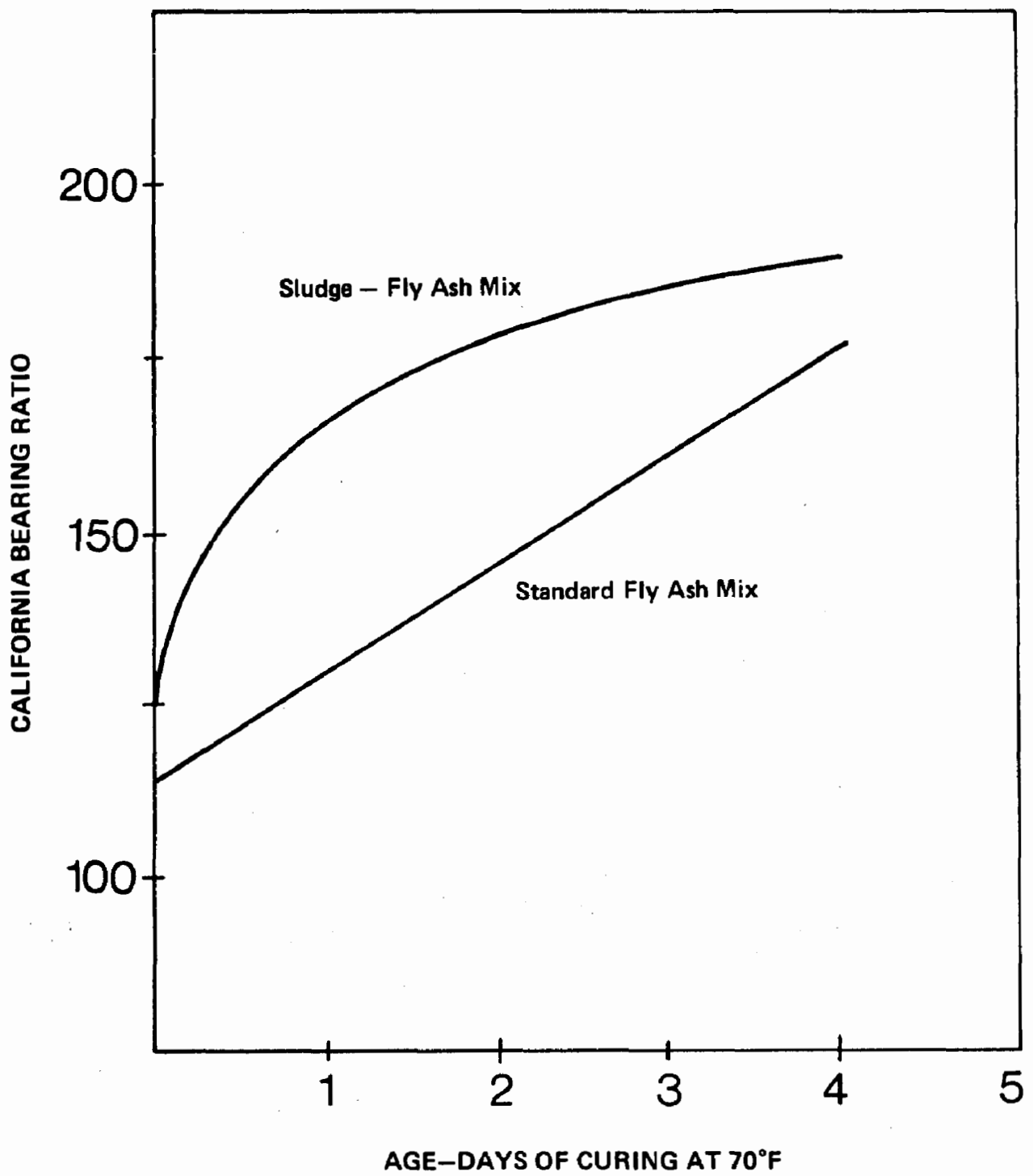


FIGURE 13 – California Bearing Ratio for Poz-O-Tec* road base.

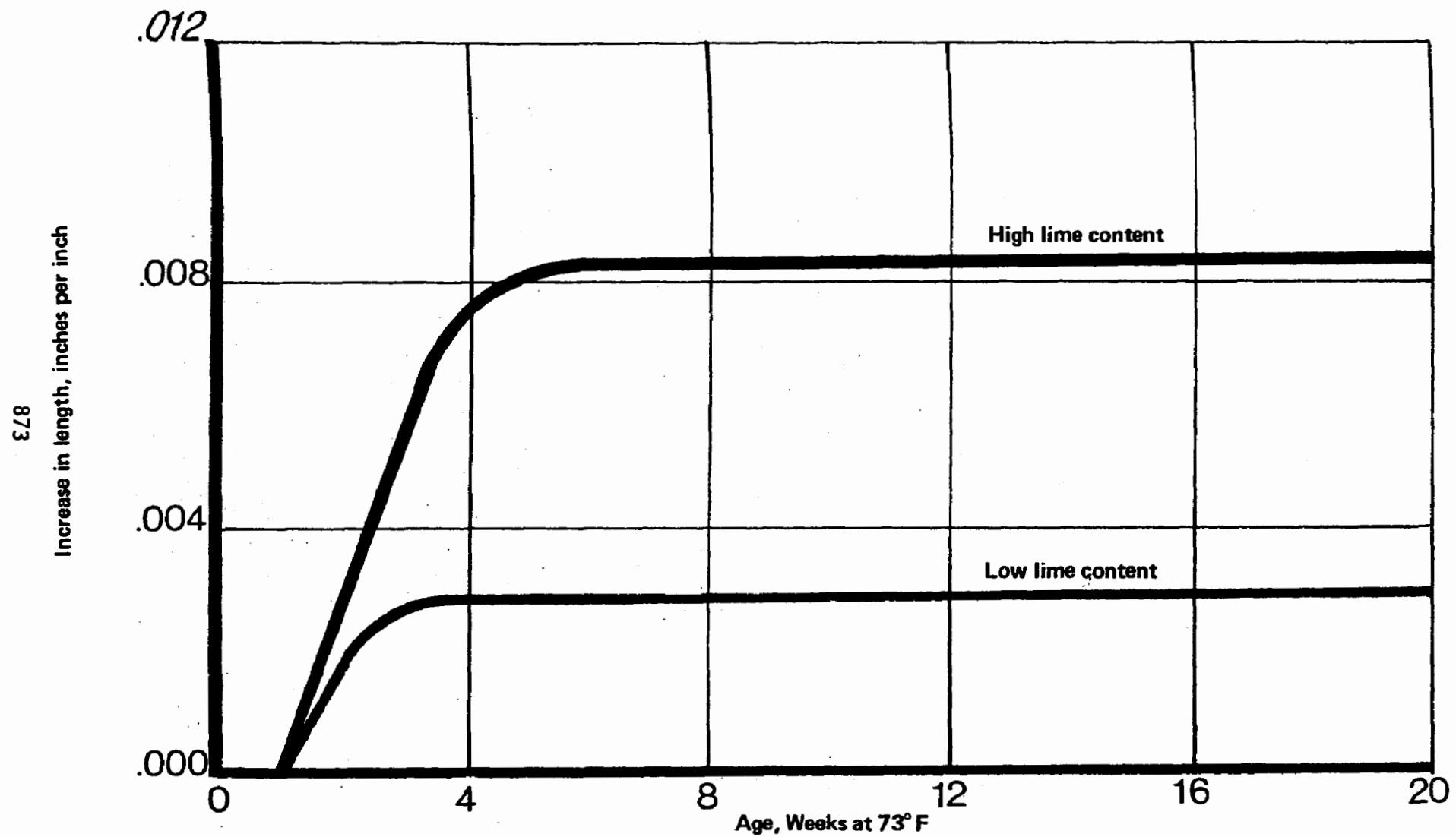


FIGURE 14 — Early expansion of fly ash-sludge mixtures.

UTILIZING AND DISPOSING OF SULFUR PRODUCTS
FROM FLUE GAS DESULFURIZATION PROCESSES IN JAPAN

by

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Utilizing and Disposing of Sulfur Products from Flue Gas Desulfurization Processes in Japan

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Japan's energy supply has doubled in the past five years depending mainly on growing amounts of imported oil. Even though nuclear energy may eventually supplant petroleum, imported oil and sulfur derived from it are likely to keep increasing for some time to come. Regulations on SO_2 emissions are becoming more and more stringent, inducing greater efforts for the desulfurization of fuel oil and waste gas. While virtually all of the by-products from the desulfurization--elemental sulfur, sodium sulfite, sulfuric acid, gypsum, etc.--have been utilized so far, it will not be long before supply of by-products runs far ahead of demand. Gypsum is generally regarded as the most rational by-product because of its several uses including land filling and also because of its ease of abandonment. Elemental sulfur is considered to be another logical by-product because it may be stored for some time for future use.

1. Characteristics of desulfurization in Japan

Of the total electric power (386 billion Kwhr) produced in Japan in 1971, about 62% depended upon oil, 12% upon coal, 22% upon hydraulic power, and 2% upon nuclear energy.¹ Heavy oil, a residue of atmospheric distillation of crude oil, has been used as a major fuel in recent Japan. Heavy oil consumption in 1971 reached 745 million barrels. About 30% of the heavy oil was burned in power plants and the rest in other industries and buildings.¹ Heavy oil from high-sulfur crude contains 4% sulfur. In 1971 nearly one-fourth of the total heavy oil was subjected to hydro-desulfurization giving 287,000 tons of elemental sulfur as by-product. Still nearly 6 million tons of SO_2 was emitted by burning the heavy oil, constituting the chief source of SO_2 emissions.

At present in Japan, more than 100 commercial and prototype plants for waste-gas desulfurization are on stream. Most of them treat either flue gas from oil-fired industrial boilers or waste gas from chemical plants, smelters, etc. Nine major power companies which produce more than 70% of total power in Japan have recently decided to build many flue gas desulfurization plants. The total capacity of the plants of the power companies will increase from 357 Mw in 1972 to 2,700 Mw in 1974 and to 4,800 Mw in 1976.

A salient feature of the desulfurization efforts in Japan is that they are oriented toward processes that yield salable by-products such as sodium sulfite for paper mills, sulfuric acid, gypsum for retarder of cement setting and for gypsum board, etc. The feature is predicated on the following circumstances: (1) Japan is subject to limitations in domestic supply of sulfur and its compounds as well as in land space

available for disposal of useless by-products. (2) Most desulfurization plants treat flue gas from oil-fired boilers, waste gases from chemical plants, etc. which contain less dust than does coal-fired flue gas and therefore are suited to the production of by-products of high purity. (3) Most steam power plants are located close to chemical plants; hence it is easy to utilize the desulfurization by-products in chemical plants.

However, since so many desulfurization plants are to be built, it is considered that in future the supply of the by-products will far exceed the demand, necessitating the abandonment of a substantial portion of them. Even now there are many small plants (less than about 30,000 scfm) which produce waste solutions of sodium sulfate, sodium sulfite, and ammonium sulfate; it is uneconomical to recover by-products at small plants.

2. By-production of sodium salts

Since 1966 more than 50 units have been built to recover SO_2 to by-produce sodium sulfite for paper mills. Some of the plants are listed in Table 1. In most of them, SO_2 is absorbed with a sodium sulfite solution to form sodium bisulfite which is then treated with sodium hydroxide to produce sodium sulfite. (By treating flue gas with a sodium hydroxide solution, CO_2 is also absorbed.) One-half of the sulfite solution is recycled to the absorber and the rest is concentrated to produce anhydrous sodium sulfite. An example of the process is shown in Figure 1. Flue gas is first washed with water in a conventional scrubber for cooling and dust removal; 60 to 80% of dust which is contained in flue gas from oil-fired boiler to an extent of about 0.1 grain/scf is removed. The purity of the product ranges from 90 to 97%; small amounts of sodium sulfate, dust, etc. are contained in the product. Sodium sulfite solution of about 20% concentration is also produced in some plants and used for paper mills.

A new semi-wet process for sodium scrubbing has been developed recently by Hitachi, Ltd. (Figure 2). Flue gas from oil-fired boiler at about 350°F after passing through a dust eliminator is introduced into a reactor into which sodium hydroxide solution is fed. By the heat of the gas, moisture is removed and powdery product consisting of sodium sulfite, sulfate and carbonate (for example, Na_2SO_3 -60%, Na_2SO_4 -20%, and Na_2CO_3 -20%) is formed which is caught by a dust separator. The product is usable for kraft pulp production.

Table 1. Major Waste-Gas Desulfurization Plants that By-Produce Sodium Salts

Process developer	Product	User	Plant site	(Charge: NaOH)	
				Unit capacity (1,000 scfm)	Date of completion
Oji Paper	Na ₂ SO ₃	Oji Paper	Kasugai	805(in 12 units) ^{a,b}	1966 - 1972
Oji Jinkoshi	Na ₂ SO ₃	Oji Paper	Tomakomai	400(in 4 units) ^a	1971 - 1972
Kureha Chemical	Na ₂ SO ₃	Kureha Chemical	Nishiki	176 ^a , 176 ^a	1968
Kureha Chemical	Na ₂ SO ₃	Konan Utility	Konan	123 ^a	1972
Showa Denko	Na ₂ SO ₃	Ajinomoto	Kawasaki	159 ^a	1971
Showa Denko	Na ₂ SO ₃	Asia Oil	Yokohama	142 ^a	1972
Bahco-Tsukishima	Na ₂ SO ₃	Daishowa Paper	Yoshinaga	129 ^b , 65 ^b , 26 ^b	1971
Bahco-Tsukishima	Na ₂ SO ₃	Daio Paper	Iyomishima	88 ^a , 70 ^a	1972
Hitachi, Ltd.	Na ₂ SO ₃	Jujo Paper	Miyakojima	57 ^a	1972
IHI-TCA	Na ₂ SO ₄	Mitsui S. O.	Sakai	88 ^a , 88 ^a , 88 ^a	1973
Mitsubishi (MKK)	Na ₂ SO ₄	Asahi Glass	Amagasaki	130 ^c	1973
Kurabo Ind.	Waste Na ₂ SO ₄	Bridgestone Tire	Tokyo	71 ^a	1972
Toyobo Co.	Waste Na ₂ SO ₃	Toyobo Co.	Shogawa	24 ^a	1971
IHI-TCA	Waste Na ₂ SO ₄	Nissan Motor	Oppama	67 ^a	1972

a: Oil-fired boiler

b: Kraft recovery boiler

c: Glass melting furnace

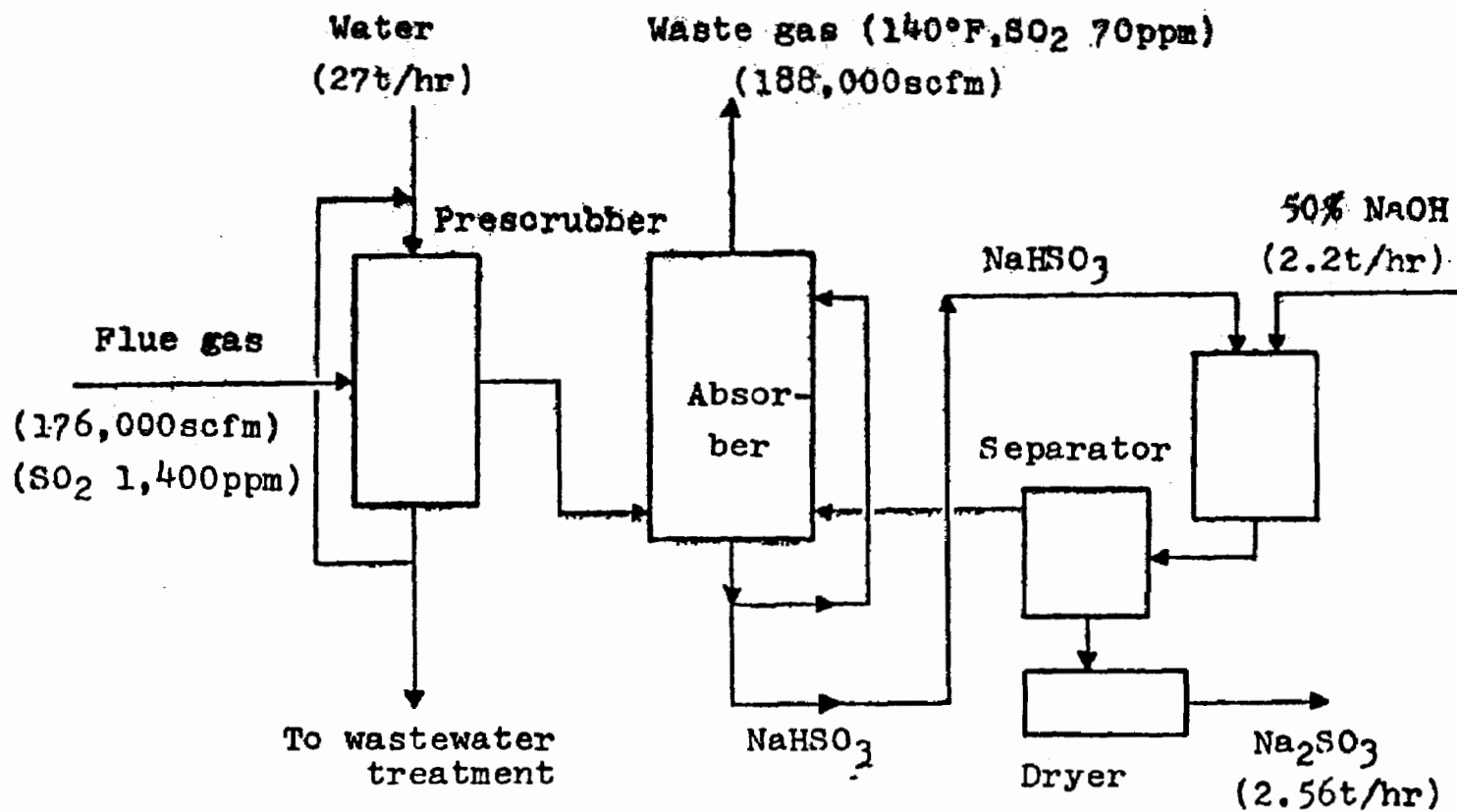


Figure 1 Flow sheet of Kureha sodium process

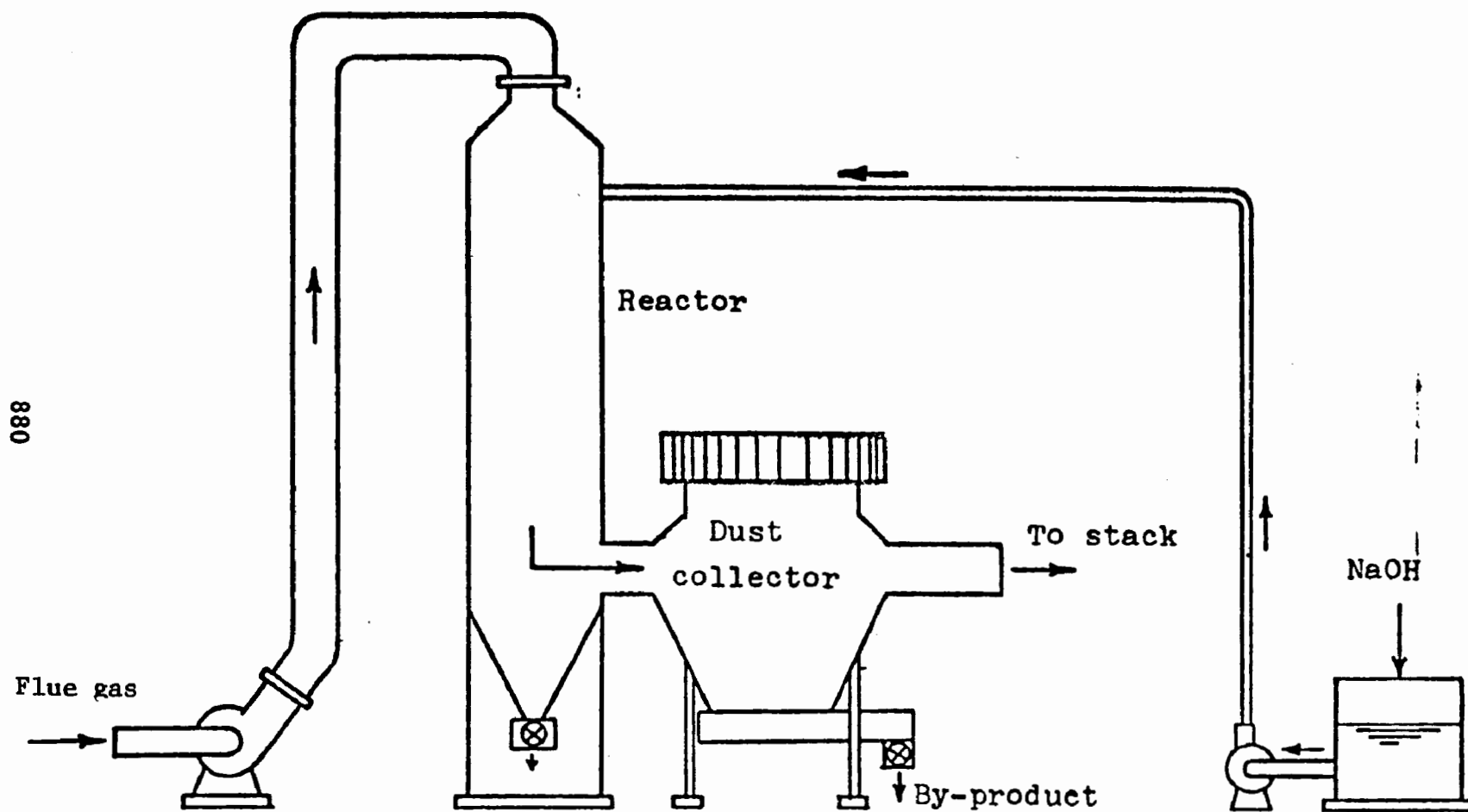


Figure 2 Hitachi semi-wet sodium process

These sodium processes are simple and are operated with ease. Investment cost is low. Demand for sodium sulfite, however, is limited. As shown in Table 2, production of the sulfite has increased rapidly with the progress of desulfurization and has resulted in a considerable price drop for the sulfite due to oversupply.

Table 2. Production and Price of Anhydrous Sodium Sulfite²

	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>
Production (1,000 t)	113	135	171	289	330
Price (\$/t)	64	62	61	58	60

Under such situation, the following ways of sodium scrubbing have been developed recently: (1) Several plants have been built recently to by-produce salable solid sodium sulfate. The sulfate is produced by air oxidation of sodium sulfite solution. Demand for the sulfate is also limited. (2) Many smaller plants have started to produce waste solution of sodium sulfate or sulfite. Some of these plants are listed in Table 2. (3) Showa Denko as well as Kureha Chemical jointly with Kawasaki Heavy Industries have developed sodium-limestone double alkali processes which are described in the present author's separate paper for the symposium entitled "Flue Gas Desulfurization Technology in Japan."

Table 3. Major Waste-Gas Desulfurization Plants that By-Produce Gypsum

Process developer	Absorbent	User	Plant site	Capacity (1,000 scfm)	Date of completion
Mitsubishi-JECCO	Ca(OH)_2	Nippon Kokan	Koyasu	37 ^d	1964
Mitsubishi-JECCO	Ca(OH)_2	Kansai Electric	Amagasaki	59 ^a	1972
Mitsubishi-JECCO	Ca(OH)_2	Onahama Smelting	Onahama	54 ^e	1972
Mitsubishi-JECCO	Ca(OH)_2	Kansai Electric	Kainan	235 ^a , 221 ^a	1974
Mitsubishi-JECCO	Ca(OH)_2	Tohoku Electric	Hachinoe	224 ^a	1974
Mitsubishi-JECCO	CaCO_3	Tokyo Electric	Yokosuka	220 ^a	1974
Babcock-Hitachi	CaCO_3	Chugoku Electric	Mizushima	170 ^a	1974
Chiyoda	H_2SO_4 , CaCO_3	Fuji Kosan	Kainan	93 ^a	1972
Chiyoda	H_2SO_4 , CaCO_3	Mitsubishi Rayon	Otake	53 ^a	1973
Chiyoda	H_2SO_4 , CaCO_3	Daicel	Aboshi	59 ^a	1973
Chiyoda	H_2SO_4 , CaCO_3	Hokuriku Electric	Shinminato	420 ^a	1974
Chiyoda	H_2SO_4 , CaCO_3	Mitsubishi Petrochem.	Yokkaichi	413 ^a	1974
Hitachi, Ltd.	Carbon, CaCO_3	Tokyo Electric	Kashima	250 ^a	1972
Showa Denko	NaOH , CaCO_3	Showa Denko	Chiba	340 ^a	1973
Kureha-Kawasaki	NaOH , CaCO_3	Shikoku Electric	Shintokushima	250 ^a	1974
Kureha-Kawasaki	NaOH , CaCO_3	Tohoku Electric	Sendai	220 ^a	1974
Nippon Kokan	NH_3 , Ca(OH)_2	Nippon Kokan	Keihin	88 ^b	1972
Chemico-Mitsui	Ca(OH)_2	Mitsui Aluminum	Omuta*	226 ^c	1972

*Producing waste calcium sulfite; gypsum will be produced in near future.

a: Oil-fired boiler

d: Sulfuric acid plant

b: Iron-ore sintering plant

e: Smelting furnace

c: Coal-fired boiler

3. Gypsum and calcium sulfite

3.1 Uses

Gypsum is considered the ideal by-product for the time being. Many processes have been developed in Japan recently that recover salable gypsum with sufficiently good quality to make it available as retarder of cement setting and for production of gypsum board (Table 3). Six of the processes which seem to be of more interest for possible application in the U. S. A. are described in the author's paper referred to above. Demand for and supply of gypsum in Japan are illustrated in Figure 3. Prices of by-produced gypsum (mainly phosphogypsum from wet-process phosphoric acid production) are shown in Table 4.

Table 4. Prices of By-Produced Gypsum (\$/t)²

<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>
4.4	4.7	4.4	6.1	6.7

All of the phosphogypsum and most of the other by-products have been used for cement and board production. As demand for gypsum has increased substantially, supply is on the short side at present, resulting in some price increase.

In order to use by-product gypsum for wall board, proper crystal size and shape and less impurity are required to ensure high strength. Phosphogypsum from the conventional dihydrate process usually has a small crystal size (10-30 microns) with much impurity and gives less strength. Japanese phosphoric acid producers have developed hemihydrate-dihydrate processes by which good crystals of gypsum (50-150 microns) with less impurity are obtained. Good phosphogypsum from these processes has a strength equal to or better than natural gypsum.

Such background has helped find outlets for by-product gypsum from desulfurization. For example, a wall board production plant of Onahama-Yoshino Gypsum Co., Ltd., using gypsum (450 t/day) recovered from the Mitsubishi-JECCO process is under construction at Onahama works, Onahama Smelting and Refining Co. Another example has been presented by Mitsui Aluminum Co. which has produced waste calcium sulfite by treating coal-fired flue gas (226,000 scfm) with the Chemico-Mitsui process. Mitsui Aluminum, jointly with Mitsui Toatsu Chemicals, Inc., has succeeded in tests to manufacture wall board from gypsum obtained from the calcium sulfite. The gypsum has a little less than 90% purity, containing fly ash and other impurities. Mitsui Aluminum plans to install a prototype reactor within 1973 to convert about one-fourth of its by-product calcium sulfite to gypsum. It is likely that a full-scale reactor will be installed in 1974.

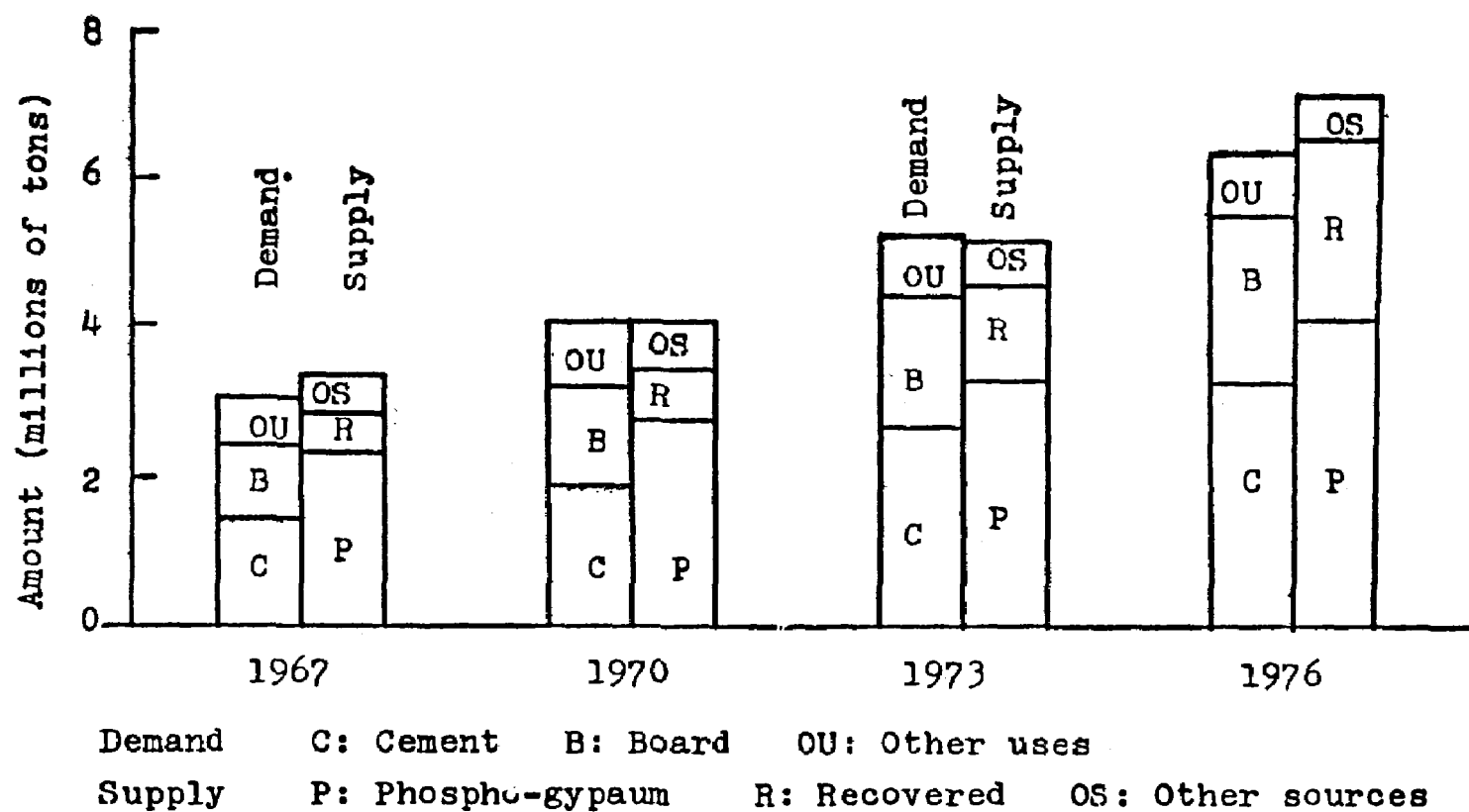


Figure 3 Demand for and supply of gypsum in Japan

By-product gypsum is available also as retarder of cement setting. Gypsum is added to Portland cement clinker to the extent of 3-4% at grinding. Nippon Kokan (Mitsubishi-JECCO lime-gypsum process) has sold the by-product gypsum for cement since several years ago. Gypsum should be charged continuously into the cement mill. Powdery gypsum with more than 10% moisture tends to form a "bridge" in the hopper and cannot be charged smoothly. By the Mitsubishi-JECCO process and the Nippon Kokan ammonia-lime process, the product gypsum from a centrifuge has a low moisture content of about 10%. Gypsum of about 90% purity containing fly ash is useful, but alkali-rich gypsum by-produced from the double alkali process would impair cement setting. New uses of gypsum and calcium sulfite have been developed recently in Japan. Mitsui Toatsu Chemicals, Inc., jointly with Taisei Construction Co. has started producing a new material "gypsum polymer composite" with gypsum and methyl methacrylate. Lion Fat and Oil Co. jointly with Idemitsu Kosan has commenced production of synthetic paper from calcium sulfite and polyethylene at a weight ratio of about 70:30. By-produced gypsum and calcium sulfite could be used if the dust in flue gas is removed reasonably well so that the color is not too dark.

3.2 Discarding

Gypsum is produced from calcium sulfite by oxidation. Oxidizer is virtually unnecessary in certain plants--such as Amagasaki plant, Kansai Electric Power (Mitsubishi-JECCO process) and Kumagaya plant, Chichibu Cement (IHI-TCA process)--which treat flue gas with relatively low SO_2 and high O_2 concentrations; essentially all of calcium sulfite is converted to gypsum in the scrubber. But normally an oxidizer (for oxidation with air) or a reactor (by the above mentioned Mitsui gypsum process in which a catalyst is used) is required which adds some cost to desulfurization. Gypsum has advantages over calcium sulfite even for land filling or discarding. Gypsum can be grown into fairly large crystals (50 to 300 microns); moisture content of the centrifuge discharge can be made as low as 10%. On the other hand, the crystal of calcium sulfite is normally very small (1-10 microns); centrifuge discharge contains about 60% moisture and is like a paste. The calcium sulfite may not suit land filling because of the high moisture which is not easily removed, while gypsum would be useful. Moreover, calcium sulfite has some danger of consuming oxygen in ambient water. In discharging in slurry form to a waste pond, gypsum precipitates much more easily in smaller volumes than does calcium sulfite, thus reducing the required pond size. In case of truck transportation, gypsum can be handled with greater ease. By the sodium-limestone processes developed recently by Showa Denko and also by Kureha Chemical jointly with Kawasaki Heavy Industries, calcium sulfite grows into much larger crystals than usual so that the above mentioned problems might be solved.³

4. Other by-products

4.1 Sulfuric acid and sulfur

There are many processes that by-produce sulfuric acid and sulfur (Table 5). By these processes SO_2 in waste gases is first absorbed with various absorbents and then recovered as SO_2 gas of 7 to 95% concentration which is used for sulfuric acid or sulfur production. Among these processes, the Wellman-Lord process is well known. In Japan plants based on this process were constructed respectively by Mitsubishi Chemical Machinery Mfg. (MCK) and Sumitomo Chemical Engineering Co. (SCEC) in 1972. The former produces sulfuric acid and the latter returns the recovered SO_2 gas to a Claus furnace to produce elemental sulfur. By magnesium scrubbing processes, magnesium sulfite formed by the reaction of magnesium hydroxide and SO_2 is calcined to recover SO_2 for sulfuric acid production. Some magnesium sulfate is also formed which is not as easy as magnesium sulfite to be thermally decomposed. The Mitsui Mining process features the by-production of some solid magnesium sulfate for fertilizer and other uses.⁴ Demand for magnesium sulfate, however, is limited. The Onahama Smelting process treats waste gas from a copper smelter containing about 20,000 ppm SO_2 to produce 6,600 t/month sulfuric acid. By the Chemico process, a new plant to treat 294,000 scfm waste gas from a Claus furnace is to be constructed by 1974. By the Sumitomo Shipbuilding process, the SO_2 absorbed on activated carbon is expelled by heating it in a reducing gas, to release SO_2 gas of 10-20% concentration which is used for sulfuric acid production.

By the Shell process, SO_2 is absorbed with copper oxide to form copper sulfate, which is then treated with reducing gas to expel SO_2 .⁵ A commercial plant is scheduled to come on-stream in a few months at Yokkaichi. The MHI-IFP process uses ammonia scrubbing with thermal decomposition of ammonium sulfite and sulfate to regenerate SO_2 (Figure 4).⁶

A commercial plant based on the MHI-IFP process will come on-stream in 1974. In these two processes, the recovered SO_2 is reacted with H_2S to produce elemental sulfur.

Supply of sulfur and sulfuric acid in Japan is shown in Table 6. Their prices are shown in Table 7. Demand for sulfur and sulfuric acid is nearly equal to the supply. There has been little import or export of sulfur and sulfuric acid. Sulfur mines in Japan are small and sulfuric acid has been produced mainly from pyrite and smelter gas. Since elemental sulfur recovered from hydrosulfurization of heavy oil has increased resulting in the lowering of sulfur price, the use of sulfur for sulfuric acid production has been started recently.

An annual increase in the demand for sulfuric acid is estimated at about 5%; some more flue gas desulfurization plants by-producing sulfuric acid will be built but not very many of them are expected.

Table 5. Major Waste Gas Desulfurization Plants that Produce Other By-Products

Process developer	Absorbent	Product	User	Plant site	Capacity (1,000 scfm)	Date of Completion
Wellman-MKK	NaOH	H ₂ SO ₄	Japan Synth. Rubber	Chiba	118 ^a	1971
Wellman-MKK	NaOH	H ₂ SO ₄	Chubu Electric	Nishinagoya	370 ^a	1973
Wellman-MKK	NaOH	H ₂ SO ₄	Japan Synth. Rubber	Yokkaichi	160 ^a	1974
Wellman-SCEC	NaOH	S	Toa Nenryo	Negishi	35 ^b	1971
Wellman-SCEC	NaOH	H ₂ SO ₄	Sumitomo C.C.	Chiba	125 ^a	1973
Mitsui Mining	MgO	H ₂ SO ₄	Mitsui Mining	Hibi	47 ^c	1971
Onahama Smelting	MgO	H ₂ SO ₄	Onahama Smelting	Onahama	78 ^d	1972
Chemico-Mitsui	MgO	S	Idemitsu Kosan	Chiba	294 ^b	1974
Sumitomo Shipbuilding	Carbon	H ₂ SO ₄	Kansai Electric	Sakai	100 ^a	1971
Shell	CuO	S	Showa Y. S.	Yokkaichi	71 ^a	1973
MHI-IFP	NH ₃	S	Maruzen Oil	Shimozu	16 ^b	1974
Nippon Kokan	NH ₃	(NH ₄) ₂ SO ₄	Nippon Kokan	Keihin	88 ^e	1972
Mitsubishi (MHI)	MnO _x , NH ₃	(NH ₄) ₂ SO ₄	Chubu Electric	Yokkaichi	193 ^a	1972
Kurabo Ind.	NH ₃	Waste (NH ₄) ₂ SO ₄	Mitsubishi Electric	Amagasaki	24 ^a	1971
Kurabo Ind.	NH ₃	Waste (NH ₄) ₂ SO ₄	Ishigezome Sarashi	Tokyo	14 ^a	1971

a. Oil-fired boiler

b. Claus furnace

c. Sulfuric acid plant

d. Smelting furnace

e. Iron ore sintering plant

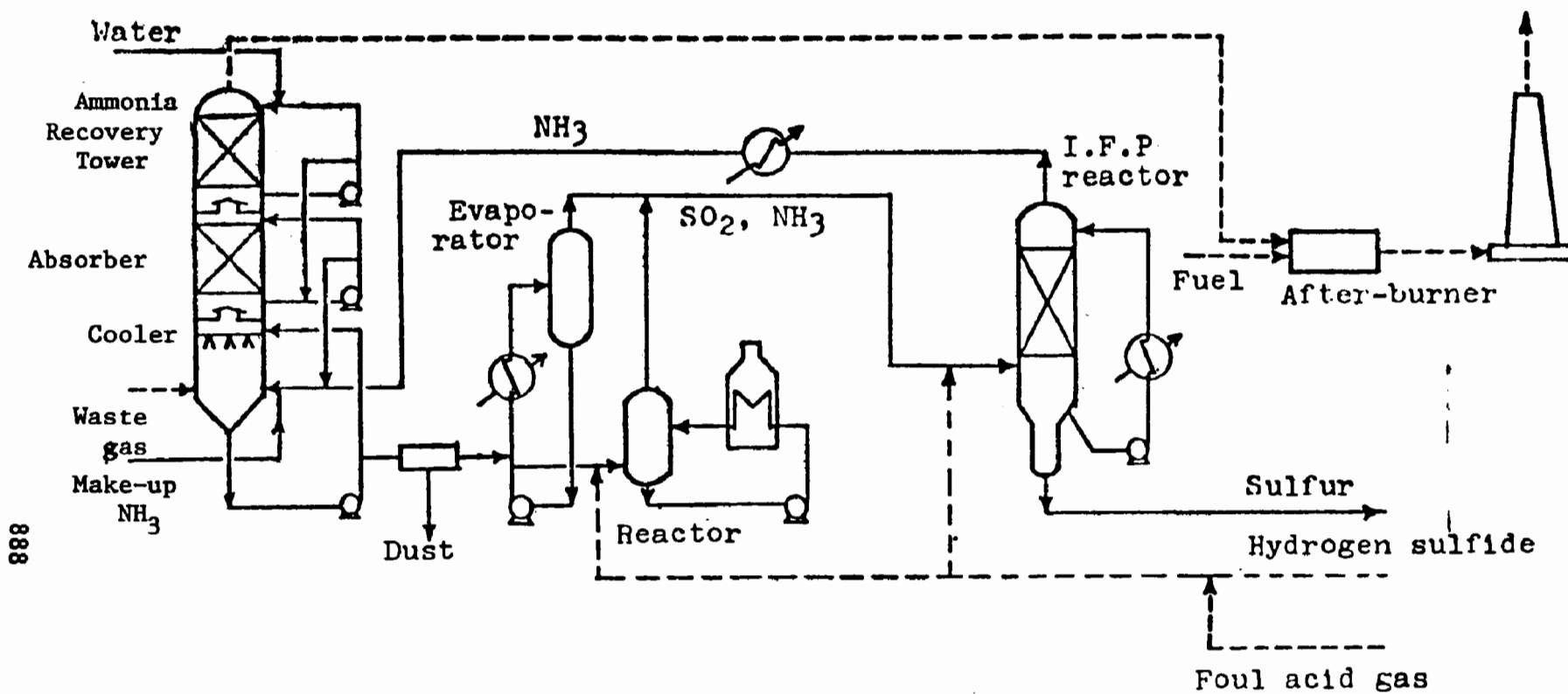


Figure 4 Flow sheet of M.H.I.- I.F.P. process

Table 6. Supply of Sulfur and Its Compounds²

(1,000 tons of material)

	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>
Sulfur					
Mined	283	180	120	47	18
Recovered	97	179	297	414	526
Total	380	354	417	461	544
Sulfuric acid					
from pyrite	4,576	4,524	4,303	3,348	2,747
from smelter gas	2,719	2,972	3,242	3,770	4,343
from sulfur	0	0	17	210	295
Total	7,295	7,496	7,562	7,328	7,385

Table 7. Price of Sulfur and Its Compounds (\$/t)²

	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>
Sulfur	73		54	68	50
Sulfuric acid	26	25	26	27	23

Elemental sulfur can be produced from recovered SO_2 easily at oil refineries which have H_2S . For plants which have no H_2S , the production may be costly because it is required to reduce two-thirds of the SO_2 into H_2S ; the desulfurization cost including production of elemental sulfur may be close to that of hydrodesulfurization of heavy oil by the topped-crude process which ranges from \$1.1 to 1.5/bl oil to reduce sulfur from 4 to 1%. When a large oversupply of sulfur and its compounds occurs due to the development of desulfurization, the sulfur production process would assume greater importance because elemental sulfur has the smallest volume among sulfur and its compounds and requires the least transportation and storage space.

4.2 Ammonium sulfate

There were several ammonia scrubbing plants a few years ago in Japan treating tail gas from sulfuric acid plants to by-produce ammonium sulfate. All of the plants have been shut down because of the oversupply of ammonium sulfate and also because double contact processes for

production of the acid has been introduced to reduce SO₂ emissions. Now there are three ammonia scrubbing plants. Two of them produce dilute ammonium sulfate solution to be discarded, and the last produces solid ammonium sulfate (Nippon Kokan process) although in this plant ammonium sulfite and sulfate are being converted to gypsum at present. In addition, ammonium sulfate has been produced at Yokkaichi Station, Chubu Electric Power, using the Mitsubishi manganese process. Due to the worldwide increase in the demand for nitrogen fertilizers, it is possible that ammonium sulfate will be produced in future from SO₂ in flue gas at a considerable number of plants in several countries. One of the problems in ammonia scrubbing has been plume formation, but the problem has been nearly solved in Japan. For plants that produce waste solution, ammonia scrubbing is less expensive than sodium scrubbing because ammonia is much cheaper than sodium hydroxide. It is likely, however, that the emission of ammonium sulfate solution will be restricted because it could cause a eutrophication problem.

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LONG RANGE MARKET PROJECTIONS FOR BY-PRODUCTS
OF REGENERABLE FLUE GAS DESULFURIZATION PROCESSES

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A B S T R A C T

LONG RANGE MARKET PROJECTIONS FOR BY-PRODUCTS OF REGENERABLE FLUE GAS DESULFURIZATION PROCESSES

If all sulfur emitted from utility stacks, smelters, etc. were to be recovered in useful form, the quantity would be so large as to have a major impact on sulfur's price and markets, with the possibility of causing severe dislocations. This paper describes a quantitative study of this proposition, using a computer model, with projections extending to the year 2020. The purpose was to provide the EPA with a planning tool for establishing the relative priorities that should be given to development of technology for recovery of "abatement sulfur" in (a) marketable and (b) non-marketable forms.

The paper describes how various abatement schedules were simulated, and the supply/demand/price implications of these schedules. Because sulfur is an international commodity, the domestic abatement schedules and their implications are placed in an international context and related to world supply/demand/price relationships. In addition, the relative values of sulfur recovered in acid and elemental form are discussed.

Note: The work on which this paper is based was performed pursuant to Contract No. EHSD 71-13 with The Environmental Protection Agency.

INTRODUCTION

In its 1970 report on "Abatement of Sulfur Oxide Emissions from Stationary Combustion Sources," a joint panel of the National Academy of Engineering/National Research Council remarked that it would be desirable to conduct a study of the long range supply and demand situation with regard to the several alternative (sulfur) by-products to aid in establishing priorities for support of control and abatement technology.

NAE/NRC's suggestion was implemented by the EPA through Contract No. EHSD 71-13 with the Government Research Laboratory of Esso Research and Engineering Company.

The full report of this study has been issued as Document No. PB 208993 by the National Technical Information Service, Springfield, Va. 22151.

PURPOSE OF STUDY

To provide the EPA with a planning tool for establishing the relative priorities that should be given to development of technology for recovery of "abatement sulfur" in marketable and non-marketable forms.

TO BE DISCUSSED

- How various abatement schedules were simulated.
- The modeling of domestic and foreign sulfur supply and demand to permit projections to the year 2020.
- The effect of stockpiling elemental sulfur.
- The price implications of the supply and demand projections, as derived by linear programming (computer) calculations.
- The relative values of sulfur recovered in acid and elemental forms.

SIMULATION OF ABATEMENT SCHEDULES

Abatement refers to removal of sulfur so that it has not emitted to the atmosphere. The degree of abatement, as treated in this study, refers to the percentage reduction from the total quantity of sulfur oxides emitted from utility stacks in 1970. This was the base year for the study. The degree of abatement does not include sulfur removed from fossil fuels, e.g., by desulfurization of petroleum, prior to combustion. This is because such sulfur was treated separately in the supply/demand calculations, so that the effects of flue gas desulfurization could be isolated.

The term "useful form" is used to distinguish between sulfur removed in elemental form or as acid from that recovered as a "throwaway" by-product. Theoretically, a given degree of abatement could be achieved with no sulfur in useful form (if only throwaway by-products were produced), or with 100% recovery in useful form, or with an infinite number of intermediate cases. However, what matters in the computer calculations is the quantity of sulfur in useful form, rather than the percentage that this quantity represents of the total amount abated or of the total abatement potential.

The total abatement potential in 1970 was the amount of sulfur actually emitted from utility stacks in that year. For the other years for which calculations were made (1975, 1980, 1985, 1990, 2000, 2010, 2020), it was necessary to project both the amounts and sulfur contents of the fossil fuels that domestic electric utilities would burn. This led to the

abatement potential without any stack-gas treatment. From these quantities, it was then possible to assume varying degrees of abatement, e.g., so that 1970 emissions would not be exceeded, and other cases in which various percentage improvements over the 1970 level would be achieved. Having done this, further assumptions were made about how much of the abated sulfur would be in useful form. These are the quantities of useful sulfur that were included in the supply/demand calculations.

It is important to recognize that the study did not forecast that any particular quantity of sulfur would be abated in any future year. What was done was to simulate a wide range of possibilities, and then to assess the implications of these possibilities in terms of the calculated value for recovered sulfur in different parts of the United States. The whole purpose was to provide the Environmental Protection Agency with a quantitative tool for exploring the consequences of different policies and technological approaches for the abatement of sulfur oxide emissions.

MODELING OF DOMESTIC AND FOREIGN SUPPLY AND DEMAND

For convenience, the study has been referred to as a "long range sulfur supply and demand model." In practice, several models and sub-models were developed, and one of these models was "computerized" for the purpose of calculating sulfur values in different locations. Two types of model were used:

- a simulation or morphological model to represent the sulfur industry and the structural way in which abatement sulfur could impact on it.

- a forecasting model to project the demand/supply/price framework of the industry at various times into the distant future.

In preparing the simulation model, it was necessary to take into account not only all of the major supply/demand regions under specific study, but also the external sources of supply and demand that could interact with the former. Thus, the starting point was the "World model" shown in Figure 1. The next step was to construct the "North American model" shown in Figure 2. The numbered boxes in this figure are the U.S. regions under specific study. The cross-hatched boxes are the extra-regional North American suppliers to the United States. For example, Calgary is the center for Canadian sulfur recovered from sour natural gas, Coatzacoalcos represents Mexican Frasch production, while Aruba represents production of sulfur from all Caribbean refineries. The cross-hatched boxes with the underscoring represent sources of sulfuric acid, rather than elemental sulfur, that is potentially available for shipment to other regions. Whether such shipment of acid will occur in practice involves economic factors, particularly transportation costs, that will be discussed later.

Figure 3, an exploded map of the continental U.S., shows the numbered regions of Figure 2 in their normal geographical perspective and also the way in which the regions coincide approximately with the Federal Power Commission's regionalization of electricity generating capacity.

The elements of the forecasting model are listed in Table 1. Unlike many long range projections that may be little more than 10-15 year extrapolations, the sulfur study is concerned with the next five decades.

For this reason, it was considered necessary to start by making economic projections, and then to use correlations to convert the levels of industrial and agricultural activity into projections of sulfur supply and demand. The principal steps are indicated in Table 1. It should be noted that a key step was to translate the projections of economic activity into energy demand. This is necessary because it is from fossil fuels that the greater part of the by-product sulfur is coming, and will continue to come, during the next several decades. In addition, the demand for sulfur, whether industrial or fertilizer demand, also correlates with economic activity and economic growth. Consequently, by basing the overall projections on correlations with constant dollar G.N.P., there is some self-compensation in the net statistics. For example, if economic development is overestimated this would have the effect both of overestimating the potential for sulfur recovery and of demand for sulfur.

Separate forecasts were developed for nuclear and hydro energy that, when subtracted from projected total energy demand, gave the fossil fuel energy requirements. The latter were broken down into individual projections for natural gas, petroleum and coal. These quantities, in conjunction with data concerning the sulfur content of these natural resources in different parts of the world, led to the amounts of sulfur potentially recoverable from each. Separate projections were made of the sulfur recoverable from smelters, pyrites and miscellaneous sources. And, finally, estimates were made of the future availability of elemental sulfur from domestic and foreign Frasch mines.

On the demand side, a set of GNP/industrial sulfur correlations was used to project industrial sulfur demand in different areas, while separate correlations were used to project fertilizer sulfur demand. Worldwide, the latter accounts for about half of the total demand for sulfur, but, because of differences in agricultural acreage in different countries and other factors, does not necessarily move in step with industrial demand for sulfur.

The sum of industrial and fertilizer demand for a particular region* is the region's total demand. The difference between this quantity and the region's internal supplies of sulfur represents either a net demand for sulfur or the capability of the region to supply sulfur to another region. For the purpose of the computer calculations, a net foreign demand was located in Northern Europe (symbolized by Rotterdam) while net supply potentials were located in Canada, Mexico and the Caribbean. These four foreign regions, together with the eleven regions of the continental U.S., comprised the "North American model" used for the computer calculations.

EFFECT OF STOCKPILING ELEMENTAL SULFUR

By 1970, stockpiles of elemental sulfur in Western Canada had reached several million tons and now approximate 8 million long tons. This sulfur is coming from sour natural gas, and must be removed before the gas is delivered to a commercial pipeline. Thus, it is the demand for natural gas, not the demand for sulfur, that has been a major factor in the rate

* as defined in Figures 1 and 2.

at which this by-product sulfur has been produced. The reason for the stockpiles is that production has greatly exceeded the demand of the markets to which the Western Canadian sulfur can be delivered economically. Recently, there have been additional restraints on movements of sulfur through the port of Vancouver and on rail deliveries to the Midwest. These factors have accentuated the stockpiling in Alberta, and have contributed to a temporary tightness in worldwide sulfur supplies. The word temporary is used advisedly because the transportation bottlenecks can be relieved and, once this happens, the Canadian stockpiles will again exert a major influence on world sulfur supplies and prices.

Transportation costs are a major factor in the sale of Western Canadian sulfur. Competition takes place at the point of delivery, e.g., Northern Europe. The price obtainable here minus the transportation cost gives the net-back to Western Canadian producer. Clearly, it is not in the interest of the producers to move sulfur into world markets that would net little or nothing back to Alberta. This is why Canadian sour gas sulfur competes in some world markets but not in others. In turn, this is why the Canadian stockpiles of recovered sulfur are growing. On the other hand, the existence of the stockpiles means that this sulfur could enter world markets on comparatively short notice provided that the price obtainable for it was sufficient to cover transportation costs and give a tolerable net-back to the producer. This statement begs the question of what is meant by "tolerable return." An elliptical answer to this very difficult question is that an incremental sale may cause the average price of all sales to be depressed thereby lowering the overall net-back. Thus, the optimum strategy

from the standpoint of a Western Canadian sulfur producer may require a combination of stockpiling and export sales.

The Canadian stockpiles differ in function from those of the Frasch sulfur producers. At present, domestic Frasch stocks are probably just below the level of 4 million long tons and have been declining slowly as sulfur demand has grown and various production and transportation bottlenecks have occurred. In principle, however, the Frasch stocks are merely a working inventory. When this inventory rises, the Frasch producers will tend to cut production; when inventory falls, there will be attempts to expand production. As discussed already, such flexibility of production is not enjoyed by producers of by-product sulfur.

What has been happening in Canada illuminates what may occur in the U.S. as and when air pollution controls force the recovery of sulfur from utility stacks. If a surplus of sulfur from this source is to be avoided, some combination of the following approaches may be necessary:

- (a) recovery of large amounts of sulfur in the form of throw-away by-products.
- (b) recovery and stockpiling of elemental sulfur.

Singly, or in combination, these approaches could be applied so as to limit the quantity of sulfur recovered in useful form to the amount that could be marketed without causing major dislocations to the industry.

There is some evidence that the application of throw-away systems may be limited either by logistics or by the possibility of water pollution from the discarded by-products. This is the reason, why the E.P.A. asked for the implications of national stockpiles of elemental sulfur to be

examined. As treated in the computer calculations, a national stockpile of sulfur is a source of "negative supply" since it removes sulfur from the market. Additionally, a national stockpile would permit the re-entry of sulfur in later years on the assumption that the general condition of potential oversupply will eventually be corrected. Conceptually, this condition could result from a continuing increase in the demand for sulfur and from an eventual decline in the use of fossil fuels for the generation of electricity, general industrial purposes, etc.

LINEAR PROGRAM FOR CALCULATION OF SULFUR VALUES

The computer calculations were made with IBM's linear program "LP-MOSS." This is a variant of the familiar transportation linear program. In addition, a number of specially developed programs and sub-routines were needed to get the information in and out of the computer. A schematic diagram of the entire procedure is given in Figures 4.

The linear program calculates the way that each of the net demand regions in Figure 2 can secure the necessary supplies at lowest cost from other domestic and foreign regions that are in a net supply position.

The net demand in a particular region is the region's gross demand minus whatever supplies of sulfur are available from within the region. The base case of net demand excludes regional abatement sulfur from the region's internal supplies. Other cases then consider varying quantities of abatement sulfur in useful form. Such sulfur is conceived to reduce the net demand of the pertinent region before the possibility of shipment to another region is considered (i.e., permitted by the computer program). The LP program also requires the following input data:

- Quantity of supply available from each extra-regional supplier.
- F.O.B. price for each source of extra-regional supply.
- Transportation costs for each linkage between the net demand regions and the extra-regional supply points.

In addition, certain special features were incorporated:

- Upper bounds on the amount of acid that may be shipped into a given region (in order to simulate the capacity of the region to accept merchant acid). The upper bounds were raised with time in order to simulate an increasing ability to accept sulfur in the form of acid.
- An acid equivalency credit, recognizing that the cost of manufacturing acid is avoided by a customer who purchases acid rather than elemental sulfur.
- Lower bounds on certain supply linkages in order to simulate the effects of marketing strengths (e.g., captive terminals in the net demand regions) and captive use of sulfur by the suppliers (e.g., the manufacture of P fertilizers by the producers of Frasch sulfur).

The output data from the LP program include a matrix of extra-regional suppliers and net demand regions which shows how demand was filled (i.e., who sold to whom), and what the delivered cost was. If no sales were made by a particular supplier to a particular demand region, the required reduction in minimum delivered cost (and, hence, in F.O.B. value) for a sale to occur is printed in the matrix. Other output programs tabulate the sales by and netback to each supplier, and the calculated delivered value of S in each region.

Each LP case calculates the value of an incremental unit of supply rather than of supply increments of any size. However, parametric cases involving substantially different quantities of abatement S. supply make it possible to obtain value estimates by interpolation. The calculated values are considered to be maxima because new suppliers would have to shave their price in order to "buy into" an existing market. These maxima are referred to later as "maximum delivered values" (M.D.V.). As a first approximation, it is postulated that a recoverer of abatement S in elemental form might expect a plant netback of about \$10/LT less than the M.D.V. The \$10/LT represents a composite of transportation and marketing costs (including price-shaving to buy into the market). Actual transportation and marketing costs are likely to vary greatly from one specific situation to another. Thus, the deduction of \$10/LT from M.D.V. to obtain the F.O.B. value (F.O.B.V.) of abatement S should be used with caution.

PRICE IMPLICATIONS OF SUPPLY/DEMAND PROJECTIONS

The computer calculations permitted the construction of correlation charts for the individual regions of the continental U.S. Examples are given in Figures 5 and 6. Each chart indicates:

- (a) The variation in net regional demand with increasing regional supply of abatement sulfur in useful form.
- (b) The maximum delivered value (M.D.V.) of abatement sulfur corresponding to a given level of supply in useful form.

In addition, a rough estimate of the F.O.B. value (F.O.B.V.) of abatement S in useful form is shown on the charts. In most cases, F.O.B.V. is M.D.V.-10 (\$/LT), i.e., it is merely the M.D.V. minus an arbitrary delivery

cost of \$10/LT. In a few cases, the F.O.B.V. refers to net-back estimated for abatement S shipped to another region. There are also cases in which it was not possible to estimate either an M.D.V. or F.O.B.V.

No charts were prepared for the year 2020 because the results obtained, while similar to those for 2010, are judged to be too sensitive to the assumptions made. Each figure is a composite of six charts covering the years 1975 through 2010. All of the charts have certain features in common:

- Regional abatement S in useful form is plotted as an abscissa.
- Net regional demand is plotted as an ordinate, with the scale at the left.
- M.D.V. and F.O.B.V. are plotted as ordinates, with a common scale at the right.
- The numbers 0, +5, +10 and +15 refer to parametric demand (as discussed in the complete report, but not here).
- All volumes are expressed in million LT of S equivalent.
- All values are expressed in \$ per LT of S equivalent.

Chicago Region (Figure 5)

This region has a significant demand for sulfur but it has an even greater potential for producing abatement S. Markets for all of this potential cannot be conceived. Hence, all of the M.D.V. and F.O.B.V. curves have sharp downturns. A calculated F.O.B.V. curve is shown for 1990, based upon the assumption that Chicago region sulfur will be moving to extra-regional markets by then. In retrospect, the contrast between the

1985 and 1990 charts suggests that a turn around may not come so quickly. However, a national stockpile in the Chicago region could be a spur to exports and could support the conditions projected in the 1990 chart.

Tampa Region (Figure 6)

The net demand in the Tampa region greatly exceeds its abatement potential. But most of the demand involves captive production of acid from purchased elemental S. The charts in Figure 6 suggest that reasonable F.O.B.V.'s may be possible for local deliveries of acid in the Tampa/Bartow area.* The downtrend in M.D.V. for the Tampa region with increasing supplies of abatement S in useful form is due to the general level of recovery in the U.S. not to the impact of the Tampa region's own abatement potential.

Implications

The years 1980 and 2000 may be used to illustrate the results of the computer calculations. The choice permits significantly different situations to be contrasted. In 1980, production of W. Canadian sulfur is expected to be at peak levels and backstopped by huge stockpiles, world markets will be under intense supply pressure, and the fitting (and retrofitting) of abatement systems in the U.S. should be beyond the demonstration stage and into widespread use. In contrast, two decades later, W. Canadian S is expected to be a minor factor in world markets, S recovered from petroleum refining will be of major importance while, in the U.S., the policies applied to abatement S in prior years will have determined the shape of the domestic sulfur and sulfuric acid industries and their relationship to world markets.

* Direct negotiations between potential producers of abatement acid and users of fertilizer acid would seem to be required.

Results that illustrate the conditions projected for the years 1980 and 2000 are given in Tables 2 and 3. The overall sulfur demand of the continental U.S. is summarized in the top segment of each table. This is followed by estimates of demand in two of the most important regions of the Model, Chicago and Tampa. In both cases, sulfur supplies from within the region are deducted to give the net regional demand. These sulfur supplies exclude abatement S in useful form.

The third segment of each table shows cases that illustrate the effects of different levels of abatement combined with different percentage recoveries in useful form and, hence, different quantities of abatement S in useful form.

The fourth segment of each table shows the net regional demand for the Chicago and Tampa regions, after subtracting the pertinent quantities of abatement S in useful form from the base case of net demand. The reason that the net demand in cases (B) and (C) is the same as in case (A) is that the two former cases make the assumption of no recovery of S in useful form. Even though cases (A), (B) and (C) represent different levels of abatement, they are identical in terms of the assumption that no useful sulfur is recovered. This implies different levels of recovery in throw-away form. However, the latter has no direct effect on the value estimated for abatement sulfur.

The fifth segment of each table shows the estimated value of abatement S corresponding to each quantity of abatement S in useful form. Here, it must be pointed out that, for both years, cases (A), (B) and (C) lie outside the area actually investigated by computer cases. This is because it is considered an unrealistic assumption that no abatement S at all will be recovered in useful form. With no useful abatement S in

the year 2000, the M.D.V.'s of \$31+ and \$30+ (obtained by extrapolation from calculated cases) might be somewhat higher. Additionally, some switching to processes not requiring sulfur would be expected since cases (A), (B) and (C) correspond to a net deficit in supplies for the continental U.S.

It may seem somewhat of a contradiction to have an M.D.V. for abatement S if none is assumed to be recovered in useful form, as in cases (A), (B) and (C). However, the M.D.V. applies, conceptually, to the first units of abatement S that would be recovered in useful form.

For 1980, case (D) suggests an M.D.V. only slightly less than for cases (A) - (C) in both regions. However, a marked difference should be noted for case (E). Here, a marginally lower value is estimated for the Tampa region while an indeterminately low value is estimated for the Chicago region. The explanation is that abatement sulfur has hardly changed the net demand of the Tampa region whereas, in case (E), it has produced a condition of gross oversupply in the Chicago region, namely a net demand of minus 0.14 million LT. Because of general conditions of oversupply corresponding to case 1980 E, no extra-regional outlet is envisaged for the Chicago region's surplus of 0.14 million LT.

The drop off in estimated M.D.V.'s for the Tampa region is attributable not to the small quantities of abatement S in useful form assumed to be produced within the region but to the corresponding quantities produced in other regions.

For the year 2000, it will be seen that both cases (D) and (E) represent a surplus of supply over demand in the Chicago region. In spite of this, significant M.D.V.'s are estimated for both cases. The explanation is that, in contrast to the 1980 cases, extra-regional outlets for Chicago

region sulfur are anticipated, i.e., the Chicago region is expected to be an "extra-regional supplier" by the year 2000. Nevertheless, if the percentage of abatement S recovered in useful form were to be only slightly greater than in case (E)-- e.g., 60% instead of 50% in useful form -- then the Chicago region would become grossly oversupplied and the estimated value of abatement S in useful form would be indeterminately low.

RELATIVE VALUES OF SULFUR RECOVERED IN ACID AND ELEMENTAL FORMS

U.S. consumption of sulfur is mostly in the form of acid. Thus, recovered sulfur has a different value depending on whether it is recovered as acid or as elemental sulfur. Theoretically, acid has the higher value because it means that the customer does not have to bear the cost of manufacturing it. However, the cost of transporting acid is at least three times as great as for elemental S per ton of S-value. In consequence, the greater value of recovering acid rather than elemental sulfur is critically dependent on assured, local markets for all of the acid produced. Unless these conditions are fulfilled, the value of acid may be low and may even be negative. Elemental sulfur can be stockpiled; in most cases at small cost. Sulfuric acid can not be stockpiled.

At the end of 1965, just over half of U.S. sulfuric acid capacity was in 6 states: Florida, Texas, New Jersey, Illinois, California and Louisiana. Today, the industry is even more concentrated on the Gulf Coast and in Florida, with a relative loss of capacity in the Midwest. The geographical trends reflect the importance of Florida's pebble phosphate deposits and the development of chemical industry on the Gulf Coast.

Most of the acid used to manufacture P fertilizers is produced captively. This is true of a significant percentage of industrial acid

as well. Some of the acid manufacturers also have captive production of S values. This applies not only to the special case of acid recovered by smelters but also to combinations of:

- Frasch S production and P fertilizer manufacture.
- S recovery from oil-and-gas operations and P fertilizer manufacture.
- S recovery by chemical companies and manufacture of industrial acid.

The structures and geography of the elemental sulfur and acid industries will make it difficult for abatement acid to enter the market. The willingness of existing acid marketers and captive users to offtake abatement acid is necessary if a significant outlet is to be developed. The incentives for such offtake have not been clearly established. Currently the acid manufacturers, particularly those who merchant industrial acid, stand to benefit if abatement S were to enter the market in elemental form but to lose if entry were to be as acid. On the other hand, a significant amount of old acid plant capacity is being shut down and this may provide opportunities for abatement acid to enter the market.

The acid equivalency credit, discussed in the computer program, is a device making it possible to deal with both acid and elemental sulfur in the same calculation. The credit was changed with time to reflect the difference between:

- (a) having to shut down existing acid manufacturing capacity in order to be able to purchase merchant acid
- and (b) purchasing acid incrementally rather than building new acid manufacturing capacity.

The structure of the U.S. sulfuric acid industry suggests that, near term, it will be essential for many power stations to recover or remove sulfur in forms other than acid. The market for SO_2 is small, and that for ammonium sulfate is declining. Hence, apart from using low sulfur fuels (if available), the only broadly applicable choices appear to be elemental sulfur and waste gypsum. This is not to say that acid recovery systems will not be useful, but it does say that the larger part of the current problem will require another solution.

TABLE 1
FORECAST BASIS

• Supply

- (1) PROJECTIONS OF : (2) CONSTANT \$ GNP
- (3) POPULATION
- (2) GNP/ENERGY CORRELATION + (2) → (5) ENERGY FORECAST
- (6) NUCLEAR AND HYDRO ENERGY FORECASTS
- (5) - (6) → (7) FOSSIL FUEL ENERGY FORECAST
- (8) BREAKDOWN OF FOSSIL FUEL ENERGY BY SOURCE
- (7) & (8) → (9) NATURAL GAS FORECAST
- (10) PETROLEUM FORECAST
- (11) COAL FORECAST
- (12) NATURAL GAS SULFUR CONTENT & (9) → (13) NAT. GAS S RECOVERY POTENTIAL
- (14) PETROLEUM SULFUR CONTENT & (10) → (15) PETROLEUM S RECOVERY POTENTIAL
- (16) COAL SULFUR CONTENT & (11) → (17) COAL S RECOVERY POTENTIAL
- (18) % RECOVERY IN USEFUL FORM FROM NATURAL GAS
- (19) % RECOVERY IN USEFUL FORM FROM PETROLEUM
- (20) % RECOVERY IN USEFUL FORM FROM COAL
- (13) & (18) → (21) S RECOVERED FROM NATURAL GAS
- (15) & (19) → (22) S RECOVERED FROM PETROLEUM
- (17) & (20) → (23) S RECOVERED FROM COAL
- (24) PROJECTION OF S RECOVERY FROM SMELTERS, PYRITE AND OTHER SOURCES
- (25) PROJECTION OF FRASCH S AVAILABILITY
- (21) & (22) & (24) & (25) → (26) TOTAL S SUPPLY (EXCLUDING STOCKPILES)

• Demand

- (27) POPULATION & GNP PER CAPITA/FERTILIZER S DEMAND/RELATIONSHIPS
- (2) & (3) & (27) → (28) FERTILIZER S DEMAND
- (29) GNP/INDUSTRIAL S DEMAND CORRELATION
- (2) & (29) → (30) INDUSTRIAL S DEMAND
- (28) + (30) → (31) TOTAL S DEMAND

• Supply/Demand Balance

- (31) - (21) - (22) - (23) - (24) → (32) NET FOREIGN DEMAND, INCLUDING ABATEMENT S BUT EXCLUDING FRASCH SUPPLY
- (31) - (21) - (22) - (24) → (33) U.S. NET REGIONAL DEMAND, EXCLUDING FRASCH SUPPLY AND ABATEMENT S

Note: The symbol & signifies the joint consideration of one factor with another, not a simple arithmetic sum of the factors.

TABLE 2

ILLUSTRATION OF U.S. SULFUR SITUATION IN 1980

● Continental U.S.

	<u>Million LT</u>
Fertilizer S Demand	7.1
Industrial S Demand	<u>6.7</u>
Total S Demand	<u>13.8</u>

● Demand in Representative Regions

	<u>Chicago</u>	<u>Tampa</u>
Gross Demand	1.66	3.19
Regional Supply (excl. Abate. S)	<u>0.59</u>	<u>0.10</u>
(A) Net Regional Demand	<u>1.07</u>	<u>3.09</u>

● Illustrative Cases of Abatement Supply

<u>Total SO_x Emitted</u>	<u>% of Abate. S In Useful Form</u>	<u>Quantity of Abate. S In Useful Form (10⁶LT)</u>	
(B) Same as 1970	None	N11	N11
(C) 40% Less Than 1970	None	N11	N11
(D) Same as 1970	50	0.49	0.02
(E) 40% Less Than 1970	50	1.21	0.06

● Net Regional Demand After Inclusion of Abate. S in Useful Form (10⁶ LT)

(B), (C)	1.07	3.09
(D)	0.58	3.07
(E)	-0.14	3.03

● Estimated Maximum Delivered Value (M.D.V.) for Abate. S (\$/LT)

(A), (B), (C)	26	23
(D)	25	22+
(E)	Indeterminately Low	21

Note: Estimates of Value are in 1970 constant dollars.

TABLE 3

ILLUSTRATION OF U.S. SULFUR SITUATION IN 2000

● Continental U.S.

	<u>Million LT</u>
Fertilizer S Demand	11.0
Industrial S Demand	<u>14.2</u>
Total S Demand	<u>25.2</u>

● Demand in Representative Regions (Million LT)

	<u>Chicago</u>	<u>Tampa</u>
Gross Demand	3.53	4.20
Regional Supply (excl. Abate. S)	<u>2.92</u>	<u>0.30</u>
(A) Net Regional Demand	<u>0.61</u>	<u>3.90</u>

● Illustrative Cases of Abatement Supply

	<u>Total SO_x Emitted</u>	<u>% of Abate. S In Useful Form</u>	<u>Quantity of Abate S In Useful Form (10⁶LT)</u>	
(B) Same as 1970		None	Nil	Nil
(C) 40% Less than 1970		None	Nil	Nil
(D) Same as 1970		50	2.35	0.13
(E) 40% Less than 1970		50	3.50	0.20

● Net Regional Demand After Inclusion of Abate. S in Useful Form (10⁶ LT)

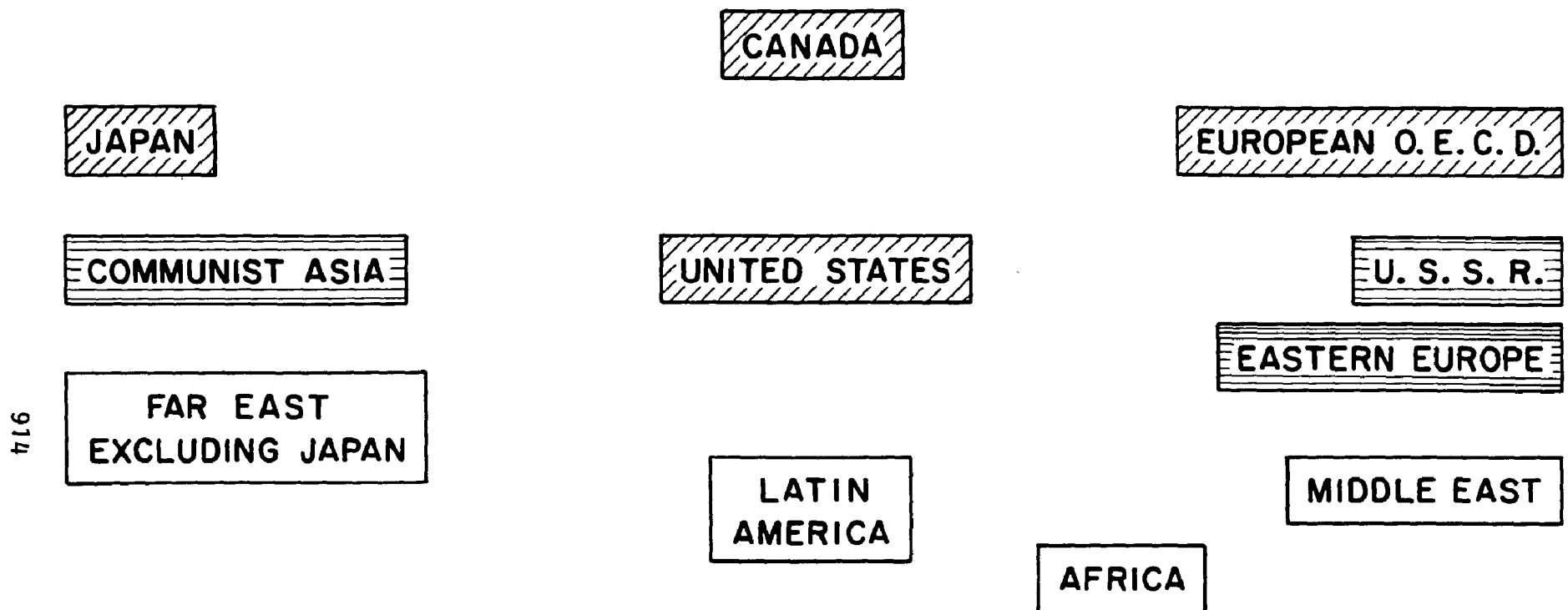
(B), (C) Same as Base Case (A)	0.61	3.90
(D)	-1.74	3.77
(E)	-2.89	3.60

● Estimated Maximum Delivered Value (M.D.V.) for Abate. S (\$/LT)

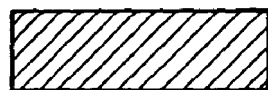
(A), (B), (C)	31+	30+
(D)	26	29
(E)	21	28

Note: Estimates of Value are in 1970 constant dollars.

Figure 1
WORLD MODEL



LEGEND



ORGANIZATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT



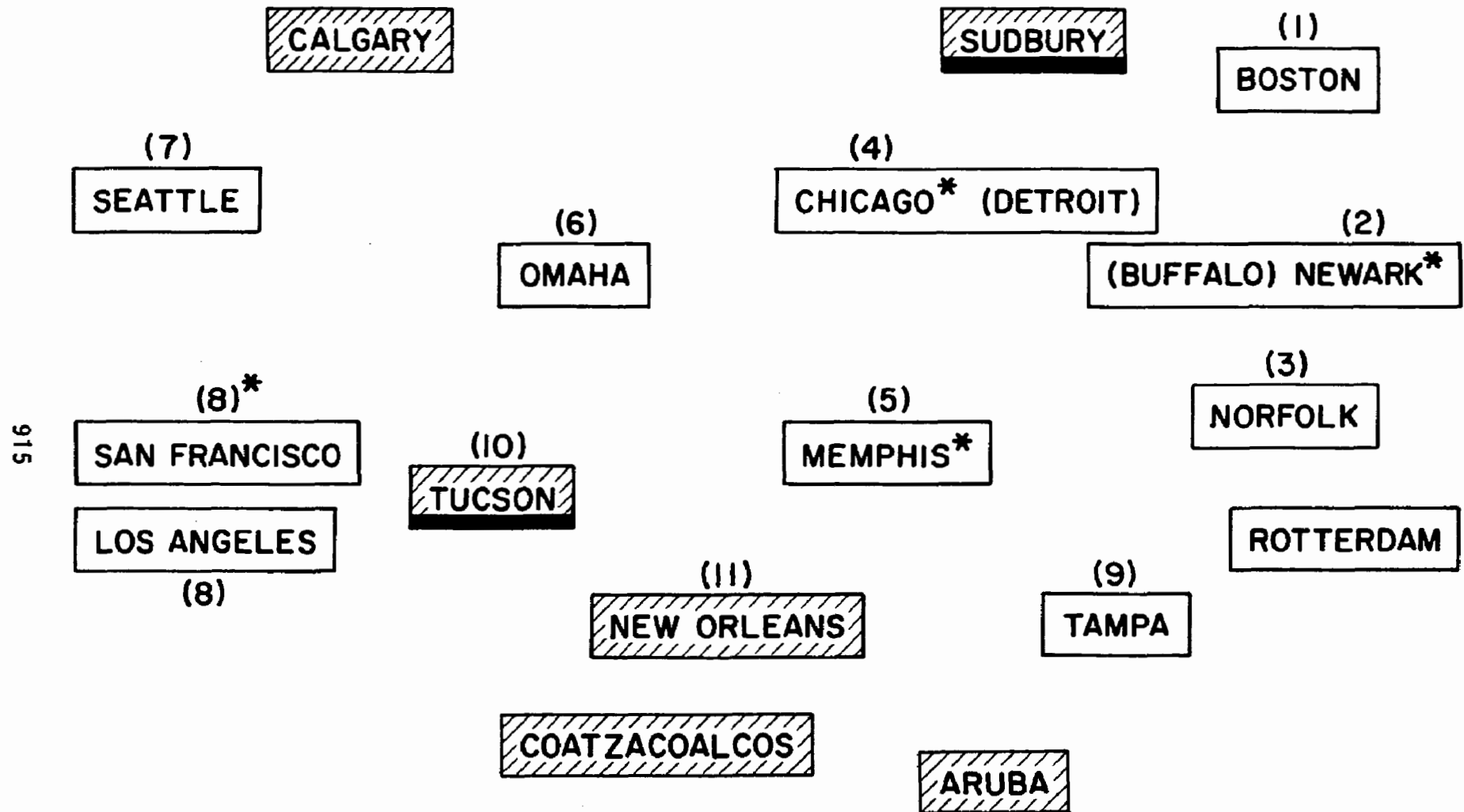
COMMUNIST COUNTRIES



"DEVELOPING FREE WORLD"

Figure 2

NORTH AMERICAN MODEL



LEGEND

- (1) - (11) DESIGNATE U.S. REGIONS
 * SOURCE OF "EXTRA-REGIONAL SUPPLY" IN LATER YEARS OF FORECAST
 () SUB-REGIONS

EXTRA-REGIONAL SUPPLIER

ACID SUPPLIER

Figure 3
U.S. REGIONS

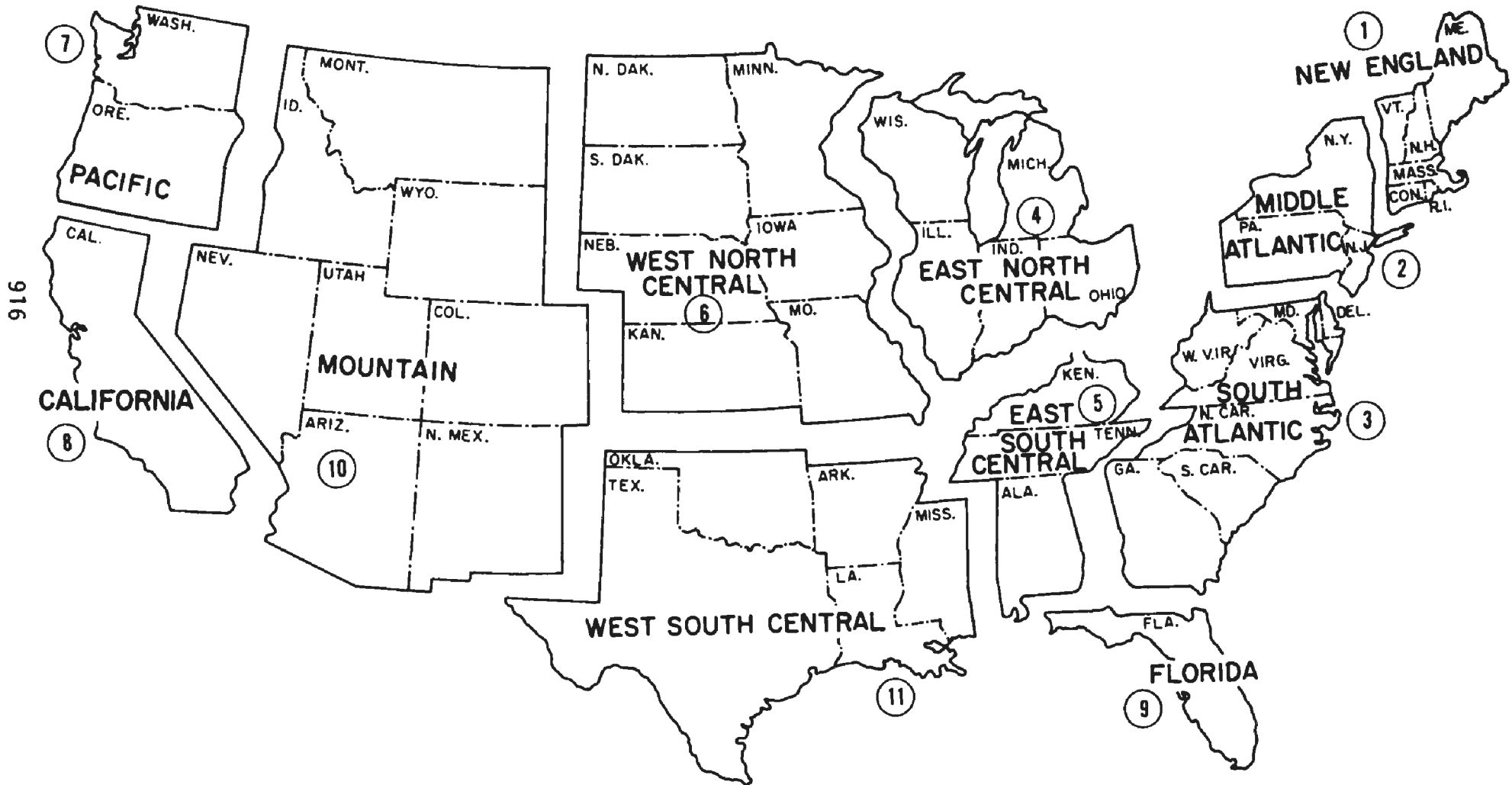


Figure 4
COMPUTER CALCULATION

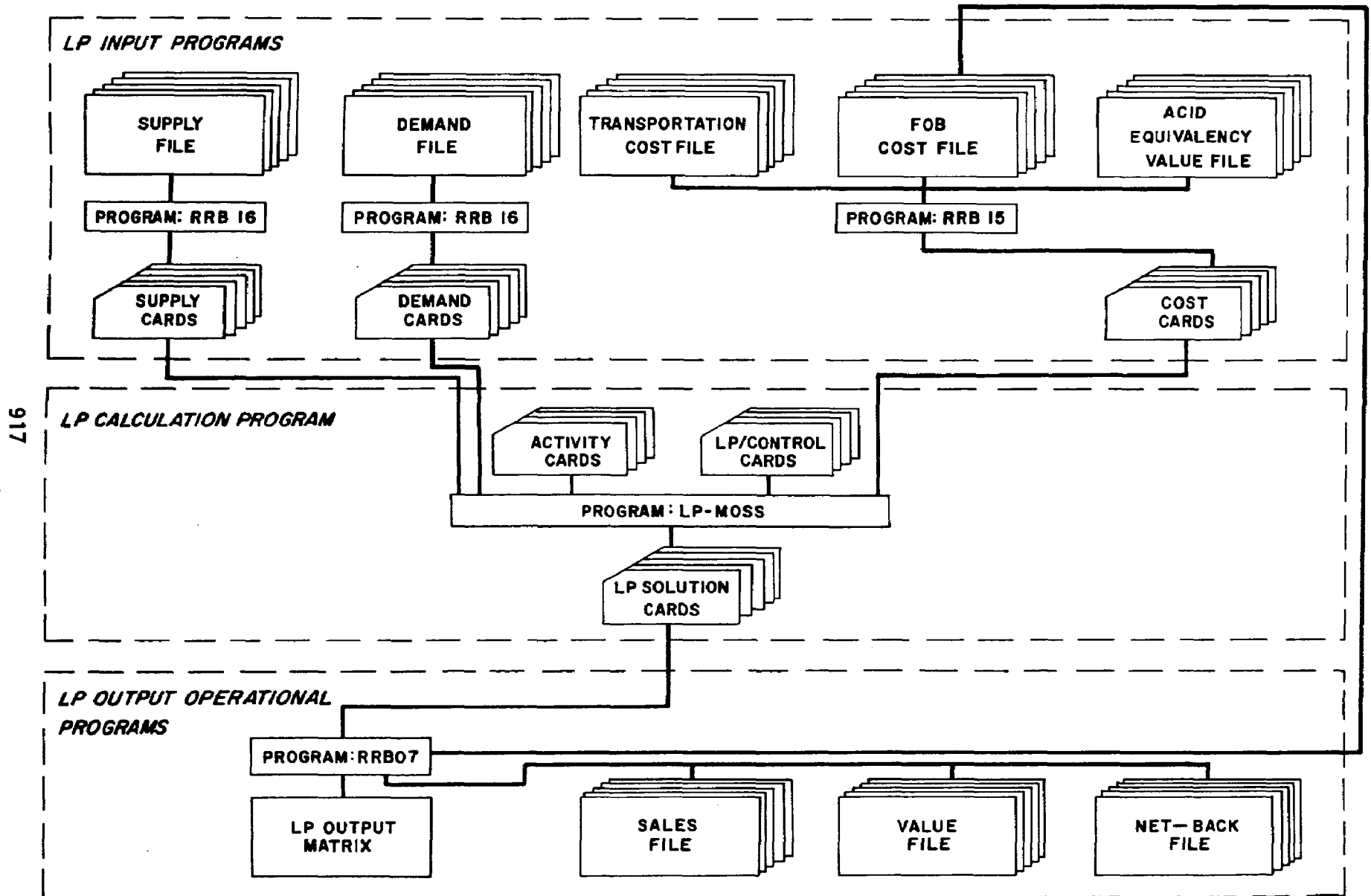


Figure 5

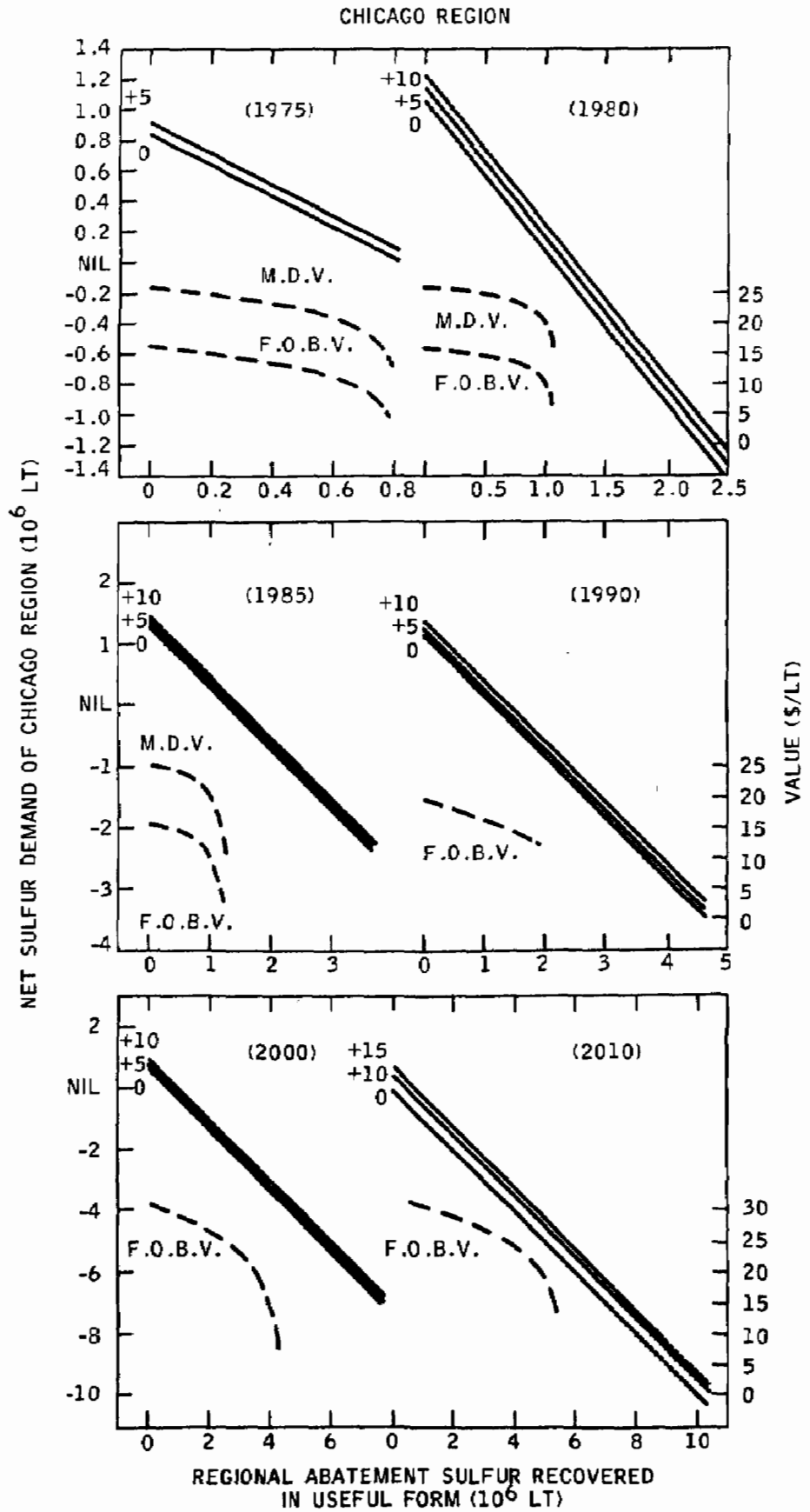
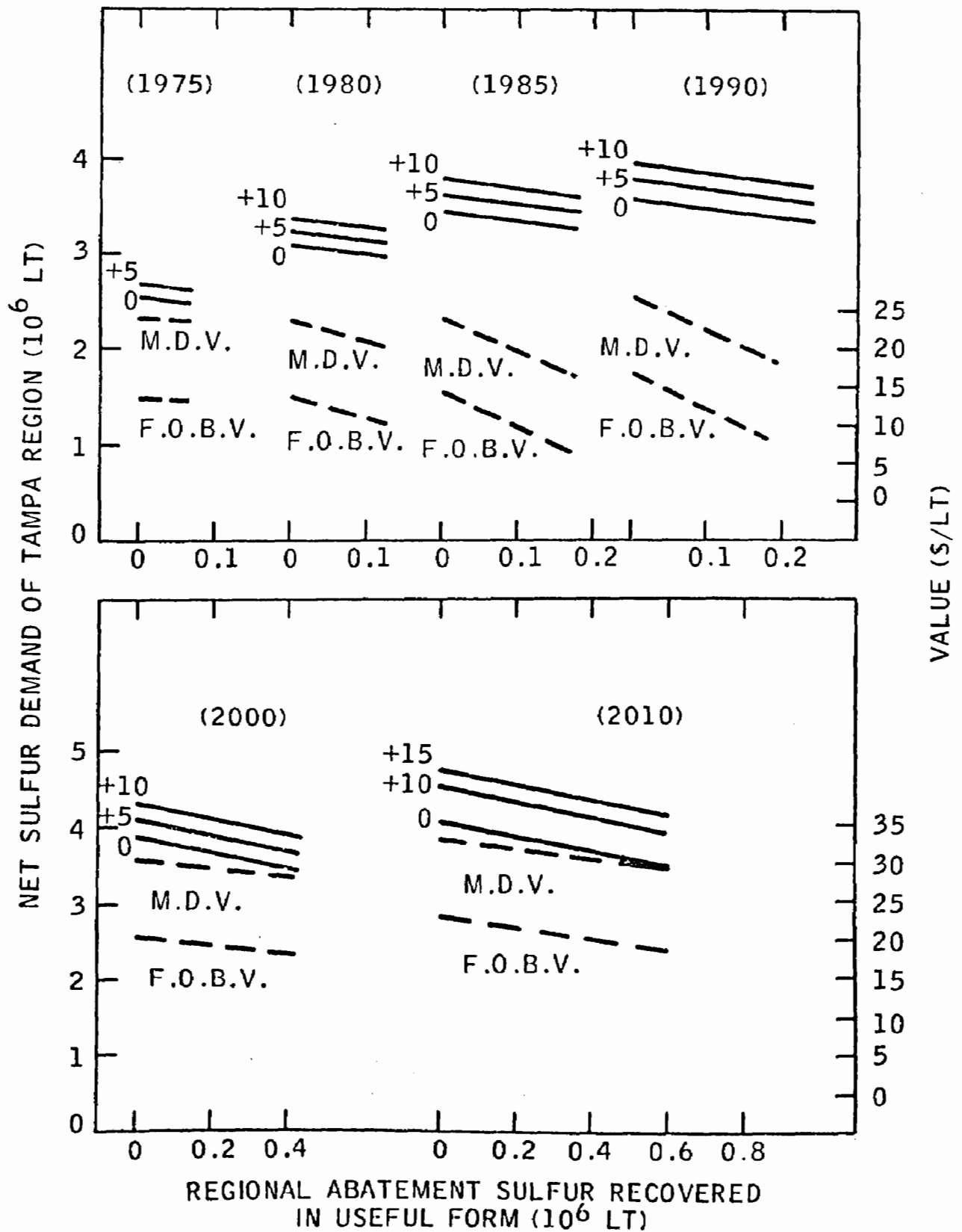


Figure 6
TAMPA REGION



NEW USES FOR SULFUR-
THEIR STATUS AND PROSPECTS

by

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New Uses for Sulfur - Their Status and Prospects¹

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Introduction

From statements and forecasts on the energy needs of our nation and the means available to fill these needs, it appears certain that high-sulfur coal will continue to play an important part in the foreseeable future. The Air Quality Criteria which are now being enacted and which are due to be fully implemented by 1977 make it equally certain that all of the sulfur content of this coal will not be allowed to escape into the atmosphere. Thus, it appears highly probable that large tonnages of sulfur will be recovered in one way or another from high-sulfur coal.

Two approaches are presently considered possible to prevent sulfur oxide emissions from coal: stack gas scrubbing and coal gasification.

The majority of the stack gas scrubber technologies near commercialization recover the sulfur values as gypsum or sulfuric acid. While these are acceptable intermediate term solutions, the problems associated with spent gypsum disposal and the general transportation and marketing problems with sulfuric acid make them unattractive and even unacceptable over the long run. Recovery as elemental sulfur appears to be the ultimate solution, from the point of view of marketing, storage, and transport of the product. Also, the processes under development for coal gasification generally recover sulfur in the elemental form. The following discussion is therefore restricted to the question of finding a market for the elemental sulfur recovered from coal as a result of air pollution abatement regulations.

The Magnitude of the Problem

Let us first put the recovered sulfur in perspective in relation to tonnage, time, and cost. It is unlikely that large tonnages of sulfur from stack gas scrubbers or coal gasification will reach the market before the 1980's. The first demonstration plants for recovery of elemental sulfur have recently been completed or are still under construction. It is likely that they will have to operate successfully for a year or two before the technology achieves general commercial acceptance. This will then be followed by an estimated three-year period between placing the order and full operation. However, by the mid-eighties it is quite conceivable that 500 million tons of high-sulfur coal per year will be consumed in the U.S. in power stations and/or coal gasification plants equipped with scrubbers recovering sulfur. Assuming an average sulfur content of 3%, about 15 million tons sulfur per year could theoretically be recovered.

The disposal of this amount of sulfur becomes of considerable economic importance. If it can be sold at a price of \$25/ton f.o.b. the

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power plant*, the U.S. utilities industry could realize an annual income of about \$375 million, to set off against the capital and operating costs of desulfurization equipment. Conversely, if no market exists for this sulfur, the storage of large quantities in heavily populated areas may cause its own pollution problems. Furthermore, the costs associated with storage of sulfur could amount to \$2-\$5 per ton per year--representing an additional cost to the industry.

The Sulfur Market

What are the possibilities of marketing the large quantities of sulfur which will be recovered from stack gases or coal gasification? To answer this, let us look at the present and probable future situation.

In 1972, Free World production of elemental sulfur reached 21 million tons. This exceeded consumption by over 1 million tons. In addition, nearly 2 million tons were imported from communist countries and, as a result, sulfur inventories increased by over 3 million tons.

Over half of the sulfur presently produced is recovered from natural gas or petroleum. The demand for natural gas and low-sulfur petroleum products will accelerate the recovery of sulfur from these sources.

The traditional uses of sulfur, that is, in the fertilizer, chemical, and other industries, are not expected to grow at an average of more than 4-5% annually. Most forecasts agree that production of recovered sulfur will grow at rates considerably in excess of this. Thus, even without any sulfur from coal, the oversupply situation can be expected to continue in the 1980's. If recovery from stack gas or coal gasification reaches the estimated levels, sulfur production in North America in the mid-1980's would outstrip consumption by a substantial margin.

Under these circumstances, the majority of utilities would be unable to sell substantial quantities of their recovered sulfur in the market.

New Uses

There are new, potentially high-tonnage uses for sulfur which, if developed commercially, can absorb the sulfur that will have to be produced if the current air quality standards are to be met. In the remainder of this paper, we will discuss with you the more promising of these new uses.

A word here about the agricultural uses of sulfur. Sulfur is essential in plant and animal nutrition, and is valuable as a soil amendment and pesticide. The Sulphur Institute is working actively with agricultural scientists and the fertilizer industry to promote and develop the uses of sulfur in agriculture. The potential market for these uses in the U.S. is estimated at between 1.5 and 2 million tons per year above the present use, but as this is, strictly speaking, not a "new" use but an expansion of an existing one, we will not discuss it further in this paper.

*This figure is given for illustrative purposes only and does not imply a recommendation or forecast of the sulfur selling price.

To alleviate the supply/demand imbalance and to be commercially acceptable, a new use for sulfur should ideally satisfy the following criteria:

1. The potential tonnage use, realistically assessed, must be large, at a minimum several hundred thousand tons per year.
2. The time and cost needed to develop the use must be reasonable.
3. The economics should be favorable, to attract industry interest and capital.
4. The new use must be ecologically acceptable, i.e., it must not create any pollution problems of its own.

The Sulphur Institute has carefully considered a great number of possible new uses for sulfur and its compounds, including sulfuric acid and sulfur dioxide. Those uses which in one way or another utilize the mechanical properties of elemental sulfur appear to have merits which match these criteria most closely. Our discussion here will be limited to these uses.

Pure elemental sulfur is familiar to most people as a rather brittle, yellow solid. However, it has a number of interesting mechanical properties, not all of which are, as yet, fully understood. These properties are dependent upon the time-temperature history of the sulfur and can be greatly modified by additives. Conversely, when sulfur is added to or incorporated into other structural materials, the mechanical properties of these materials are often improved.

The following examples will demonstrate some of the commercially interesting utilizations of these properties.

Sulfur-Asphalt Paving Materials

Processes for improving the properties of asphalts by treatment with sulfur were first introduced over 100 years ago, but have generally not become commercially successful. Most of this early work had as its objective to chemically react sulfur with asphalt. The new technology described below relates to the physical addition of sulfur to asphalt-aggregate mixtures. Chemical reaction between the sulfur and asphalt is deliberately minimized to prevent the evolution of H_2S which generally accompanies the reaction of sulfur with hydrocarbons.

The composition of sulfur-asphalt paving materials varies considerably, but a typical material consists of about 13% sulfur, 6% asphalt, and 81% sand, by weight. This material is interesting for two reasons:

1. It has certain technical advantages over conventional paving materials. In general, addition of sulfur to asphalt paving material can increase durability, strength, and resistance to water. Also, there are indications that the material may be particularly suitable for direct application on weak subgrades, without prior excavation and backfilling.
2. In many areas of the country (Gulf Coast region, Pacific Northwest, Great Lakes region) good quality aggregate is becoming scarce and increasingly expensive. Sulfur-asphalt permits the use of low-cost, widely available sand instead of aggregate.

The composition and cost of sulfur-asphalt paving materials compares with those of conventional asphalt paving materials approximately as follows:

	lbs/cu ft	% by wt	% by vol	cost ¢/cu ft
<u>Conventional asphalt material*</u>				
Asphalt	8	6	13	14
Aggregate, crushed & screened	135	94	81	27
Air voids	--	--	6	--
Total	143	100	100	41
<u>Sulfur-asphalt material*</u>				
Asphalt	8	6	13	14
Sulfur	17	13	14	21
Sand	105	81	65	2.5
Air voids	--	--	8	--
Total	130	100	100	37.5

*Assuming asphalt at \$35/ton, aggregate at \$4/ton, sand at \$0.50/ton, and sulfur at \$25/ton.

There are indications that it may be feasible to use lower grade asphalts in the sulfur-asphalt mix. This would further improve the economics of this material.

Approximately 22 million tons asphalt are used each year in the United States for road building. For the non-communist world as a whole, the corresponding figure is about 45 million tons. Any sizable penetration of sulfur-asphalt into this market clearly could consume multi-million tonnages of sulfur.

Further work is needed in several areas before sulfur-asphalt paving materials can become a commercial reality. Although H_2S formation during manufacturing and transport does not appear to be a problem, it must be studied further before the technology is released for general use. Durability comparisons of sulfur-asphalt with conventional materials require considerable time, and the introduction of new paving materials into general use is often a slow process.

The most extensive work on sulfur-asphalt paving materials has been carried out by Shell Canada, Ltd., in British Columbia and Ontario. Trials have also taken place in France, Japan, and Scandinavia. The Sulphur Institute has recently concluded an agreement with Shell whereby the development of sulfur-asphalt pavements in the U.S. will be carried out under a joint government-private industry program. Initial development work is now under way at the Texas Transportation Institute, Texas A & M University. Following preliminary familiarization work this year, road tests are scheduled for 1974.

The sulfur-asphalt paving materials so far developed do not result in a decreased consumption of asphalt per unit of road. The existing and projected shortage of domestically produced petroleum may make it necessary to limit the consumption of petroleum products, including

asphalt, where satisfactory substitutes exist or can be developed. As large quantities of sulfur become available from increased use of domestic coal, a partial substitution of sulfur for asphalt would seem to make sense both from the national economy and ecology points of view.

There are indications that satisfactory sulfur-asphalt materials containing less asphalt may be possible. If the asphalt is eliminated completely, the result is a sulfur-sand concrete, and we will discuss this next.

Sulfur Concretes

Mixes of molten sulfur with sand and/or aggregate set on cooling to form concretes with properties equal or superior to those of Portland cement-aggregate concretes. Sulfur concretes set and reach full strength in a matter of minutes, as opposed to one or more days for the conventional materials. There is also the advantage that the large quantities of water required for conventional concretes are not needed.

Preparation of the mix is simple: the sand or aggregate (70% by weight) is pre-heated to about 325° F and sulfur (30%) is added. Mixing is continued until all the sulfur is melted and the mix is then poured, tamped, and left to harden.

Using this technique, tiles, blocks, bricks, and other structural elements have been produced. In 1972, part of an experimental house was built near Montreal by McGill University staff, using interlocking sulfur-concrete bricks, without mortar or other joining material. Reports indicate that the walls built using this technique are structurally sound and weatherproof.

Sulfur concretes may be particularly attractive in countries with no indigenous supply of Portland cement, but with a readily available supply of sand and sulfur. Northern Canada, western U.S., and several Middle Eastern countries fall into this category. Sulfur concretes may also have application in remote areas where the cost of casting and curing Portland cement concretes is excessive. Another potential use is as an emergency patching material for highways.

Sulfur concretes are at an early stage of development. Their eventual acceptance and the size of the market are matters for speculation. However, the potential market is very large if the technique is basically acceptable in housing and road construction. For example, building a 2-lane highway suitable for heavy traffic would require about 1,800 tons sulfur per mile.

Surface Bond Construction

Low-cost easily built structures can be erected by surface-bonding concrete blocks with a sulfur formulation. This technique has interesting potential applications in low-cost housing, storage buildings, silos, etc.

The sulfur-surface bond construction technique is simple both in concept and practice. It is applicable to structures utilizing lightweight concrete blocks or other block or block-like materials.

No mortar or joining material is used between the blocks; they are simply stacked dry, one upon the other, until the desired wall configuration is achieved. A thin single coating of molten mixture, consisting primarily of sulfur with small percentages of glass fibers and other additives, is applied over the outside and inside of the wall. Within seconds, the molten coating solidifies and forms a hard, impervious surface. If a color other than yellow is desired, pigments can be added to the formulation or the coating may be painted over with conventional house paint. Walls constructed using this technique are much stronger than walls using conventional masonry construction. In particular, sulfur surface bond-constructed walls have considerable strength in tension, whereas conventional masonry walls primarily show strength in compression and very little in tension.

Using this technique, a building was constructed in 1963 at the Southwest Research Institute, San Antonio, Texas. Unskilled labor with no previous experience in applying hot coatings of this type carried out the work, using regular paint brushes to apply the sulfur.

Concrete block walls are highly porous and must be properly sealed after installation. At the Southwest Research Institute, there are conventional concrete block buildings, some of which are more than 15 years old, which have required sealing, caulking, and re-sealing from time to time, and still leak when subjected to a hard driving rain. No leaks have ever occurred in the sulfur building, nor have any cracks developed. The building has not presented any problems and as a consequence has not received any maintenance. No cracking, spalling, or other deterioration of the sulfur coating has occurred.

The performance of the sulfur building over a period of ten years under the climatic conditions prevailing in San Antonio has convincingly demonstrated the practicability of the technique. Another sulfur-surface bond building was recently completed at the U.S. Bureau of Mines research facility at Boulder City, Nevada, using recently developed spray equipment to apply the sulfur-fiber formulation.

The difficulty and cost involved in changing building codes and practices probably preclude the near-term use of the technique for human dwellings in the U.S. and other developed countries. However, it would appear to have considerable potential in the construction of warehouses, utility buildings, silos, and similar structures. A proposal to evaluate the technique in Latin America and Africa has been accepted in principle by U.S.A.I.D. The economics of the technique appear favorable, and the advantages of higher strength and improved water resistance should make it attractive in many applications.

Sulfur as a Coating Material

Sulfur formulations similar to those used in surface bond construction are being tested as low-cost coating and repair materials. Sulfur coatings can provide both chemical (corrosion) and mechanical (erosion) protection. For coatings of maximum mechanical strength, glass or other fibers are added to the formulation, but in many cases this can be dispensed with and coatings consisting essentially of sulfur with small amounts of organic modifiers can be used.

Sulfur coatings are being evaluated or considered for a number of applications: protection of concrete structures in corrosive environments, stabilization and erosion control of earthworks and storage ponds, and stabilization of mineral tailings piles.

Sulfur is also being evaluated as a repair material for cracks in Portland cement and asphalt concretes, for example, in roads, airport runways, and swimming pools. Several federal agencies recognize that inexpensive coatings and repair materials can fill an important need, and are investigating various applications.

A different, but potentially very important application of sulfur coating relates to its use in fertilizer technology. In particular, sulfur-coated urea (SCU) shows signs of becoming commercially accepted for use on a number of agricultural crops in several regions. By coating urea with sulfur, the dissolution rate of this nitrogen fertilizer is considerably reduced. This results in more efficient utilization of the nitrogen by plants and reduced loss of nitrogen to the environment by leaching and run off. Many other methods of providing slow-release nitrogen have been suggested, but SCU appears to be the only one that is cheap enough for general use. The Tennessee Valley Authority has been pioneering the development and testing of SCU, and is presently considering the construction of a full-scale plant. A typical SCU product contains about 10-15% sulfur. With world production of urea for fertilizer use at about 15 million tons annually, this clearly represents a considerable outlet for sulfur.

Sulfur Impregnation

Ceramic and other porous materials can be impregnated with sulfur, thereby improving the chemical resistance and the mechanical properties of the material. Bonded abrasive grinding wheels impregnated with sulfur have improved strength; the sulfur also acts as a lubricant and coolant during grinding. Sulfur impregnation of ceramic tiles results in lower water adsorption, making the tiles frost resistant for external applications. Impact and compressive strengths are also improved. Corrosion of concrete sewer pipes is a serious problem in many localities. Impregnating the pipes with sulfur has been estimated to extend the life of the pipe by a factor of 10, and to double the flexural strength.

Impregnation of ceramic and concrete materials is generally carried out by immersion in molten sulfur. Use of vacuum to remove air from the pores of the material prior to immersion in the sulfur speeds the rate of impregnation.

Research and development on sulfur impregnation is in its infancy. Potential applications are numerous, particularly in building and construction.

Sulfur Foams

Using small amounts of additives, sulfur can be turned into a foam with interesting properties. The foamed sulfur is lighter than water (typical densities are in the range 0.2-0.5); the compressive strength is in the range 50 to several hundred psi, higher than typical organic polymer foams. The foam shows excellent thermal insulation properties.

One promising application of foamed sulfur is as a sub-base for highways and airport runways in cold climates. Polystyrene foams are being used experimentally to prevent freeze and thaw damage to highways and runways, replacing costly and unreliable methods like deep sub-base beds of stone or gravel. Foamed sulfur is being evaluated as an alternative to polystyrene foams in this application. One inch of polystyrene or sulfur foam is equivalent in insulating value to 24 inches of gravel. Sulfur foams have higher compressive strength than polystyrene, they are less expensive and can be foamed in place. Construction of a 1,000-mile, four-lane highway would require about 400,000 tons of sulfur.

Several other potential applications of sulfur foams are being investigated.

Conclusions

By the early 1980's, it is probable that large tonnages of sulfur will become available from utilization of high-sulfur coal through stack gas scrubbing, coal gasification, or both. These tonnages, when added to those resulting from other sources, will be considerably in excess of sulfur demand. Because the electric utilities will be producing sulfur at a large number of locations often unfavorably situated for the sulfur markets, disposing of this sulfur in an oversupplied market can be expected to be initially difficult, and eventually impossible. Stockpiling the recovered sulfur would impose an added financial burden on the industry. However, if new uses were developed, this sulfur could be marketed, resulting in added income for the industry, partly offsetting the cost of desulfurization.

The potential new uses outlined above, could, if developed commercially, absorb the foreseeable supply of sulfur. They fulfill the criteria stated earlier to the extent that they are large-volume uses and they are ecologically acceptable. They also appear to have favorable economics, and the time and cost needed for commercial development do not appear excessive.

It would be wishful thinking, however, to expect these new end-use markets to materialize automatically, or that their development will be eagerly undertaken by private industry. In most cases, the potential financial rewards will be insufficient to entice firms which do not have an interest in sulfur or fuels to commit funds. Up to now, the burden of supporting the development of new uses for sulfur has been carried by the main suppliers of sulfur, i.e., the Frasch producers and the oil and gas companies. As new sources of sulfur become increasingly important, the originators of the new supply will have to bear a portion of the burden to develop the new uses needed to absorb this increased production. Several federal agencies, notably the U.S. Bureau of Mines, have recognized the implications of cutting down the emission of sulfur oxides and are actively sponsoring or cooperating in sulfur development programs. The electric utilities industry, potentially the largest sulfur supplier in the country, has a special responsibility in this regard. Although large-scale sulfur production by the utilities may be several years in the future, now is the time to research and develop the needed markets. We invite the utilities industry, in its own interest, to actively support sulfur development work, either through the Edison Institute, through cooperative programs with Federal agencies, or through The Sulphur Institute.

PANEL DISCUSSION:

DISPOSAL AND USES OF BY-PRODUCTS
FROM FLUE GAS DESULFURIZATION PROCESSES

PANEL DISCUSSION

A. V. Slack (TVA)— We have had an extended discussion of about all the problems we can think of in regard to disposing of the products that we will be making when we go extensively to recovery or to ridding stack gases of the sulfur compounds. We now have our panel assembled, including Mr. Fike (H. L. Fike - The Sulphur Institute) co-author of the last paper; so we are ready for any questions that either the panel or the audience may wish to pose. I would like to ask Dr. Minnick (L. J. Minnick-IU Conversion Systems) and Bill Taylor (W. C. Taylor - Combustion Engineering) a question. If we are able to convert the sludge to useful construction products (and it seems quite obvious that we can) what proportion of our sludge production do you think that we could ultimately (say, within 10 years) convert to this useful purpose?

L. J. Minnick— I do not think I can project the finished statistics. I think that I would like to comment to this extent. The utilization of the technology which was described and illustrated is something that is here. It is our mission, as far as IUCS is concerned, to take on projects as they develop and really turn out to be the garbage man, to take the problem off the hands of the utility entirely. That is our mission so that they are not involved with the running of chemical plant or process. Now the thing that dictates whether or not it is a good idea to do it, of course, is the economics; and the answer to your question really is that each situation has its own logistics. If you are going to consider stockpiling aggregate and you have a place to stockpile it in an ecologically safe way, fine. If there is a market for aggregate, you may sell enough

of it to justify some costs. If it is simply disposal of a product that's going to be put into a landfill or land improvement project, what land improvement project or what kind of land is available? If you are near a strip mine and you want to rehabilitate it, then it makes a lot of sense. We have looked at a lot of projects across the country. Now as I say, I can not give you a statistical number; but I can assure you that many, many of the situations that are opening up in the southwest and eastern United States do lend themselves to the conversion system approach. The quantities of materials that are involved, the very fact that there is lot of it, make it much more economical. If someone says that we have one million or two million tons of material to convert a year, it makes a lot more sense than if you are just handling a small quantity. So what the exact amount is, I can not answer that.

A. V. Slack— All I was looking for was a guess.

W. C. Taylor— Well, I agree with John (Minnick) in that the question bears on many factors; but I see no reason why you could not use 100 percent of the sludge. I said in my talk that in Germany now they use 80 percent of all the flyash that they manufacture. About 80 percent of all of the construction of say less than 8-story buildings in Europe now has a lot of the flyash in it; they are now digging up some of the flyash that they buried to use in construction. But there are many factors in this country that will determine whether or not we use large quantities of the stuff. In my slide, I mentioned my one brief moment of glory when we had thought that in the laboratory we had proved the technical feasibility of utilizing this material in a number of areas. Several different useful products pertained to building and highway con-

struction. If you used it in sub-base for highways, you could use all the material. If you look at the highway building program, you can see that we use about 15 billion tons of stone in this country every year for construction. But, like we said, the flyash brick that the University of West Virginia came up with was supposed to be economic and it was cheaper than the clay. It was lighter and cheaper to ship. Structurally, it was sounder. Everything was better than the clay brick; but, you could not get anyone to buy it. You could not get anyone to put up a plant to make it. So this is the problem you have — the old inertia. A guy has been getting his clay brick from a distributor for years. He has established his rapport. He is not going to change all of a sudden just because you say, "Look, I've got some bricks and I can give you 2 cents off per brick." I think it is a big marketing problem. Frankly, we are now looking at some throwaway processes because we feel that, until the marketing problem is solved, we will be throwing it away in the beginning. But if someone has a lot of money and wants to make a lot more money, we have a lot technically proven processes that he can use and he can start buying some sludge.

A. V. Slack— Are there any questions that the panel members now would like to put to each other?

J. Ando(Chuo University)— May I ask a question of Mr. Minnick? I think the use of the sludge for road construction is a very good thing. I must say I have English trouble and I am afraid I may not understand you, but would you say it is mainly a matter of our economy? I think, it is rather that if the material is very cheap and if its use is technically feasible, it is economically feasible.

L. J. Minnick— Well, first of all, as we look at it, we do not attempt to take credit for the sale of the product. We feel that the cost of

conversion is a disposal cost. Now one of the reasons that the aggregate is useful is that it can be stockpiled. It is important that the power plant stay on stream; it must run; and every minute of the day the sludge is coming out and you have got to do something about it. Now if you convert it to aggregate and stockpile it, in the construction season the stockpiles are depleted; when the construction season is off, like in the wintertime or something of that sort, you can still operate and just pile up the material. But whether or no you sell it is a function of the market. If you are in an area where there is lots of cheap aggregate, you're not going to sell it. If you are in an area where there is a depletion or shortage of aggregate, yes, you can sell and sell it at a profitable price. And again, it's the logistics of it, the individual situation. But in our approach to it, we are looking at it as a disposal charge and then these other things are credits that can come back and give you some economic trade-offs.

A. V. Slack— I have a question here from Bill Richardson of Bechtel who is concerned with about 6 million tons of gypsum that we import each year into this country. So the question is, "Do we need to import it since we have this great tremendous source of gypsum or we could make gypsum by oxidizing our sludge?" I do not know exactly who on the panel to address that to. Does anyone have any views on it?

W. C. Taylor— That was a question I was going to ask Dr. Ando because they seem to be very successful in Japan in utilizing the gypsum, and I think one of the things there is that there is a shortage of gypsum and it probably costs them a lot to export it. I look at his slides and see the equipment that has to be used to go from, say the sludge,

to get this 95 or >90 percent gypsum. Here you can mine 99 percent pure gypsum and you can float it down on a barge for practically nothing. It would cost, it seems to me, in this country about 5 times as much to get 90 percent gypsum from sludge as it would be to float it down at 99 percent. And unless we are talking reverse economics, I do not think even (though we are now looking at wallboard) that so far it looks like it is much more expensive to try to recover it than to just mine it.

J. Ando—Yes, I believe we agree that byproduct gypsum cannot compete with your pure cheap natural gypsum, it is true; but I think that in certain areas byproduct gypsum may be used because you are still importing some. And in Japan, until about 10 years ago, we had plenty of byproduct gypsum from wet process phosphoric acid production. No one used it and we were still importing because they had no experience using it; they thought the use of byproduct gypsum might give bad results for cement and plaster board. I worked in the field and made some reliability tests and showed it could be used, but no one believed it. Now all of them are using it and now we have a shortage of gypsum. Every bit of gypsum is now used. I think there is a similar situation in this country.

A. V. Slack—Of course, it does depend on what it costs to make this gypsum. Since there are various processes in Japan for making it, I suppose we really need an economic comparison. Now may we have questions from the floor.

John Salm (Pioneer Service & Engineering)—On the matter of gypsum, even the naturally occurring gypsum in the United States has various degrees of effectiveness when used as a moderator or regulator in the setting of Portland cement. I was wondering how much work has been done

on testing the gypsums that are formed in these various processes to see how reactive they are, how effective they are in actual use of Portland cement? I talked with Dr. Ando in the intermission; he indicated that it has been used successfully in Japan, but there have also been some problems with the use of the artificially produced gypsum. I just wanted to throw that out to find if there had been any actual research done in that regard over here?

J. Ando.—In Japan, phosphogypsum has been the problem if it can be used for cement or not. Until about several years ago, cement companies did not want to use it. The main reason is that some small amount of P_2O_5 (phosphoric acid) and also a fluorine hindered the cement setting. Since that time they have improved the process of the production of gypsum so that now the P_2O_5 in the gypsum can be reduced to below 12.1 percent and it can be used without any problem. Also many cement companies recently have tried to use byproduct gypsum from coal-fired boilers produced by Mitsui in Omuta by the Chemico and other processes: the Chiyoda process and the Mitsubishi-JECCO process. All of the byproduct gypsum can be used without any problem. The only problem is, if it contains too much moisture, it cannot be put into the cement mill; but if the moisture is about 11-12 percent or less it can be used without any problem. In the Mitsui case, if the flyash content in the byproduct gypsum is less than about 10 percent it can be used in cement.

Ken O'Brien (R. W. Beck).—I have two questions. The first one is to Dr. Minnick. I am wondering about the ratio of flyash to calcium sul-

fite or sulfate. Would you say that what comes out of an average coal-fired power plant is compatible to make these building products or is there likely to be a large surplus or a lack of one or the other? My other question is to anyone who can answer it. Assuming flyash is one of the products necessary to make a building product, what do you do on an oil-fired plant? Involved in a particular project, we are oxidizing to sulfate. It probably wouldn't do the job because the landfill would be under water.

L. J. Minnick—Both of those points were covered in the written portion of my paper. But very briefly, the answer is "yes" to your first question. For most coals (those with 3, 4, even 5 percent sulfur), assuming you have 8, 10, 12 percent ash, you have the right proportion. The only place where you get out of line is when you have a boiler that produces a very low flyash; such as the centrifugal or, what do you call it, cyclone boiler which produces most of the ash in the form of bottom ash. In this case, you are short of flyash. In connection with oil, the system that I presented depends on flyash; that's the magic ingredient. And if you don't have flyash available somewhere, you don't get the chemistry that was described.

Max Schmidt (The university of Wurzburg, Germany)—I want to ask Dr. Platou (J. S. Platou, The Sulphur Institute), the last speaker, just one question. You showed us very nice slides on the use of sulfur in the construction business. You showed us a house which was built in Texas about 10 years ago and another one just under construction in Montreal. Now you are talking about sulfur, talking about millions of tons of sulfur, but what do you mean by sulfur? It is not pure sulfur. Can you tell us something about the additives, the cost of the additives

compared with the elemental sulfur itself?

J. S. Platou — The sulfur mixtures, the sulfur formulations that we used in the surface bond construction used in constructing these houses are approximately 90 percent elemental sulfur. The remaining 10 percent is composed largely of fibers; glass fibers have been used mostly up to now and a very small amount of organic additives in an order of a few percent. Does that answer your question?

M. Schmidt — I did ask for the cost average of the organic additives or thiocols. What is the price of sulfur? Not what is the price of the additives.

J. S. Platou — Harold (Fike), do you want to comment on that? I would think that probably thiocols are not exactly what we would want to talk about now.

H. L. Fike — Over the years, Prof. Schmidt, we have looked at a good many additives. As you recall, we did use many of the thiocols, which cost roughly \$1.00 per pound 8 or 10 years ago. Now we have primarily concentrated on some unsaturated hydrocarbons, particularly the dipentene, the terpene-type products, the dicyclopentadienes. We have looked at various other crude aromatic unsaturated compounds which come from refineries, some of which are available for 8-10 cents per pound. We feel that if these additives are used in the amount of 3, 4, or 5 percent they will still represent a rather large portion of the costs of the sulfur coating. It will still be a coating which will be perhaps slightly less than most of the standard asphalt coatings and much less than the asphalt emulsion coatings. In some of the cases where we have used this, we have been more or less competing against the epoxy materials and, of course, there it was only a fraction of the cost.

A. V. Slack—Two of our panelists may have to leave early and I have a couple of questions I would like for them to cover. One to Jerry Rossoff (Aerospace Corporation) and again I am concerned with this dewatered sludge that we may produce and what happens to it when it rains? Have you gotten into that problem much, Jerry?

J. Rossoff—Well, we have some limited data and we are working with one sludge from the TVA Shawnee plant that shows it will absorb and re-absorb water and bloat and hold it. So as far as rain goes, if the sludge is not thick and you do not have any way to let it drain through and carry the water off, it will absorb the water again.

J. W. Jones (EPA) —I would like to make one comment on that. That particular material was allowed to settle naturally and then air-dried; isn't that right, Jerry?

J. Rossoff—Yes.

J. W. Jones—There was no compaction or any treatment, any physical treatment of it?

J. Rossoff—Right, there was no treatment whatsoever. It was allowed to dry out. And it will reach a saturation point and will hold so much and that is it, but it will regain water. I think that was the question; if it rains, it will pick it up and bloat.

A. V. Slack—And let me get one more question in to Mr. Farmer (M. H. Farmer, Esso Research) who may have to leave. In your model, did you include what we mentioned earlier, the possibility of building a fertilizer plant at a power plant or smelter and thereby affecting the economics in the market?

M. H. Farmer—Well, in a way, yes. Of course, there were many things

covered in the full report, a very heavy thing, that is not even in the handout material that most of you probably have. The Western smelters were considered in some detail and some of them, of course, particularly those in the more northern copper mining states, are tied in with fertilizer production. But those in the southern part of Arizona have a particular problem. But the study did not get into local marketing situations. We wish that we had been able to do so, but it was outside of the scope of the program.

Fred Grozinger (Potomac Electric Power Company)—I would like to ask Mr. Farmer a question. I am somewhat confused about the overall practicality and objectives of the report that you did for EPA. Could you possibly explain if there's anything in this country in general? Or is it going to be specifically a tool for EPA?

M. H. Farmer—Well, I hope that it will be of some benefit to the utility industry; but of course the terms of work, the scope of work, was decided by the EPA. Working with Norman Plaks (EPA), we were able to expand the original terms somewhat and I think we made it more useful as the project developed. But it had a specific purpose to help them in establishing their research priorities; I believe that it has had some impact on those decisions already. But also it was my hope at least that, by placing the industry in its world context, it would make it easier for a utility perhaps or any other individual to fit his piece of the puzzle into a broader context. Now, a lot of times a suggestion is made, "Well, surely such and such a thing could be done," and the suggestor does not realize what the problem really is in accomplishing what he wants to do. Just one quick example. I read a suggestion

some time ago that phosphogypsum should be used as a soil conditioner. Well, of course, most of the fertilizer gypsum is produced in Florida and most of the soil conditioning goes on in California. So the transportation cost is a very, very important part in the utilization of any low unit value material. I am sorry if I have not answered your question.

F. Grozinger — That is fine. I was just a little confused on the actual objective.

J. Salm — On the subject of utilizing sludge as a construction material, what experience has there been with regard to the resistance of this material to freezing and thawing cycles? Or to, say, gully washing type rains in the Southwest? Have these materials actually been tested for all of these requirements?

L. J. Minnick — Well, yes. As I mentioned, this is sort of an outgrowth that was done with Poz-o-Pac. The test procedures have been established by Federal highway departments and ASTM and so on. They are very well known, freezing and thawing being a case in point, and the answer is "yes." They have been fully evaluated from that standpoint.

J. Salm — One other question, Mr. Minnick. On the expansiveness of this material, is that a controlled expansion, like that of cements that can either be expanded or . . . ?

L. J. Minnick — Exactly. That is the way to look at it, as an expansive cement. Ettringite formation in Portland cement can cause deleterious reactions if the ettringite forms after the cement sets. In the case that we have here, the ettringite is the setting process and it forms during the hardening and therefore does not cause deleterious expansions. The expansions are beneficial, just like you have with an

expansive cement. Same idea.

J. Salm—Could I ask one question of Mr. Platou, please? On the use of sulfur in the construction materials, you are talking about very high percentages of sulfur. What is the fire hazard? Would OSHA agree with it?

J. S. Platou—It is a good question, sir. There are several aspects of this, of course. Before going any further, I would just say that additives have been developed, they are even patented, that will make sulfur non-sustaining of combustion. In other words, they comply with one of the ASTM standards. Self-extinguishing. Another aspect is that when you add a certain amount of aggregate or other non-combustible material to the sulfur, this will of course also act as a heat sink and again contribute to making the material self-extinguishing. This is a problem that we are aware of, It is, of course, being evaluated for these various uses. Do you want to add to that, Harold?

H. L. Fike—About the only thing I might add to this is the thought that where many people think that they are going to be just storing sulfur out in the country, it does pose a potential danger to just store tremendous piles of it in the country. It could catch fire there. And this is one of the reasons where I think the beneficial use (for example, in a sulfur-asphalt road or a sulfur foam as an underlay for a pavement material) would not really create any problem as far as being combustible. But it is a problem which we would like to face up to more directly than we have. In fact, we would like to come up with something which would actually make the sulfur non-burning, We have not done this as yet. And it is not really a very promising endeavor.

Jacques Dulin (Industrial Resources)—We have heard today discussions of taking care of the waste products from the calcium systems (specifically, scrubbers) and also what to do with the sulfuric acid and the sulfur. Tomorrow we are going to hear something in connection with sodium systems and ammonia systems. I wonder if the panel could jump ahead just a little bit and perhaps give a few moments of discussion to the state of the art in connection with the disposal of sodium sulfite or sulfate from those types of systems. There is one aspect that I would like to mention for them to direct their attention to. We have heard here specifically of scrubbers and not of baghouses and the use of reactive filter aids in connection with the baghouses to produce (rather to react with) SO_2 , and to take it out of the air along with the particulates. I wonder if they could direct their attention to the disposal of that type of baghouse waste product material as well.

A. V. Slack—Well the question of sodium sulfate as a throwaway product I suppose is best discussed by Dr. Ando and he covered that to some extent but . . .

J. Ando—Again, there is a big difference in circumstances. Japan is a small country and surrounded by sea. We can just put it in the sea. We can deliver what is going directly to the sea, so sodium sulfate is no problem.

A. V. Slack—Would any member of the panel or any member of the audience like to discuss the throwing away of sodium sulfate in the United States?

W. C. Taylor—Well, I would like to express Combustion's apologies for not having considered that at all. We seem to be pretty well tied up, looking at the calcium sulfate sludges. While I am speaking, I might clarify Combustion's point of view on this in that we at CE are really not in the waste disposal business. We thought that we had to do this because at the time we began there was no one else worrying about the disposal. And there was a lot of talk going on that we had a potential problem, but no one seemed to be solving it. We thought we had to do something. Once some of these other companies seem to be coming up with processes for disposing of the sludge, we would be very glad to let them handle our problem. We were only offering this in-between service.

H. L. Fike—May I make one brief comment on that as well? The Sulphur Institute is very interested in finding uses for sulfuric acid and SO_2 . We just concentrated on the one effort today; but I think I would have to say that over the longer term we have not been able to see any future market for sodium sulfate in the United States. As you know multi-million ton quantities are used today by the pulp and paper industry. From what I can see from the general direction that this industry is going and from the people I talk with who are quite knowledgeable in this, I certainly get the suggestion that they are going to non-sulfur using pulp and paper processes. Probably about the time the utility industries might have this available, it will not be used to any great extent in North America.

Don Gylfe (Atoms International)—I'd like to answer part of the question of disposal of sodium sulfate in this country; a partial answer, anyway. We have a system that uses sodium carbonate that

we are trying to promote. It turns out that in the western states where the sources of the trona are located (in general in such areas as dry lakes in the California area), you can bring the spent product, the sodium sulfate, back to such lakes. It is being done currently in Owens Lake in Owens Valley, in connection with an operation there. The California Water Resources Board has told us that a similar process could be done at Searles Lake. That is not a general answer on what you do with sodium sulfate in all locations, but at least in the western U.S. It is one possibility for an interim solution.

G. A. Hollinden— I would like to ask Dr. Ando one question. When the team was over there in Japan last August, we were told by MKK that they were going to use sodium sulfate as a soap binder and they showed us a product of that. Do you know anything further on that, Dr. Ando?

J. Ando — Yes, they may use it, but actually they are wasting their sodium sulfate to the sea. MKK is discarding the The Wellman-Lord process waste water containing sodium sulfate is still. . .

G. A. Hollinden — Are they discarding any other products over there too, in the sea, Dr. Ando?

J. Ando — Yes, MKK recently built another plant in which they recover sodium sulfate. It is sodium scrubbing of waste gas.

H. L. Fike — I believe there is a sizable quantity if you talk in terms of millions of pounds of sodium sulfate added to detergent to protect the aluminum in washing machines, but this would not utilize the types of tonnages which the utility industry will produce. But I think most detergent formulations in the United States contain 3 or 4 percent sodium sulfate if I recall correctly.

J. Dulin—Seeing as to how we have heard a few plugs from people, our company is of course very deeply interested in sodium systems since we have a couple hundred million tons of the stuff to sell out in Colorado, specifically a sodium bicarbonate mineral called nahcolite. We have addressed ourselves to that problem and have found ways in which to insolubilize the sodium sulfate as an easily dewaterable granular precipitate, which is a double salt of sodium sulfate and ferric sulfate. And the material, you are not talking about 60 percent solids sludge, you are talking about really a material that is 100 percent solids—the water just drains right out of it. The water will then be suitable for the very simplest type of landfill. We can not say to you that it is 100 percent available today, because we are still doing research on it and answering the hundreds of questions that people have in connection with it. But it can be done. We are also handling a couple of other methods as well. I think this should alert the industry to the fact that whereas there has been a focus on calcium systems because of the end-product theoretical insolubility, there has been an earlier recognition of the advantages of a clearwater liquor type of scrubber or dry baghouses for use with sodium systems. The problem with the sodium systems has always been, "What do you do with the sodium sulfate or sulfite that you get at the back end?" We think we have an answer to that and I would like to alert you to the fact that sodium systems should be considered more carefully than they have in the past.

H. W. Elder (TVA, Muscle Shoals)— I have a question for the Sulphur Institute. Have you considered how there can be equitable competition in a market where there's an oversupply between a regulated and a non-regulated industry?

J. S. Platou—Since the Sulphur Institute has as its members both the Frasch industry and the industry which recovers sulfur, such as natural gas producers, I cannot comment on that question. I am sorry.

J. Ando— May I ask one question to Dr. Taylor? You showed me that sludge is usable for the production of lightweight aggregate. How could you make it?

W. C. Taylor— Yes, well, any product made from sulfate sludge that requires sintering would have to have a sulfur recovery process with it. We have considered that. At the time we were looking at beneficiation processes, we looked at everything for which flyash had been used. Among these were making lightweight aggregate, making sintered brick, or anything like that. That is one of the reasons for our extensive thermal studies of the material. And we found that you could not sinter the material without recovering the sulfur. Again, at that time we were considering a sulfur recovery process with a number of thermal sintering processes for utilization of sludge. Once you get off the SO_2 you are right back to something like a lignite flyash. And you can make the same type of sintered products that you could from the lignite ash.

Russ Eberhart (John Hopkins Applied Physics Lab)— Question for the gentlemen from The Sulphur Institute. What kind of landfill preparation, pitlining, or whatever would be necessary to stockpile sulfur? That is, to protect (if any protection is necessary), groundwater, and so on.

J. S. Platou—Are you referring to possible oxidation of the elemental sulfur into sulfate and getting it into groundwater?

R. Eberhart— Anything you can think of; that is, if a power company were required to stockpile this sulfur because the market were not available, what would they have to do in terms of preparing the ground

or the pit in which the sulfur would be stored?

J. S. Platou — I do not know to what extent I am qualified to answer that question as of now. It would of course depend very greatly upon the location of the sulfur stockpile, whether under average conditions or under conditions of high rainfall. Probably the people who would have most experience in that field would be the Frasch industry who, of course, maintained large stockpiles of sulfur. I do not really think I can answer that question too well. Harold, do you have any comment?

H. L. Fike — Probably all I can do is to add to the problem rather than to solve it. Sulfur is very susceptible to both chemical and biological oxidation, and as a result could cause a problem in certain areas of the country. I think that we should also recognize that practically all the sulfur sold in any large quantities in North America, particularly the United States, is now delivered in liquid form. What they do now, of course, is just put it in forms, vat it, and let it sit there. If it were going to be sold, it would have to be remelted and put into tank cars. Now to avoid that up in Canada, because they are no longer allowed to ship solid sulfur through the port of Vancouver, they have gone into a slating process. In other words, as the liquid sulfur comes, they put it on a roll and actually make small slates out of it. They can load this in the port of Vancouver and this minimizes the danger from dust explosions which they had a real problem with in the past. I only point this out because I think your question, as one gets down to it, would require a good many hours of thought and conjecture and certainly a great deal more knowledge than I possess.

A. V. Slack — Well, Harold, could you continue with that discussion and cover the H_2S emission problem? I have heard about it, but I do not

know much about the details. I have heard that on some of the, what do you call it, blocks of sulfur in Canada, they are considering having to put hoods over them to recover the H_2S . Is this true, or what is the extent of the problem?

H. L. Fike—I do not know. I am trying to check into that. You, as with many of these problems, perhaps get a different answer from different individuals. However, I think it is generally accepted that as it comes out of a Claus kiln, liquid sulfur will contain fairly sizable amounts of hydrogen sulfide. In the liquid sulfur, it is more soluble hot than it is cold, so when it does cool down and crystallize you now have a potential problem of its emitting hydrogen sulfide. I do not think this will be a problem in rural areas. I do not think the concentrations will perhaps be so large. In metropolitan areas I imagine it could be a problem, but I could not quantify it closer than that, Archie.

A. V. Slack—How does sludge smell? I am not sure.

John Rasile (Ebasco Services) — We have done some work on the disposal of these waste sludges from a number of power plants. We have found that there are in most cases, in fact all cases, concentrations of boron, cadmium, nickel, and silver which far exceed drinking water standards. In all of effluents from both wet particulate scrubbers and sulfur dioxide absorbers, there seems to be a certain lack of experience in these things. I just thought I might add that. Somebody asked a question about lining. In the few plants that have either proposed or put in wet scrubbers or sulfur dioxide absorbers, synthetic materials have been required for the lining. Clay has been found to disintegrate under the action of high calcium and magnesium salts contained in the scrubbing liquor and it's not considered an acceptable lining material. Therefore, you normally have to go to something synthetic. The Bureau of

Reclamation has actually designed and is requiring the installation of an extensive monitoring system at the Mohave plant, just to make sure that the synthetic lining does not fail or, if it does fail, to observe when it fails. What I am trying to say, I guess, is that I do not think there is going to be any acceptable disposal procedure which is not going to be associated with lining and extensive monitoring.

W. C. Taylor — I would like to make on comment on that. I have heard of this problem of potential hazards associated with sludge. But I would like to mention that you have been ponding flyash now for a number of years and we are now talking about maybe 25-30 million tons a year flyash in ponds. Now the use of sulfur from air pollution control sludge... in other words, when you added the limestone or the calcium sulfate to it, you have not increased these potential hazardous elements. Any hazardous elements that were there, were probably associated with the coal and it's been with the coal long before you started adding limestone to it. So what? You are not aggravating any problem here; you may be accentuating it or thinking about it.

J. Rasile — We have not found that to be the case. We have run leachate tests on flyash that was collected dry. We have stirred vigorously for 18 hours and determined how much leaching of the same trace elements comes out and I think the highest we ever got on anything was boron and that was 1 part per million, on trying to leach it out of dry flyash. As a contrast, when you scrub it out of a wet particulate scrubber, when you are scrubbing the particulates out, we have reached 60 parts per million of boron with no trouble at all. This has been observed in about three plants. So there seems to be some chemistry involved. In other words, it is not the same procedure.

W. C. Taylor— May I ask what are you adding to the flyash now? You are saying the scrubbing process itself makes the flyash more soluble?

J. Rasile— No, I am saying, what I think is happening. What perhaps should be determined is whether we are removing elements which used to go up the stack.

W. C. Taylor— Well, it was a hazard in any case, wasn't it?

J. Rasile— Well, except we are talking here about the disposal of waste products. And it is too bad it was a hazard. Yes, but right now somebody is going to be sitting there monitoring and if they did not monitor the stack well, somebody got away with a lot a while ago. But it is not going to be the situation any longer.

A. V. Slack— I might point out again, as I did earlier, that tests in Lunen, Germany, have not, I believe, established any leaching at all in test wells. Tests from Ontario Hydro indicate, I believe, that the liquid phase pretty well stays occluded in the sludge and doesn't get washed out. These are just bits of data.

J. Rossoff— Well, I have my own observations on that. I would not want to doubt your fears, but I have to agree with Bill. You know that you are not adding any new elements. They may be in a different form. I would just like to ask you whether you are basing your feelings on actual leaching test data to the soil or whether you are basing it on concentrations within the solid sludge itself. Or are you talking about concentrations in the liquid form, which are now in solution?

J. Rasile—The concentrations I referred to are those which were in the supernatant scrubbing liquor, the clarified scrubbing liquor. The same trace elements exist, for example, in flyash, in roughly the same proportions they did in the original coal. They stay there. I have no proof of this but my feeling at this point in time is that we are scrubbing the gases or vapors, these volatilized materials, out of the gas. We are not adding anything. But now that it is in the water (and it is in the waste water) you are trying to discharge it at the rate at which waste water will leach.

A.V. Slack—Well, of course. May I ask, though, that if we did agree that there is no leaching downward, are you saying that this waste water could leach sideways because we planned to recycle it?

J. Rasile—By what definition is it not going to leach downward?

A.V. Slack—I said tests have indicated that. Now, of course, we need to corroborate those. But if you assume this were true, then would there be a problem?

J. Rasile—Well, about the tests, not knowing anything about the tests, I would say you would have to know something about the soil

characteristics to determine whether it is going to leach downward or not.

A. V. Slack — Well, this liquor is staying in the solids. It does not make any difference about the soil underneath. Well, I think perhaps we are exhausting the subject.

J. Rossoff — May I ask one more? When Dick Stern (R. D. Stern, EPA) spoke here Monday, he made a plea for cooperation and help. Since that time I have had a lot of offers, gracious offers, to send me carloads and 55 gallon drums. If you would like to part with that data we would be happy to use it and compare with ours and include it. I think it would be very helpful.

Jim Henderson(ASARCO)— I don't quite understand the opinion expressed that we are not adding anything, because we are certainly adding lime rock. And in looking at various lime rocks in the vicinities of our smelters, we see a wide variation in the trace elements present in the lime rock itself. So I think we truly are adding something, as compared to flyash.

W. C. Taylor — Well, that is why I asked what were you adding? The limes that we have been adding and have been testing have not had any higher quantity of trace elements than we had in the ash. So I imagine you can get limestone in any purity that you want. And maybe some of them are contaminated. But I guess you would have to look at your limestone then if you were concentrating trace elements.

J. Rasile — It is not the quantity of concentration I'm speaking of. The total gross quantity of trace elements is going to be increased as compared to the flyash depending on what's in the limestone.

Howard Hesketh(Southern Illinois University)— It kind of surprises me in one respect that we are talking about a problem here with not only the sludge or the sulfur storage. You realize that here in the same discussion we have been talking about the fact that you can use the sludge as a retainer for city water supplies, you can use the sulfur as a waterproof barrier, and so on, I really see that we have the answer right here, should we want to use it.

A. V. Slack— If we can get somebody to buy the stuff. There is a practical problem here.

H. Hesketh-- I am talking about the power plants utilizing their own material to solve their own problem.

A. V. Slack— I think your material balance might be a little out of perspective there.

R. H. Borgwardt(EPA)— I have a question for Bill Taylor or anyone else who might know, concerning the magnesium that enters the scrubber with the limestone. All limestones contain magnesium in some degree or another. In our pilot plant, the evidence seems to indicate that the magnesium leaves primarily in the solid (rather than in the liquid) purge. We do not know, however, whether it is in the form of magnesium carbonate (that is, the carbonate entering just didn't dissolve and leaves with the solid) or whether it dissolved and was precipitated as possibly the magnesium sulfite and leaves as magnesium sulfite.

W. C. Taylor— Well, I'm sorry you asked me that. But maybe there is someone here from Combustion. Is there anyone here from Combustion that could help me out on this? I do know that the magnesium hydroxide is fairly insoluble and if you had a high enough pH, you would not have considerable magnesium in your. . . .

R. H. Borgwardt — I am talking about the limestone scrubbing system.

Robert Van Ness (Louisville Gas & Electric) — One of the reasons we are using carbide lime is because of this particular point. Carbide lime slurry contains probably the range we are using, probably from 0.04 to 0.07 percent MgO. Now the lime that the carbide was originally made from was about 1 percent MgO and I believe the same thing would happen in Japan because MgO is vaporized in the furnace, and it was already in the atmosphere. So you are not adding again. If you are using limestone, then you do have the problem. But that is one of the reasons we chose carbide lime. Because it was cheaper also. But this is another point. We would not have high MgO levels.

Joe Selmeczi (Dravo Corporation) — As a "has-been" geologist I would like to make a stipulation relative to the magnesium content. It's one of the paradoxes of geology that calcium and magnesium carbonate has a lower solubility than calcium carbonate or magnesium carbonate alone. Yet, you cannot synthetically make dolomite. Now when somebody is trying to use dolomitic limestone (where the combination is not a camouflaged dispersion of the magnesium in a calcium structure, but a dolomite structure) then the magnesium will go through undissolved because it will be a lot less soluble. In other words, equilibrium and kinetic-wise, one way a field geologist determines the difference between calcium carbonate and dolomite is to drip 4 percent hydrochloric acid on a stone. Now if he observes a fast evolution of carbon dioxide, it is

limestone. If the evolution is very slow, it is dolomite. I do not know how much this is worth but probably it has something to do with the way magnesium is leaving a system of limestone scrubbing. Now relative to the trace elements. We have been working with western coals (I am sorry, eastern coals) primarily at Dravo and we have run several leachability tests on flyashes and the sludges generated primarily by lime scrubbing. Now we found that in all cases the trace elements were lower than you would get from flyash leaching alone. In one case only the arsenic content was in excess of Federal regulations for drinking water. And even in the case of arsenic, the flyash leachate (the leachate from flyash) contained higher arsenic content than the sludge. One reason for that is perhaps that the sludge is creating its own reducing condition and arsenic is not thermodynamically present as arsenate in a reducing condition. Now if you are slurrying and a dissolution experiment is done in a highly oxidizing condition, you may dissolve more arsenic from your sludge. Now western coals do contain a great deal more arsenic than eastern coals. As a matter of fact, mine leaching (mine discharge waters) in the West contain arsenic in excess of what's permissible by drinking water standards. People we talked to at EPA are not concerned about mine acid waters in the East, as far as arsenic content is concerned.

Steve Smith(Koch Engineering Co)— I have a question for Bill Taylor regarding the spray drying of the sludges from the scrubber with the waste heat of the boiler gas. We think there may be some trend for the unreacted limestone in the sludge to reactive SO_2 and also it looks like there might possibly be some oxidation of the sulfite to sulfate. Has your work turned up anything on this?

W. C. Taylor— We have gone to people like you and other spray dryers. But address that to Rao again. Rao, did you hear the question?

M. R. Gogineni— I did not quite understand the question. Could you repeat the question? Maybe I can help.

S. Smith— Yes, in spray drying the sludge from a limestone scrubber, have you found any reaction between the SO_2 and the limestone, the unreacted limestone in the sludge? And have you found any oxidation from the oxygen, the flue gas of the sulfite to sulfate?

M. R. Gogineni— I think in saying we have done work, I think it is not experimental work. It is still in the paper evaluation and we have done some pilot plant tests using the, I think, air at the temperature of the flue gas. But there was no SO_2 removed in the spray dryer as a result of reacting with the unreacted calcium carbonate that was present in the sludge.

S. Smith— Okay; I think, depending on the amount of limestone in the sludge, of course, that this will vary. I think there may be a little

bit of removal.

M.R. Gogineni — Maybe.

S. Smith — Okay.

M.R. Gogineni — Or maybe not, if it is solid.

W. V. Botts (Atomic International)-- I might just comment on spray drying. We have some data that suggest, even with the lime, that you do get SO₂ removal. We are selling systems of a spray drying nature using sodium carbonate. A spray dryer is probably one of the most efficient contactors that you can come up with for contacting flue gas with a reactant, and we are using sodium carbonate. In our tests at the Mohave station, we ran some lime dilute solutions and got quite good SO₂ removal. So if there is any lime in the sludge, you do indeed get SO₂ removal.

J. Selmeczi — I do not think I have to introduce myself again, but I remember what I wanted to say. As far as the heavy metals leaching into the soil and the probes, valve points, or whatever devices you try to determine, their transferral in the groundwater depends entirely on the soil conditions. As geochemists know, humus is a very good ion exchanger which you probably find close to the surface. As a matter of fact, this is how we detect buried deposits of valuable minerals. Clays also have fantastic capacities for heavy metals in the cationic form; not in the anionic form, however. Now, for example, with cesium (which was conducted under the supervision or sponsorship of AEC), a

radioactive cesium was found to be most economically removed by clay or just natural soil, mixing radioactively contaminated water with natural soil. So just to sound a little bit of a hopeful note, heavy metals if they do leach into the ground and if the ground is not porous sandy soil, but contains even a small amount of clays, the clays will remove the heavy metals.

J. Ando — Let me just mention just one thing about the spray drying of the sludge. I don't think that desulfurization takes place by the calcium carbonate temperature which is not very high. But I am sure that considerable oxidation of calcium sulfite will occur in the spray drying.

M.R. Gogineni — Regarding the spray drying and SO_2 removal in the spray dryer. I think the gentleman commented about the fact that he was getting some SO_2 removal when he tried to dry sodium carbonate. Am I right? It may be due to what's in the solution rather than what's in the solid form.

REMOVAL OF SULFUR DIOXIDE FROM STACK GASES
BY SCRUBBING WITH AMMONIACAL SOLUTIONS:
PILOT SCALE STUDIES AT TVA

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PILOT SCALE STUDIES AT TVA

ABSTRACT

The Tennessee Valley Authority and the Environmental Protection Agency have pursued an ammonia scrubbing program at TVA's Colbert pilot plant since 1969. This effort began as a wholly funded EPA program with the objective to fully characterize ammoniacal liquor scrubbing of SO_2 -laden flue gases. Since 1971, the program has become a jointly funded effort in which the operational phase of ammonia scrubbing was coupled with a regeneration scheme for producing a concentrated stream of sulfur dioxide. The principal advantage in the EPA-TVA process is economic regeneration by acidulation with ammonium bisulfate produced from thermal decomposition of ammonium sulfate. This paper highlights the activities during the continuing test program.

In general, SO_2 recovery is excellent and NH_3 losses are low using ammoniacal scrubbing solutions. However, the following problem areas have been established:

- Fume formation in the scrubber and after discharge from the stack
- Fly ash separation
- Ammonium sulfate separation

Under proper operation of the system, it is possible to control fume formation inside the scrubber while operating at relatively high salt concentrations. Avoiding fume formation on days of low temperature and high relative humidity may be impractical to achieve. While fly ash and ammonium sulfate separation have not been satisfactorily demonstrated, several promising leads will be investigated in a modified process sequence.

The double alkali approach is another possible scheme to utilize ammonia in recovering oxides of sulfur from stack gases. This approach also will be studied.

Introduction

The Tennessee Valley Authority and the Environmental Protection Agency embarked on an ammonia pilot plant scrubbing project 4 years ago. The pilot plant treats 2600 standard ft³/min*slip stream from a TVA coal-fired steam generating station located in northwestern Alabama. The objectives of the study were to establish the ability of ammoniacal solutions to efficiently remove dilute quantities of sulfur oxides from flue gas with extremely low gaseous ammonia losses. Trouble-free operation of equipment during the first 1-1/2 years of testing promises a highly reliable, low-maintenance scrubbing system.

Because of the cost of ammonia and the extreme solubility of the ammonium salts, the process is not amenable to throwaway operation. In this light, a regeneration scheme ("bisulfate process") was adopted that appears to have several advantages over other regenerative systems.

This paper describes the pilot plant operation incorporating that portion of the total system--absorption plus regeneration--that is currently available from a 1-year period of testing.

Background

Several regenerable or semi-regenerable ammonia scrubbing processes have been developed and are, or have been, in full-scale operation. The earliest of these was pioneered by The Consolidated Mining and Smelting Company (Cominco) in Trail, British Columbia.¹ The process consists of aqueous ammonia scrubbing followed by acidification of the sulfite liquor with sulfuric acid to evolve SO₂ and produce ammonium sulfate. The SO₂ is sent to a sulfuric acid plant and the ammonium sulfate is further processed for sale as a fertilizer. The process has been operating continuously and reliably on smelter gas since the mid-1930's and is still in operation. Work on adapting the method to power plant stack gas was carried out by TVA (pilot plant scale) in 1953-54.² The absence of a large market for ammonium sulfate, however, severely limits the applicability of this otherwise excellent process in the United States.

Quite similar processes have been developed and are in full-scale operation on sulfuric acid plant tail gases in Czechoslovakia and Romania.^{3,4} In these methods, the effluent scrubber liquor is acidulated with nitric or phosphoric acid; and the process, therefore, must be integrated with fertilizer plants to provide an outlet for the ammonium nitrate or ammonium phosphate formed. Again, the limited marketability of the fertilizer products and constraints as to the location of the SO₂-emitting plant near a fertilizer manufacturing center limit their wide use in this country.

*See English units and metric equivalents on page 996.

A regeneration process producing SO_2 only was postulated and tested in the 1930's by H. F. Johnstone.⁵ Steam stripping was employed to recover SO_2 and to regenerate the ammoniacal solution for reuse in the scrubber. Since concentrated SO_2 is the major product, either sulfuric acid, liquid SO_2 , or elemental sulfur can be the final product, depending on the need of the user. Development of the Johnstone process has been vigorously pursued in the U.S.S.R. A 140,000 standard ft^3/min (60 Mw) unit was installed near Moscow in 1952 and operated continuously until 1967 at which time it was disassembled because the power plant was converted from coal to natural gas. It is reported that the cyclic ammonia process will be installed on a 200 Mw coal-fired utility boiler in the U.S.S.R. in 1973. Although the Johnstone process has been shown to be feasible and presupposes no link to a complex fertilizer plant, it possesses some undesirable characteristics. Energy requirements for the process are high, approximately 12 lb steam per pound of SO_2 . Oxidation products may be difficult to purge from the system without loss of active species thereby resulting in a higher effective oxidation. The occurrence of undesirable disproportionation reactions in the steam stripper further aggravates the oxidation problem.

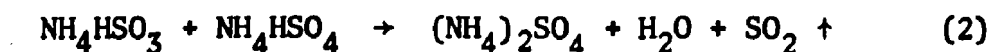
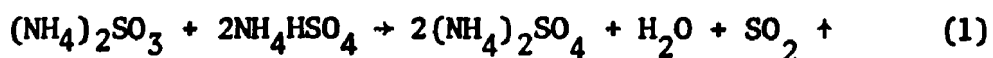
TVA-EPA Ammonium Bisulfate Process

In the decomposition of sulfites with an acid, it may be possible to regenerate the acid, thereby avoiding the need for disposal of the acid salt. Such an acid regeneration process⁶ has been known in the fertilizer industry since the 1920's. In this process, the ammonium sulfate is heated to drive off ammonia and produce acidic ammonium bisulfate, which is then used as an acidulant to release SO_2 .

In more recent work, an engineering company has incorporated the bisulfate technique in various fertilizer flowsheets⁷ and has carried out pilot plant work for converting ammonium sulfate to bisulfate. The process involves direct heating of the ammonium sulfate with combustion gas. The decomposition reaction is highly endothermic.

This work is being expanded currently to a large-scale test program, on a scale equivalent to the size required for a 30 Mw power plant burning 3.5 percent sulfur coal. Several other research organizations have also worked on the conversion step but in a less extensive way.

Application of the bisulfate technique to regeneration of ammonia scrubber liquor in an SO_2 removal process was proposed by Hixson and Miller in 1944.⁸ Ammonium sulfite-bisulfite liquor is pumped from the scrubber to an acidifier-stripper where the following reactions take place:



Essentially all of the SO_2 is released from the concentrated liquor in the acidifier-stripper. If a condenser is employed on the offgas, virtually a 100 percent stream of SO_2 can be obtained. The resulting stripped solution, containing mainly $(\text{NH}_4)_2\text{SO}_4$, is sent to an evaporator-crystallizer where the water is removed. Ammonium sulfate crystals are then transported to the decomposer where the $(\text{NH}_4)_2\text{SO}_4$ is thermally dissociated into NH_4HSO_4 and gaseous NH_3 . The bisulfate is returned to the acidifier and the ammonia to the scrubber.

Pilot Plant Equipment and Operation

The pilot plant is designed to treat 4000 actual ft^3/min flue gas at 300°F . Stainless steels (304 and 316) and rubber are used in all wetted sections for corrosion protection. The gas ducts are all mild steel. For simplicity, the plant is divided into the absorption and regeneration sections.

Absorption: The absorption section is shown in Figure 1. The scrubber is a three-stage, marble-bed unit which was available from a previous ammonia-scrubbing study. The three scrubber stages can be operated to maximize the $\text{SO}_2:\text{NH}_3$ ratio in the product liquor while limiting the SO_2 and NH_3 content of the scrubbed gases to 250 and 50 ppm, respectively.

The source of the pilot plant flue gas is downstream of the electrostatic precipitator on Unit No. 4 at TVA's Colbert Power Plant. Most of the fly ash is removed in the precipitators. However, the remaining fly ash (up to $0.5 \text{ gr}/\text{ft}^3$) enters the pilot plant scrubber where a portion of the ash is removed and accumulates in the scrubber solution at a rate of 1 to 10 pounds per hour, depending on the efficiency of the precipitator.

Most of the fly ash settles out and accumulates in the scrubber product storage tanks, F-5 and F-6. (Each of the storage tanks has a capacity for approximately 24 hours' absorber operation.) Periodically, the settled material is purged from the system. In later work, the settled material will be sent to a tub filter and the cake washed in a batch-wise operation. The wash from the filter will enter the absorber cycle as make-up water.

An alternative method of fly ash removal is to scrub the flue gas with water ahead of the absorption sections. With this scheme, a small amount of fly ash in the gas stream, as well as entrained mist, will get through the fly ash scrubber even though a high efficiency scrubber is used. Thus, a portion of the carry-over fly ash will be collected in the absorber, necessitating a purge cycle. A portion of the make-up water will be used to wash the fly ash cake from the purge cycle.

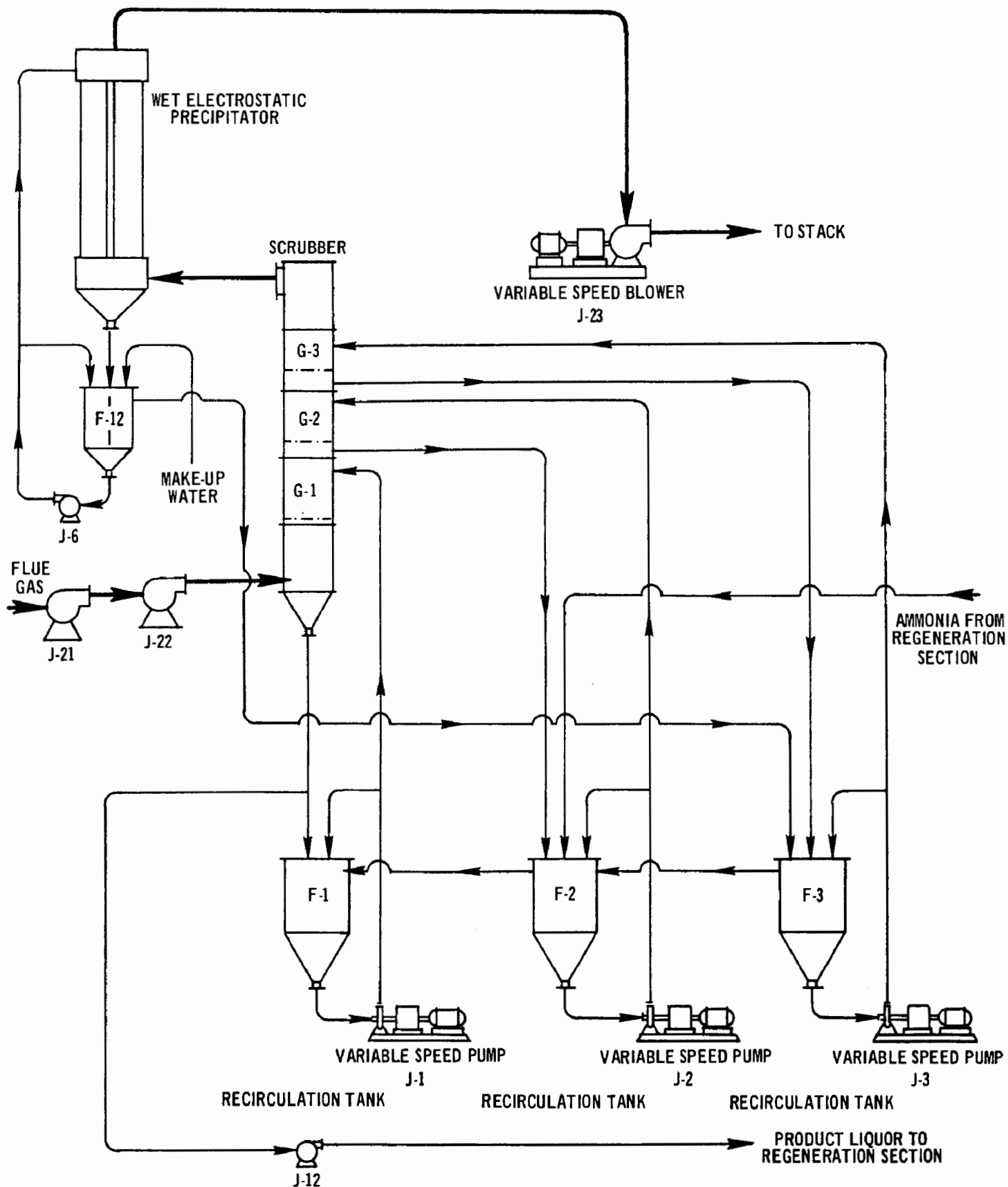


Figure 1. Absorption section ammonia scrubbing-ammonium bisulfate regeneration process.

Regeneration: The regeneration section shown in Figure 2 is designed to process liquor produced in the absorber section. Originally, the pilot plant regeneration process was designed to include the following steps:

1. Acidulation of the absorber product with ammonium bisulfate melt to release SO_2 and form ammonium sulfate.
2. Stripping of the released SO_2 from the ammonium sulfate solution.
3. Crystallization of ammonium sulfate from the mother liquor.
4. Separation of ammonium sulfate from the mother liquor.
5. Generation of ammonium bisulfate for the acidulation step by heating a 1:1 mole ratio of H_2SO_4 and ammonium sulfate.

The acidulation is accomplished in a vessel made from a 6-foot section of a 12-inch stainless steel pipe. The vessel is coated internally with DuPont's TFE Teflon for corrosion protection. Mixing of the incoming scrubber liquor and ammonium bisulfate is accomplished in a cone mixer in the upper part of the acidulator. Released SO_2 flows from the acidulator to the stack after joining the effluent from the stripper vessel. The acidulator is mounted so that the point of gravity overflow from the acidulator to the stripper can be raised or lowered to vary the retention time of material in the acidulator from zero to a maximum of 4 minutes.

The Teflon-lined stripping vessel is 1 foot in diameter by 6 feet high and contains a 4-foot section of 1/2-inch ceramic Raschig rings. Acidulated liquor enters the top of the vessel and flows countercurrent to a stream of stripping gas entering the vessel near the bottom. In the pilot plant, provisions are made to use either steam, air or scrubbed flue gas as the stripping gas.

Ammonium sulfate solution from the stripping vessel flows by gravity to crystallization tank F-7 where water is evaporated. The concentrated solution then flows to F-8 where cooling and crystallization take place. The saturated solution, containing crystals of ammonium sulfate, is centrifuged to separate ammonium sulfate crystals from the mother liquor. The filtrate is returned to the absorber section.

In a completely closed-loop ammonium bisulfate regeneration scheme, all the ammonium sulfate produced in the acidulation step would be thermally decomposed. The resulting ammonium bisulfate is fed to the acidulation step and the ammonia is returned to the absorption section (to recirculation tank F-2).

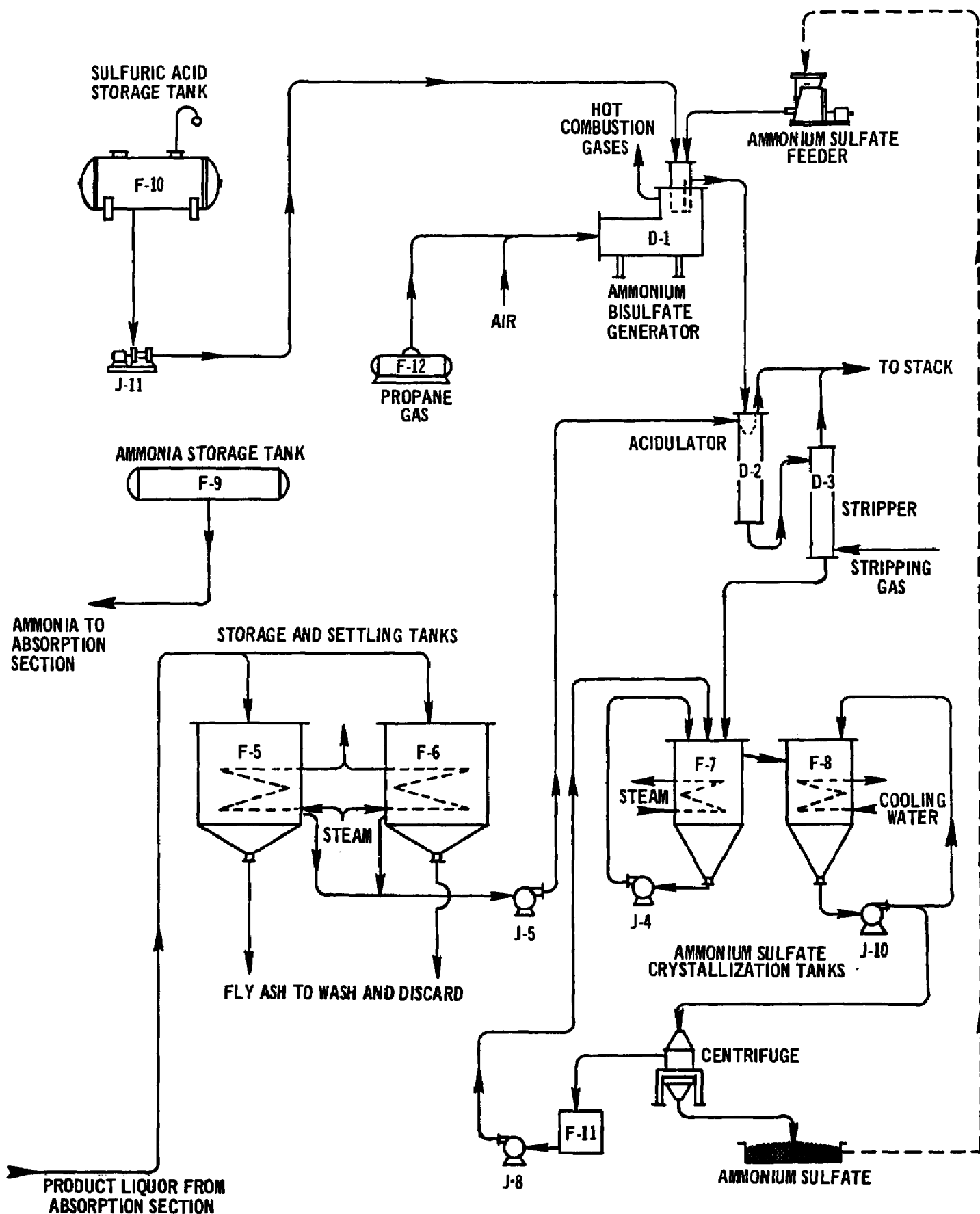


Figure 2. Regeneration section ammonia scrubbing-ammonium bisulfate regeneration process.

In the present pilot plant study, the thermal decomposition stage was omitted and the acid ion was furnished as sulfuric acid. Ammonium bisulfate will be the source of the acid ion later. The required ammonium bisulfate will be generated by heating a 1:1 molar mixture of sulfuric acid and ammonium sulfate. The sulfuric acid and the ammonium sulfate (from the centrifuge) will be fed separately and continuously to the ammonium bisulfate generator, D-1, a Teflon-lined stainless steel vessel. Here, sufficient heat will be added to the acid-ammonium sulfate mixture to evaporate the moisture added with the acid and to bring the mixture to about 350°F. The ammonium bisulfate melt will then be fed to the acidulator.

Since ammonium sulfate is not decomposed in the present study, no ammonia is available from the regeneration section. The makeup ammonia is fed to the absorption section from the ammonia storage tank, F-9. During the present pilot plant operation, the ammonia is fed undiluted directly to the points of use in the absorption section. Provisions will be made later to simulate ammonia recovery from a thermal decomposition process.

Vent System: The scrubbed flue gas is vented to the atmosphere for plume observation. The recovered SO₂ from the acidulator and stripper can be vented into the power plant stack. The storage tanks containing ammoniated solutions can be vented to the absorber or to the stack.

Instrumentation: The pilot plant is instrumented throughout so that all pertinent liquid and gas flows are monitored and values are recorded. All signals are electrically transmitted from the sensing element to the recorder-controller.

The gas flow through the scrubber system is monitored using a flange orifice in the duct leaving the scrubber. A differential pressure cell senses the pressure differential across the orifice and sends a signal to a recorder-controller on the pilot plant instrumentation board. Any deviation from the preset values on the recorder-controller causes a signal to be sent to the variable-speed drive mechanism on the induced draft blower (J-23) to correct the deviation. This arrangement assures that a constant gas flow through the scrubber system is maintained even though the pressure drop across the system may change.

Sulfur dioxide levels in the gas to the scrubber and after each scrubber stage is monitored using an ultra-violet analyzer. The analyzer has three ranges of SO₂ values: zero-4000, zero-1000, and zero-100 parts per million full-scale reading. The sample point is changed manually from station to station to avoid the possibility of leaks from an automatic sample sequencing system. Periodic checks by wet-chemical methods rarely differ from the analyzer reading by more than 5 percent.

An NO_x analyzer has been installed in the pilot plant but has not been activated. It is expected that this instrument will be available to monitor the inlet and outlet NO and NO₂ levels in future pilot plant runs.

A smoke detector is used to monitor the intensity of the plume at the stack exit. The instrument uses a light source and a photocell to measure the plume intensity. The digital readout is in Ringelmann units.

Gaseous ammonia is metered to the system as required by the use of a differential pressure cell coupled with a recorder-controller and a flow control valve. Liquid flows are sensed by magnetic flowmeters which send electronic signals to recorder-controllers. The required flows of recirculating liquor to the scrubber stages are controlled by variable-speed pumps (J-1, J-2, and J-3). Variable-speed pumps are used for flow control instead of valves because fly ash removed in the scrubber could cause plugging and erosion of control valves. Automatic flow control valves are used to control the flow of the remaining liquid streams.

Temperatures throughout the system are sensed with thermocouples and are recorded on strip charts in the control room.

Problem Areas

Fume: The most apparent problem surfacing during the past and the current TVA-EPA work with the ammonia-scrubbing process is that of fume formation. Figure 3 shows a typical ammonia-based plume including steam emitted during routine pilot plant operations with no gas reheat (exit temperature is approximately 125°F). The plume was formed during operation using three scrubbing stages, no prior humidification, and while producing a liquor with a C of about 10 and an S/C of 0.8 (C = moles of ammonia as sulfite and bisulfite per 100 moles water*, S = moles of sulfite and bisulfite sulfur per 100 moles water). Sulfur dioxide removal efficiency under these conditions is typically about 90 percent.

Efforts to reduce or eliminate the plume through manipulation of the pH of the scrubber liquor and the addition of a humidification step ahead of the scrubber did not reduce the plume opacity significantly. However, under these test conditions, the steam plume may have masked any reduction in the ammonia-based plume. Adding a wet electrostatic precipitator after the scrubber failed to produce significant results at the normal gas flow rate of 2600 standard ft³/min. (The precipitator was found to be 50 percent efficient in removing the particulate mass at this flow rate--15 ft/s shell velocity through the precipitator.)

*combined and uncombined



Figure 3. Typical plume during routine operation; high scrubber liquor concentration ($C = 10$); no reheat.

Chemical and petrographic analyses of the plume collected in an impaction sampler (Brinks mass sampler) indicate that the major fraction of the ammonia-sulfur salt is ammonium sulfate. It is probable that the particulate was formed in the vapor phase as ammonium sulfite and then oxidized to the sulfate form in the sampler. A portion of the particulate has been analyzed as ammonium chloride. (The coal used during these tests normally contained 0.1-0.2 percent chlorides.) Tests showed that a water wash ahead of the scrubber materially reduced the chloride content of the gas entering the scrubber.

Personnel from the Southern Research Institute of Birmingham, Alabama, determined the fume particle size to be 0.25 micron with 10^7 particles in the size range of 0.005 to 0.5 micron per cubic centimeter.

Reheating the scrubbed gas was effective in reducing plume opacity. These data also show that plume opacity is greater at higher salt concentration (high C's) than at lower salt concentration (low C's).

Solids Separation: Other problems identified in the pilot plant program are not as visible as the plume problem but may be difficult to solve. These are the problems of fly ash separation and ammonium sulfate separation. As stated earlier, the fly ash is expected to separate by gravity in the absorber product storage and settling tanks. These tanks, which have capacity for about 24 hours' retention time, are effective in removing most of the fly ash. However, the small quantity in the supernatant liquor from the tanks may be sufficient to adversely affect the production of crystalline ammonium sulfate further downstream in the process. Also the fly ash which contains iron may catalyze the decomposition of ammonia during thermal decomposition of ammonium sulfate. The cracking of ammonium caused by iron and other contaminants in the fly ash during the ammonium sulfate decomposition step will be examined by the Eugene Kuhlmann Company in France. The work will be done in a pilot plant sized to handle the production from a 30 Mw power plant.

Attempts to remove the product liquor from the settled fly ash by filtration in a tub filter failed because of blinding of the filter media. The fly ash was settled from scrubber product liquor with C's of approximately 10 and containing from 10 to about 30 percent by weight ammonium sulfate. The blinding was caused by gelatinous, thixotropic material composed of finely divided fly ash and tiny needle-like crystals of ferrous ammonium sulfite which precipitated from the scrubber solution. The iron in this compound is believed to come from fly ash. The quantity of iron dissolved in the solution is small--on the order of 0.01 gram per liter. Use of filter aids and precoat on various types of filter media failed to prevent blinding.

An equipment company specializing in solids separation made filtration tests on the scrubber product liquor containing fly ash and also on the mud from the bottom of the settling tanks. They recommended use of drum filters and filter aids on both materials.

Separation of ammonium sulfate crystals from the acidulated and concentrated liquor in the regeneration loop, though difficult, may be easier than fly ash separation. As stated earlier, the liquor concentration and crystal growth take place by evaporating water from the solution in a tank at atmospheric pressure. Crystal growth cannot be controlled in this equipment and attempts to separate the small crystals in the pilot plant centrifuge and drum filter have failed. Petrographic analysis indicated that ferrous ammonium sulfite was present in the material blinding the separation equipment as was the case in the fly ash separation tests.

Bench-scale work using solutions from the pilot plant operation produced adequate crystals for filtration. Filtration rates of over 200 gallons per hour per square foot were obtained in these tests which produced much larger crystals than those produced in the pilot plant. The ferrous ammonium sulfite did not cement together the larger crystals produced in the bench-scale work. The use of an evaporator-crystallizer is expected to produce the required crystals although the small amount of fly ash in the solution may influence the design (and cost) of the unit. The equipment manufacturers contacted concerning the sulfate crystal growth and separation were of the opinion that the standard sulfate crystallizer equipment would be sufficient. However, all stated that they could not guarantee this equipment without making tests using the actual solution containing fly ash.

Once adequate crystals of proper size are produced, separation would be accomplished by the standard centrifugation method used in the ammonium sulfate industry.

Pilot Plant Test Results

Routine Operation: Aside from the aforementioned problems, performance of the pilot plant in removing SO_2 from the flue gas and in subsequently releasing the absorbed SO_2 has been good. Table I shows data from a typical pilot plant run when producing an absorber liquor with a C of 10 and an S/C of 0.8. The ammonia required to react with the SO_2 was added to the second-stage absorber loop (tank F-2). Under these conditions, the SO_2 removal was approximately 90 percent. When the S/C was raised to 0.85, the removal efficiency, as expected, dropped (to 85 percent). Approximately 13 percent of the absorbed SO_2 was oxidized to ammonium sulfate. The Murphree tray efficiency for the marble-bed scrubber was about 0.90.

The regeneration loop was operated using sulfuric acid (93 percent) to acidify the liquor from the absorber section. Typical data from these tests are shown in Table II. Sulfuric acid was used for acidulation instead of ammonium bisulfate because no ammonium sulfate crystals were available from the pilot plant for production of the bisulfate. Clarified liquor from the absorber section was pumped to the acidulator at approximately 0.4 gal/min, the rate the liquor is produced in the absorber.

TABLE I

Typical Absorber Loop Data

<u>Test Conditions</u>	<u>NH₃ to F-2 tank (Normal Operation)</u>
Gas to scrubber	
Flow rate, ft ³ /min at 32°F	2650
Temperature, °F	285
SO ₂ , ppm	2360
Gas leaving first stage	
Temperature, °F	127
SO ₂ , ppm	1440
Gas leaving second stage	
Temperature, °F	125
SO ₂ , ppm	360
Gas leaving scrubber	
Temperature, °F	122
SO ₂ , ppm	280
SO ₂ removal, %	88
Stoichiometry ^a	1.45
Forward feed flow rate, ^b gal/min	1.3
Liquor to top stage	
C	1.4
S/C	0.78
pH	6.1
Specific gravity	1.036
Liquor to middle stage	
C	5.1
S/C	0.62
pH	6.8
Specific gravity	1.098
Liquor to bottom stage	
C	10.8
S/C	0.81
pH	5.7
Specific gravity	1.200
Product from scrubber	
C	10.4
S/C	0.84
pH	5.7
Specific gravity	1.202
Flow rate, gal/min	0.41

^aStoichiometry is the ratio of moles of gaseous ammonia added to the moles of SO₂ in the gas stream.

^bThe only forward feed added to the system was water.

TABLE IITypical Regeneration Loop Data

<u>Test Conditions</u>	<u>Acidulation with H₂SO₄ Only</u>
Acidulator	
Liquor feed in	
C	9.8
S/C	0.83
pH	6.0
Specific gravity	1.193
Flow rate, gal/min	0.36
Sulfuric acid	
Flow rate, gal/min	0.11
Percent sulfuric acid	93
Stoichiometry ^a	1.2
Liquor flow out	
C	1.3
S/C	1.0
pH	2.0
Specific gravity	1.194
Percent SO ₂ release	85
Stripper	
Stripping gas	
Type gas	Air
Flow rate, ft ³ /min at 70°F	12
Liquor flow out	
C	0.2
S/C	1.0
pH	2.1
Specific gravity	1.188
Percent SO ₂ release	83
Overall % SO ₂ release	97

^aStoichiometry is the ratio of moles of acid ion to moles NH₃ as ammonium bisulfite and ammonium sulfite in the liquor to the acidulator.

Sulfuric acid was pumped to the acidulator at a rate to give a ratio of 1.2 moles of acid (hydrogen) ion per mole of sulfite and bisulfite sulfur in the feed liquor to the acidulator. (The 1.2 ratio was used for convenience in these preliminary tests; the theoretical requirement is 1.0.) Approximately 85 percent of the absorbed sulfur as sulfite and bisulfite is released from the acidulator. The remaining 15 percent of the SO_2 flowed to the stripper where air at 12 ft³/min was added to remove the residual SO_2 . Approximately 83 percent of the residual SO_2 to the stripper was removed by the stripping gas to give an overall removal efficiency of 97 percent in the combined acidulator and stripper.

The acidulated and stripped liquor was concentrated to about 45 percent by weight as ammonium sulfate and then cooled to near 100°F to precipitate crystalline ammonium sulfate. However, as noted earlier, the ammonium sulfate could not be separated because of blinding of the equipment by extremely fine crystals of ammonium sulfate and ferrous ammonium sulfite.

Double Alkali Tests: Production of liquors with low C's is uneconomical for use in the ammonium bisulfate regeneration process because of the energy requirements to concentrate the solutions in the regeneration sections. However, scrubbing with solutions of low C's has possible application in the double alkali process being considered as a backup system for TVA's Widow's Creek Power Plant located in northeast Alabama. In the double alkali process based on sodium as the absorbent, the concentration of sodium in the absorber loop is limited to about 0.17 mole per 100 moles of water because of solubility limitations in the regeneration section. Ammoniacal solutions, which are not limited to low concentrations in the regeneration loop, would offer economic advantages because the size of the regeneration equipment could be reduced. When using an ammoniacal solution with a C of 0.5, the regeneration equipment size could be reduced to about one-third that required when scrubbing with sodium solutions.

A test series was made to determine whether a plume would be present under scrubber conditions similar to the proposed Widow's Creek operation. The test series was made using the flow configuration shown in Figure 4. Water was used on the bottom stage for humidification and fly ash removal. Fresh makeup water was added to this loop at the rate required to maintain the temperature of the gas leaving the bottom (G-1) stage at 120°F. Forward feed liquor (ammoniacal solution) was pumped to the middle (G-2) stage at 30 gal/min on a once-through basis and then drained to the product liquor hold tank. In one test, two-stage scrubbing was used to increase SO_2 removal. The forward feed liquor was pumped at a rate of 30 gal/min to each of the middle and top stages. The gas leaving the scrubber was reheated to 150, 175, and 200°F during most of the test series by direct heating with a propane torch.

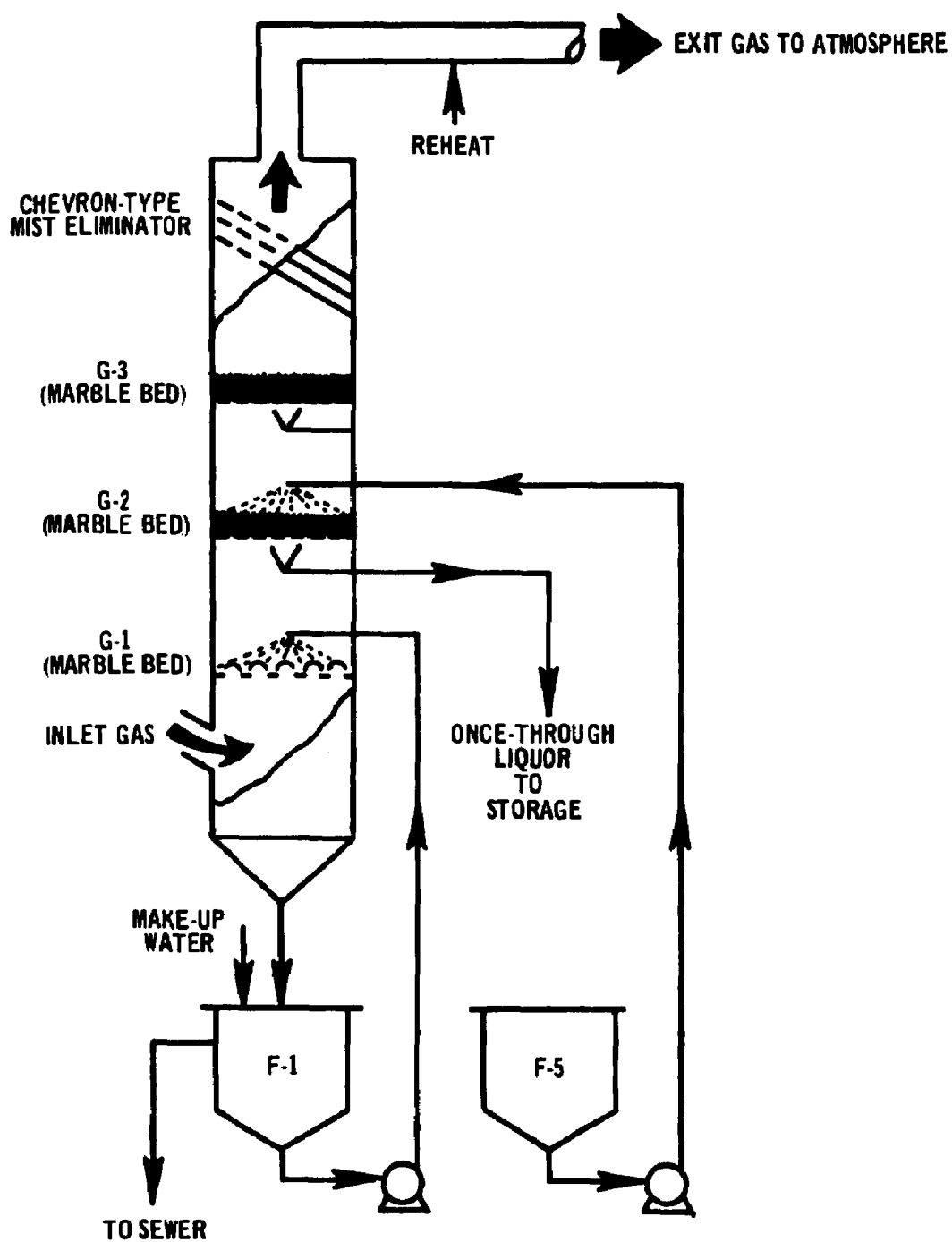


Figure 4. Flow configuration for once-through liquor on G-2 and water on G-1.

A steam plume, as well as a minor residual particulate plume, was present when scrubbing flue gas with water only (Figure 5). The steam component of the plume was dissipated when the exit gas was reheated to 175°F, but a light particulate plume remained (Figure 6). An additional plume component was present when an ammoniacal solution was used. The plume produced when scrubbing with a solution having a C of 0.5 or 1.0 was reduced to an opacity of 10 percent or less, below the maximum specification of 20 percent, by reheating the stack gas to 175°F. Figure 7 shows the severe plume while scrubbing with a solution having a C of 1.0 and with no gas reheat. Figure 8 shows the reduced plume from this operation while reheating to 175°F. The SO₂ removal efficiencies varied from 75 to 85 percent during these tests.

A second absorber stage was added in one test sequence to increase SO₂ removal efficiency. An average removal of 92 percent resulted when operating with solutions having a C of 1.8 to both scrubbing stages. Reheating to 200°F was required in this test sequence to lower the plume opacity to 20 percent or less (Figure 9).

From these tests it was concluded that the plume produced when scrubbing with solution having low ammonia content is significantly lower than the plume produced during routine scrubber operation. Also, the plume produced under these low salt conditions could be made acceptable by reheating the exit gas to temperatures necessary to dissipate the steam component of the plume. This temperature will vary according to the ambient air conditions--temperature and relative humidity.

Modified Operation: The absorption section of the ammonia scrubbing-ammonium bisulfate regeneration process pilot plant was operated from April 16 to May 4, 1973, to study additional methods of minimizing the plume from the absorber. Two basic flow configurations were used: a recirculation system using one, two, or three stages of absorption (Figure 10); and a once-through system using one stage of absorption (Figure 11). This operation was carried out in cooperation with Air Products and Chemicals, Inc., Allentown, Pennsylvania.

The tests were made to determine whether the plume leaving the absorber could be reduced to an acceptable level by operating under the following conditions:

- Insulated absorber
- A water wash ahead of the first absorber stage
- A water wash after the absorber stage
- Reheating the scrubbed flue gas



Figure 5. Plume emitted while scrubbing with water only; no reheat.



Figure 6. Particulate plume emitted while scrubbing with water only; 1750 F reheat.



Figure 7. Plume from operation with scrubber solution having $C = 1.0$; no reheat.



Figure 8. Plume from operation with scrubber solution having $C = 1.0$; 1750° F reheat.



Figure 9. Plume from operation with solution having $C = 1.8$; two scrubber stages; 200°F reheat.

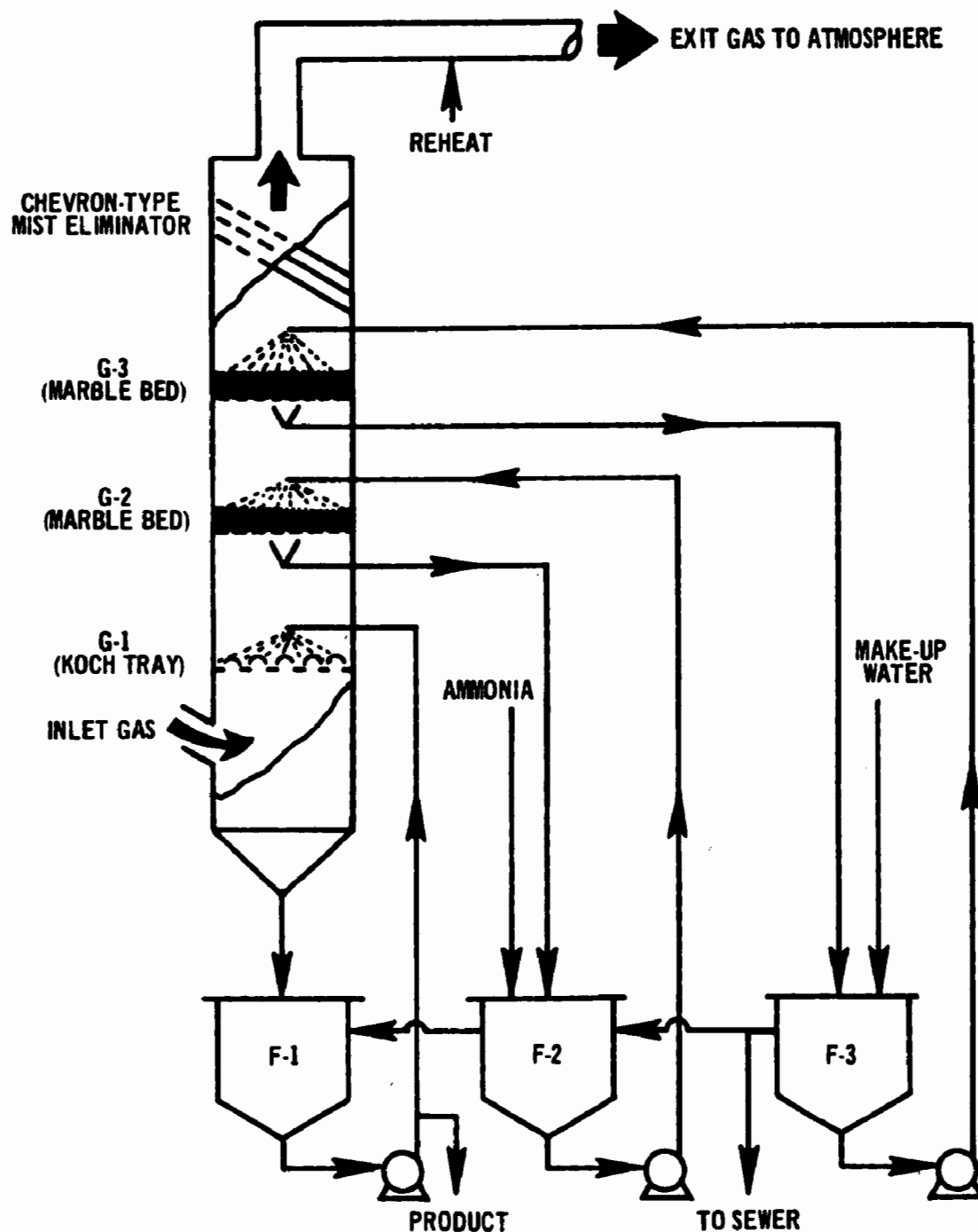


Figure 10. Normal recirculating flow configuration.

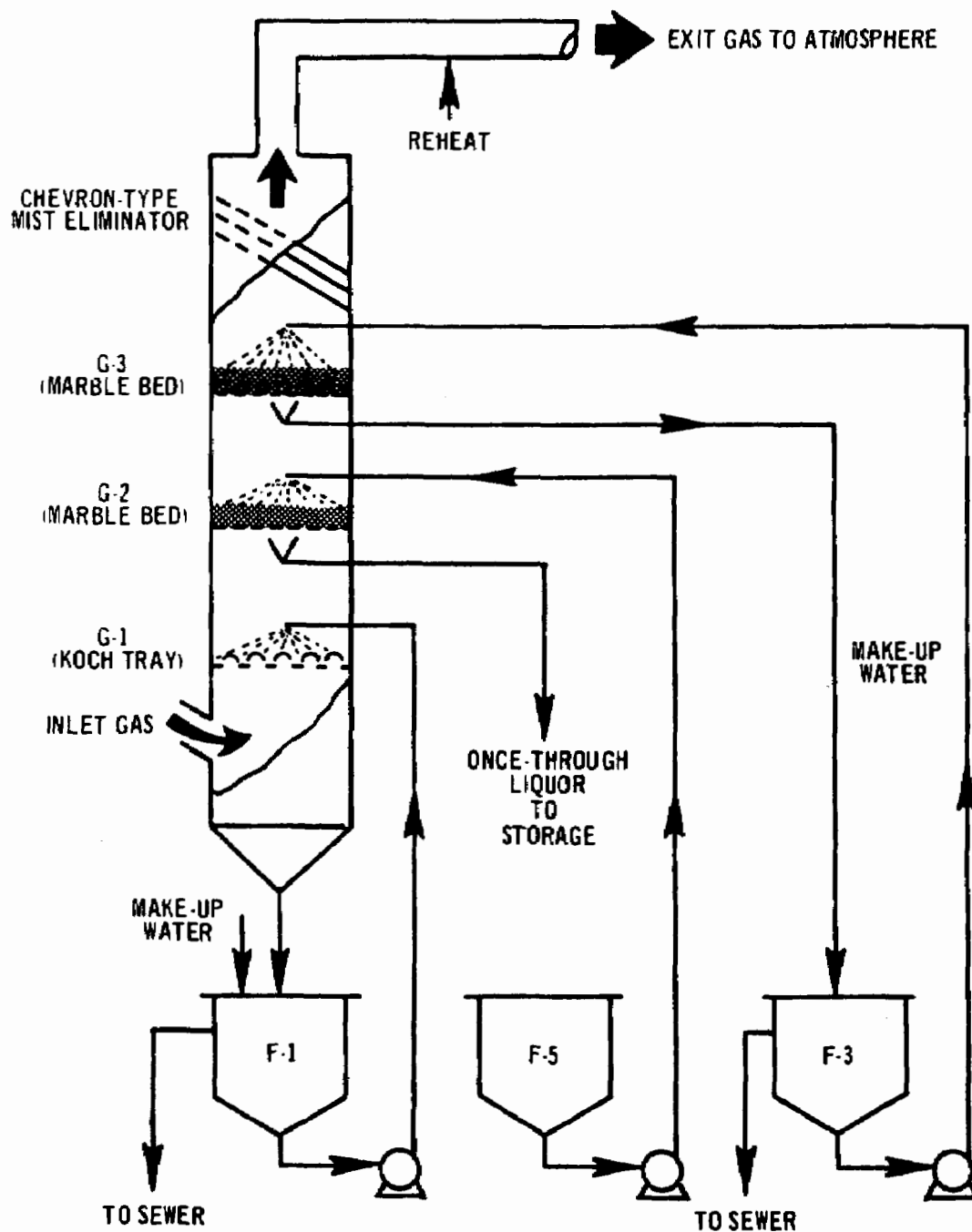


Figure 11. Once-through flow configuration.

An acceptable plume for the pilot plant was defined as one having a maximum of 5 percent opacity. The opacity readings were made by qualified observers who successfully completed the EPA-prescribed visual emissions school. The absorber and all downstream ductwork were insulated for reasons that Air Products and Chemicals, Inc., consider proprietary. The water wash ahead of the first absorption stage was used to humidify and cool the hot flue gas; to remove chlorides and, thereby, prevent formation of an ammonium chloride plume; and to remove fly ash. It was expected that cooling the flue gas would reduce the ammonia-based plume containing sulfur. The moving marble bed of the bottom stage (G-1) used in previous work was replaced with a multi-venturi FlexiTray manufactured by Koch Engineering Company, Inc. No downtime was required when this type of tray was deactivated during absorber operation. (The glass marbles had to be removed from the marble bed scrubber when the unit was deactivated to prevent damage from thermal shock should the scrubber liquor accidentally come in contact with the hot bed.)

The water wash after the absorption stage was to decrease the salt content of the entrained mist leaving the absorber. Reheating would have evaporated the mist and produced an increased concentration of ammonia and sulfur dioxide in the exit flue gas which could have then reacted to form a plume. The top stage of the absorber (G-3) was used for this wash. The gas leaving the absorber was directly reheated with a propane torch to destroy the particulate matter present and eliminate a steam plume. The retention time of the heated flue gas in ductwork was 1.5 seconds.

A summary of the test conditions and the opacity readings for each test are given in Table III. These tests show that an acceptable plume was obtained during production of liquor with high C's when:

- Water wash was used ahead of the first absorber stage.
- Absorber and all ducts were insulated.
- Reheat was applied as required to dissipate the steam plume.

Comparison of Figures 12 and 13 shows the effect of the water wash ahead of the first absorber stage. In Figure 12, the water wash was not employed and the opacity was 5 percent. The water wash was activated and the opacity dropped to 0 percent (Figure 13).

The concentration of ammonia salts in the water wash (G-3) after the absorption stage did not show any significant effect upon the plume formed in the range studied ($C = 0.1$ to 3).

TABLE III
Summary of Operating Data for the
Test Series, April - May 1973

Test No.	0	I-1	I-2A	I-2B	I-2C	I-2D
Date	4/19	4/20	4/20	4/20	4/20	4/20
Time	11:00 a.m.	1:00 p.m.	1:45 p.m.	2:15 p.m.	3:15 p.m.	3:40 p.m.
Liquor flow configuration	←			→		
Flow						
Liquor, gal/min						
To G-1 (bottom stage)	30	30	33	31	31	30
To G-2 (middle stage)	30	30	30	30	30	30
To G-3 (top stage)	15	15	15	15	15	15
Gas, ft ³ /min	2700	2700	2700	2700	2700	2700
Liquor Ca						
G-1-I ^b	28.1	13.21	12.6	14.0	-	13.0
G-1-O ^c	-	13.09	13.0	13.8	-	13.6
G-2-I ^b	9.52	4.90	5.2	4.9	-	4.5
G-2-O ^c	9.48	4.73	5.2	5.0	-	4.5
G-3-I ^b	1.35	-	0.1	0.1	-	1.2
G-3-O ^c	1.88	0.10	0.6	0.4	-	1.4
Liquor S/C ^d						
G-1-I ^b	0.76	0.82	0.85	0.81	-	0.79
G-1-O ^c	-	0.83	0.84	0.82	-	0.79
G-2-I ^b	0.58	0.55	0.55	0.56	-	0.60
G-2-O ^c	0.59	0.57	0.57	0.57	-	0.62
G-3-I ^b	0.62	-	0.84	0.85	-	0.72
G-3-O ^c	0.60	0.86	0.58	0.61	-	0.70
Liquor pH						
G-1-I ^b	5.90	5.75	5.80	5.80	5.80	5.80
G-1-O ^c	-	5.75	5.75	5.75	5.90	5.90
G-2-I ^b	6.70	7.25	7.10	7.10	6.80	6.80
G-2-O ^c	6.70	6.95	6.95	6.95	6.70	6.70
G-3-I ^b	6.70	7.20	7.25	7.25	6.50	6.50
G-3-O ^c	6.80	7.10	7.15	7.15	6.50	6.50
SO ₂ , ppm						
Entering G-1	2600	2320	2440	2600	2400	2400
Leaving G-1	1700	1860	2000	1880	2040	1640
Leaving G-2	80	400	300	160	160	240
Leaving G-3	40	100	40	60	60	160
Percent removal	98.5	95.6	98.4	97.7	97.5	93.3
NH ₃ leaving G-3, ppm						
	47	47	51	51	51	50
Temperatures, °F						
Liquor						
From G-1	141	131	131	130	131	131
From G-2	126	127	127	127	126	128
From G-3	125	126	126	126	125	125
Gas						
To G-1	282	290	289	286	290	290
From G-1	144	132	133	132	133	133
From G-2	130	127	127	126	127	127
From G-3	126	125	125	125	125	126
Exit gas	200	150	200	220	225	200
Ambient	73	84	85	85	82	84
Relative humidity, %						
	80	49	47	47	42	42
Predicted temperature at which steam plume forms, °F ^e						
	152	120	120	120	124	120
Reheat temperature, °F						
	200	150	200	220	225	200
Percent opacity						
	25	65	15	20	10	15

^a Moles of active ammonia as ammonium sulfite-bisulfite per 100 moles of water.

^b Inlet sample.

^c Outlet sample.

^d Mole ratio of SO₂:NH₃.

^e Calculated temperature at which steam plume can form regardless of dilution; does not include a solid particulate plume, that is, an ammonia salt plume.

TABLE III (continued)
Summary of Operating Data for the
Test Series, April - May 1973

Test No.	I-3	I-4	I-5	I-6A	I-7	I-8A	I-13
Date	4/20	4/20	4/23	4/23	4/23	4/23	4/24
Time	5:55 p.m.	6:05 p.m.	2:15 p.m.	1:45 p.m.	2:40 p.m.	3:05 p.m.	3:15 p.m.
Liquor flow configuration	← Recirculating →		← Once through →				
Flow							
Liquor, gal/min							
To G-1 (bottom stage)	29	30	31	32	0	0	30
To G-2 (middle stage)	30	30	31	32	30	30	30
To G-3 (top stage)	15	15	15	15	17	17	15
Gas, ft ³ /min	2700	2700	2700	2700	2700	2700	2700
Liquor C ^a							
G-1-I ^b	0.85	0.85	0.30	0.30	-	-	0.12
G-1-O ^c	1.50	1.50	0.50	0.50	-	-	0.11
G-2-I ^b	10.6	10.6	10.1	10.1	9.1	9.1	1.9
G-2-O ^c	10.4	10.4	10.1	10.1	8.9	8.9	1.9
G-3-I ^b	0.14	0.14	0.21	0.21	0.30	0.30	0.33
G-3-O ^c	0.31	0.31	0.38	0.38	0.41	0.41	0.29
Liquor S/c ^d							
G-1-I ^b	0.95	0.95	0.93	0.93	-	-	0.50
G-1-O ^c	0.93	0.93	0.88	0.88	-	-	0.70
G-2-I ^b	0.78	0.78	0.77	0.77	0.77	0.77	0.76
G-2-O ^c	0.79	0.79	0.78	0.78	0.79	0.79	0.81
G-3-I ^b	0.99	0.99	0.72	0.72	0.93	0.93	0.78
G-3-O ^c	0.95	0.95	0.81	0.81	0.90	0.90	0.91
Liquor pH							
G-1-I ^b	5.10	5.10	4.70	4.70	-	-	2.40
G-1-O ^c	5.70	5.70	5.90	5.90	-	-	2.30
G-2-I ^b	5.90	5.90	6.00	6.00	5.80	5.80	6.00
G-2-O ^c	5.90	5.90	6.00	6.00	5.80	5.80	5.80
G-3-I ^b	5.70	5.70	4.70	4.70	5.10	5.10	3.10
G-3-O ^c	4.90	4.90	5.00	5.00	4.20	4.20	3.10
SO ₂ , ppm							
Entering G-1	2520	2520	2560	2480	2480	2480	2480
Leaving G-1	1760	1760	2600	2520	2480	2480	2520
Leaving G-2	920	920	880	880	920	920	480
Leaving G-3	920	920	680	720	780	780	560
Percent removal	63.5	63.5	73.4	70.9	68.5	68.5	77.4
NH ₃ leaving G-3, ppm	87	-	47	47	79	-	37
Temperatures, °F							
Liquor							
From G-1	121	121	125	127	-	-	125
From G-2	129	129	130	130	128	128	126
From G-3	122	122	130	127	124	124	125
Gas							
To G-1	270	270	290	290	290	288	288
From G-1	124	124	127	128	274	285	125
From G-2	129	129	130	130	138	128	126
From G-3	121	121	125	125	124	124	125
Exit gas	160	-	150	200	150	200	150
Ambient	83	83	72	70	72	72	65
Relative humidity, %	42	42	84	84	80	80	93
Predicted temperature at which steam plume forms, °F ^e	124	124	159	160	154	154	181
Reheat temperature, °F	160	None	150	200	150	200	150
Percent opacity	Nil	5	20	5	30	5	90/15 at lip

^aMoles of active ammonia as ammonium sulfite-bisulfite per 100 moles of water.

^bInlet sample.

^cOutlet sample.

^dMole ratio of SO₂:NH₃.

^eCalculated temperature at which steam plume can form regardless of dilution; does not include a solid particulate plume, that is, an ammonia salt plume.

TABLE III (continued)
Summary of Operating Data for the
Test Series, April - May 1973

Test No.	I-14A	I-15	I-16A	I-17	I-17	I-18	I-18
Date	4/24	4/24	4/24	4/26	4/27	5/1	5/2
Time	3:45 p.m.	4:30 p.m.	4:10 p.m.	3:05 p.m.	1:45 p.m.	1:00 p.m.	4:00 p.m.
Liquor flow configuration	←—Once through—→			←—Recirculating—→			
Flow							
Liquor, gal/min							
To G-1 (bottom stage)	30	0	0	30	31	30	30
To G-2 (middle stage)	30	30	30	30	30	30	30
To G-3 (top stage)	15	15	15	25	26	25	25
Gas, ft ³ /min	2700	2700	2700	3000	3000	2900	2700
Liquor Ca							
G-1-I ^b	0.12	-	-	0.03	0.03	-	0.04
G-1-O ^c	0.11	-	-	0.03	0.03	-	0.04
G-2-I ^b	1.9	1.8	1.8	11.6	11.6	11.62	7.61
G-2-O ^c	1.9	1.7	1.7	11.8	11.8	11.72	8.39
G-3-I ^b	0.33	0.23	0.23	0.29	0.29	2.06	2.94
G-3-O ^c	0.29	0.24	0.24	0.38	0.38	2.39	3.21
Liquor S/cd							
G-1-I ^b	0.50	-	-	-	-	-	-
G-1-O ^c	0.70	-	-	-	-	-	-
G-2-I ^b	0.76	0.78	0.78	0.74	0.74	0.75	0.82
G-2-O ^c	0.81	0.86	0.86	0.75	0.75	0.75	0.79
G-3-I ^b	0.78	0.95	0.95	0.93	0.93	0.93	0.95
G-3-O ^c	0.91	0.95	0.95	0.93	0.93	0.89	0.92
Liquor pH							
G-1-I ^b	2.40	-	-	2.30	2.30	2.20	2.40
G-1-O ^c	2.30	-	-	2.20	2.20	2.20	2.30
G-2-I ^b	6.00	6.00	6.00	6.00	6.00	6.00	5.80
G-2-O ^c	5.80	5.70	5.70	5.90	5.90	5.90	5.70
G-3-I ^b	3.10	3.10	3.10	5.30	5.30	5.60	5.40
G-3-O ^c	3.10	2.90	2.90	5.50	5.50	5.60	5.40
SO ₂ , ppm							
Entering G-1	2600	2600	2600	2620	2840	2640	2520
Leaving G-1	2600	2540	2540	2440	2560	2480	2400
Leaving G-2	440	440	580	600	680	560	560
Leaving G-3	560	600	64	680	400	440	800
Percent removal	78.5	76.9	75.4	74.0	85.9	83.3	68.3
NH ₃ leaving G-3, ppm							
	39	34	34	89	70	93	85
Temperatures, °F							
Liquor							
From G-1	125	-	-	124	120	125	110
From G-2	126	128	126	128	128	134	125
From G-3	125	126	125	124	121	129	122
Gas							
To G-1	286	286	284	280	272	295	294
From G-1	126	268	255	124	120	125	115
From G-2	127	127	127	128	128	133	124
From G-3	126	125	124	124	120	127	121
Exit gas	200	150	200	200	160	200	160
Ambient	66	66	66	60	57	74	80
Relative humidity, %	93	92	92	96	51	64	56
Predicted temperature at which steam plume forms, °F ^e	181	181	181	198	170	141	131
Reheat temperature, °F	200	150	200	200	160	200	160
	0	80/30	5	40/5	15/10	10/5	5
Percent opacity		at lip		at lip	at lip	at lip	

^aMoles of active ammonia as ammonium sulfite-bisulfite per 100 moles of water.

^bInlet sample.

^cOutlet sample.

^dMole ratio of SO₂:NH₃.

^eCalculated temperature at which steam plume can form regardless of dilution; does not include a solid particulate plume, that is, an ammonia salt plume.



Figure 12. Operation with no water wash ahead of first absorber stage.



Figure 13. Operation with water wash ahead of first absorber stage.

The chloride concentration of the inlet flue gas was approximately 30 ppm and in the exit gas was about 3 ppm. The effect of chloride removal on plume reduction could not be separated from the effects of cooling and humidifying the gas ahead of the first absorber stage.

Heat losses were minimized by insulating the absorber system. The difference between the liquor temperature and the outside absorber skin temperature averaged about 1 °F. In operation without insulation, differences as great as 30 °F have been measured. No definite conclusions were drawn about how effective the insulation was in preventing plume formation.

The reheat required to dissipate the steam plume is a function of the ambient temperature and relative humidity. The reheat temperature required to avoid formation of a steam plume can be predicted for a given gas composition and known ambient conditions.⁹ The predicted reheat temperature for each test is included in Table III. Reheating the gas to a temperature above the predicted reheat temperature resulted in an acceptable plume when a water wash was used ahead of the absorber. In one test (I-4), an acceptable plume was obtained without reheating (Figure 14). In this case, the gas leaving the absorber had a higher temperature than the predicted reheat temperature. In those tests without a water wash, reheating decreased the plume opacity and in two tests (I-8 and I-16) the decreased opacity reached an acceptable level.

Tests I-17 and I-18 were extended runs designed to show the reheat required as a function of the ambient conditions (temperature and relative humidity). The plume opacity was maintained at a constant 5 percent by adjusting the reheat temperature of the scrubbed flue gas (maximum temperature set at 200°F). Data from these tests show that the reheat requirements for an acceptable plume increase with increased relative humidity. These data, as well as the predicted reheat temperature necessary to avoid formation of a steam plume and the opacity reading of the stack, are given below.

Relative Humidity, %	Ambient Temp, °F	Predicted Reheat Temp Required to Eliminate Steam Plume, °F	Reheat Temp, °F	Opacity Reading, %	
				At Stack Exit	10 Feet Above Stack
94	62	189	125	50	60
			(No Reheat)		
94	62	189	200	5	30
80	65	166	193	5	10
69	63	162	196	5	10
62	68	152	197	5	5
53	57	170	180	5	5
42	60	154	175	5	5
32	82	124	158	5	5



Figure 14. Acceptable plume with no reheat.

Formation of a high-opacity plume several feet from the discharge of the stack occurred on days when the relative humidity was high (see above data). Figure 15 shows a plume reforming downwind from a clear stack. Reheat temperatures required to avoid formation of a plume on days of high relative humidity and low temperature are impractical to achieve.

Conclusions

The ammonia bisulfate process is a promising candidate for second generation SO₂ removal systems. The following conclusions are reasonable for the bisulfate process:

- Under proper operation of the scrubber, fume formation can be controlled in the scrubber while producing a liquor having a high salt concentration ($C > 12$).
- For low salt concentrations, there is much greater flexibility in the manner of scrubber operation. However, such low concentration is prohibitively expensive in the bisulfate process, but very reasonable in the double alkali approach.
- Avoiding steam plume formation outside the stack on days of high relative humidity and low temperature may be impractical to achieve.
- Adequate separation of fly ash and ammonium sulfate crystals has not been effective in the pilot plant equipment; with proper equipment, adequate separation is expected.



Figure 15. Plume reforming downwind of stack.

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Conversion of English Units to Metric Equivalents

<u>Multiply English Unit</u>	<u>By</u>	<u>To Obtain Metric Equivalent</u>
ft ³ /min	0.0283	m ³ /min
lb	0.454	kg
°F	°C = $\frac{5}{9} (°F - 32)$	°C
gr/ft ³	2.288	g/m ³
in.	2.54	cm
ft	3.281	m
gal/min	3.785	l/min

AN EPA OVERVIEW OF SODIUM-BASED DOUBLE ALKALI PROCESSES

PART I. A VIEW OF THE PROCESS CHEMISTRY OF IDENTIFIABLE AND ATTRACTIVE SCHEMES

by

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INTRODUCTION

"Double" or "dual" alkali scrubbing involves circulating a clear liquor solution of a soluble alkali salt (Na , K or NH_3), with scrubbing taking place by absorption and reaction to form the bisulfite from the sulfite. The spent scrubbing liquor is treated with limestone and/or lime which precipitates the absorbed sulfur as CaSO_3 (and possibly some CaSO_4) and regenerates the alkali scrubbing solution. Refinements may involve additional regeneration of the sulfate which is formed by oxidation.

Double alkali flue gas desulfurization processes have received increased attention in recent years because of some potential advantages over competing scrubber systems.

The circulation of a clear liquor removes many erosion, corrosion and solid deposition problems. The regeneration using limestone and/or lime is relatively cheap and simple and the solid formed is acceptable as a throwaway product. The system appears to be versatile in terms of modes of operation and may even be used to produce a salable product. Both installed and operating costs for such systems appear to be very competitive with other flue gas desulfurization systems at comparable levels of development.⁽¹⁾

A number of organizations, including the Environmental Protection Agency, have become involved with major double alkali development efforts. General Motors has been heavily involved in the development and design of double alkali systems for use in its industrial facilities.⁽²⁾ Other major double alkali development efforts have been conducted by the Tennessee Valley Authority, Arthur D. Little, Inc., FMC Corporation, Envirotech Corporation and others. The

Environmental Protection Agency is funding a contract with Arthur D. Little, Inc. to aid the development of this promising flue gas desulfurization technology. Major aspects of the process chemistry and the attractive operating schemes which are under development by various organizations will be discussed in this paper. The particular systems under development by the various organizations are discussed in greater detail in Part II of this paper.

The mention of company or product names is not to be considered as endorsement or recommendation for use by the Environmental Protection Agency.

PROCESS DESCRIPTION

Absorption

A simple flow scheme for a double alkali process is shown in Figure 1. The clear alkali solution is circulated through a scrubber where SO_2 is absorbed and some oxidation takes place. The type of scrubber used depends somewhat on the concentration of the alkali scrubbing solution, but the clear scrubbing liquor circulated allows flexibility in scrubber selection. Some of the effluent liquor from the scrubber is recirculated and the remainder is sent to the regeneration system.

Regeneration

The liquor from the scrubber is treated with either limestone or lime (Ca(OH)_2) to precipitate the absorbed sulfur as calcium solids. After separating the precipitated solids, the regenerated scrubbing liquor, which has a high sulfite to bisulfite ratio, is sent back to the scrubber loop.

Oxidation and Sulfate Control

Oxidation of absorbed sulfur may require additional regeneration of the sulfate formed. A separate stream from the primary bisulfite/sulfite regeneration system may be treated specifically for sulfate regeneration to remove sulfate from the system as an insoluble solid product.

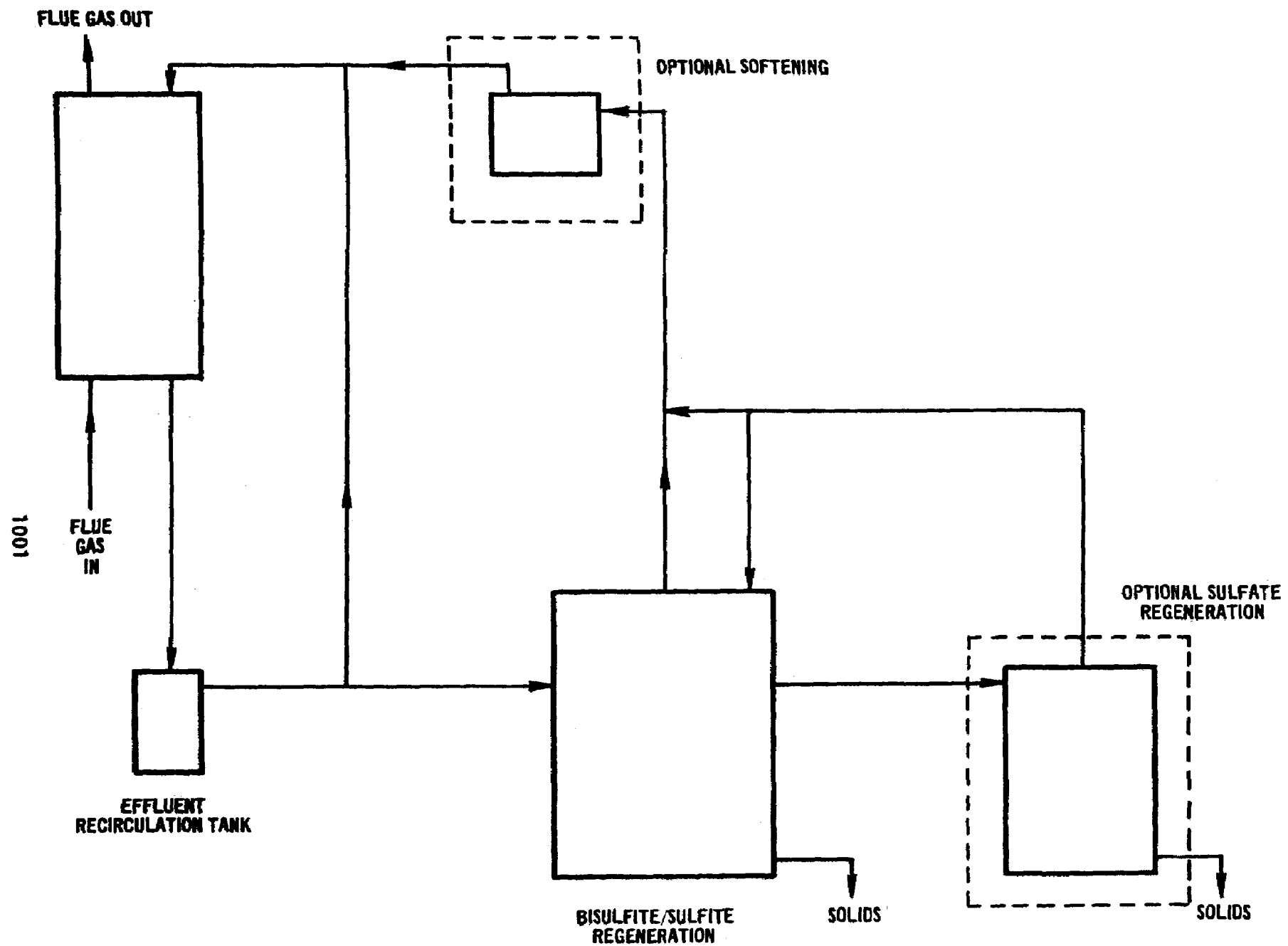


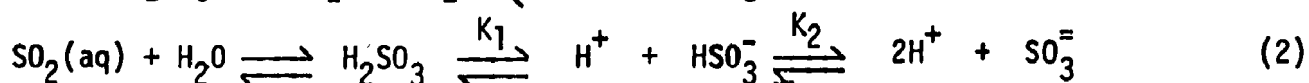
Figure 1. Double-alkali process flow scheme.

PROCESS CHEMISTRY

Generally, sodium-based double alkali systems are the only systems receiving major development emphasis. Since sodium-based systems are under major active development in this country and appear to have promise with respect to flue gas desulfurization, this paper will deal only with sodium-based systems.

Absorption

The scrubbing step involves absorption of SO_2 in a scrubbing solution of sodium sulfite, bisulfite and sulfate. The absorbed SO_2 reacts with the sulfite in solution to form bisulfite (reaction 1). The scrubbing solution is actually a buffer system of sulfurous acid (reaction 2). The pH range over which the scrubber systems may operate is from ~ 6 to 8.5. Figure 2 shows the major species in solution as a function of pH. Solutions of higher pH, with sulfite as the major species, are circulated into the scrubber while the lower pH (higher bisulfite concentration) spent solution from the effluent recirculation tank is sent to the regeneration system.



Regeneration

Spent scrubbing solution, with a low sulfite to bisulfite ratio, which is sent to the regeneration system is treated with limestone or lime to precipitate the absorbed SO_2 as calcium solids by reactions 3 and 4. The bisulfite is neutralized and sulfite is regenerated as the "active" scrubbing agent.

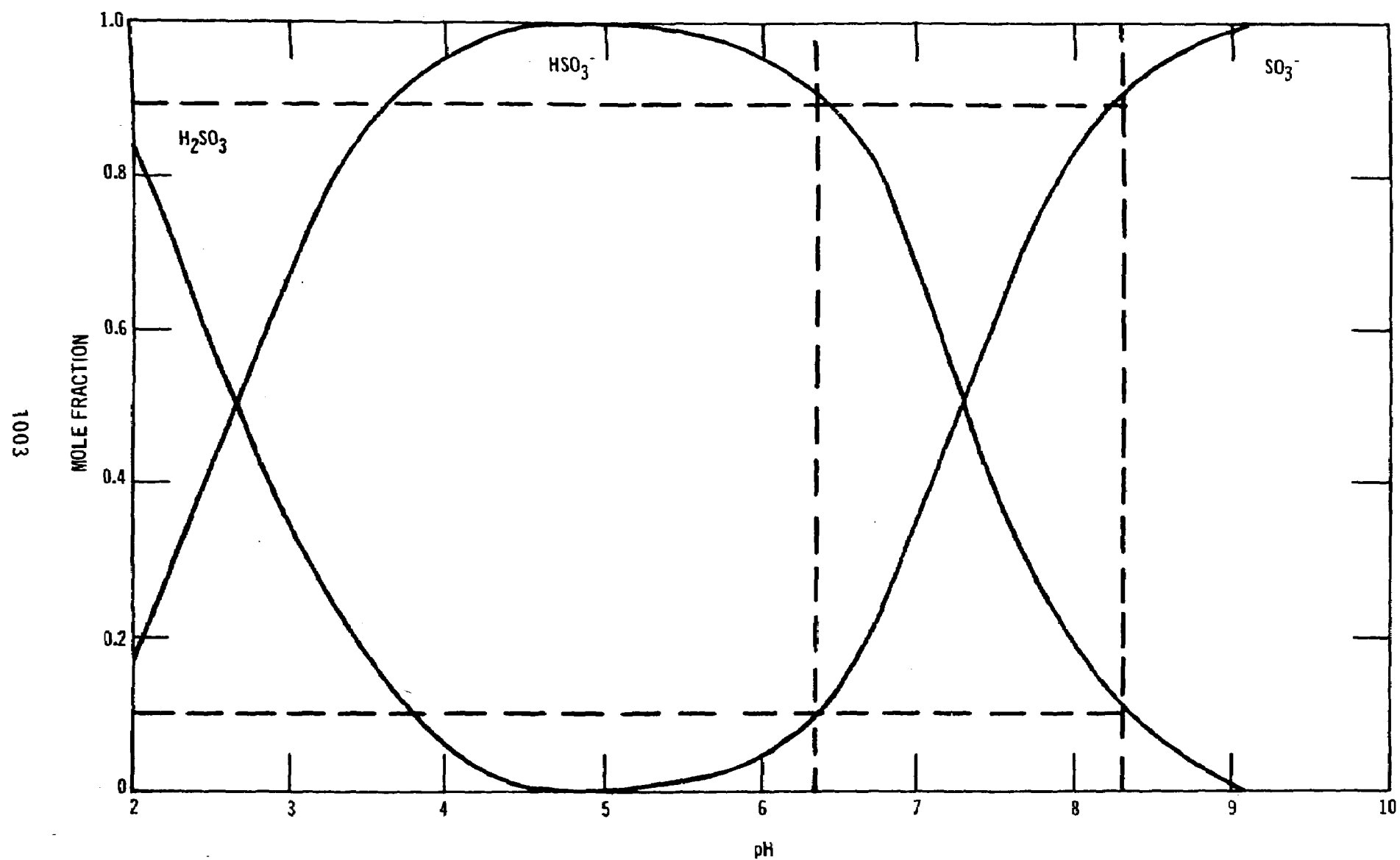
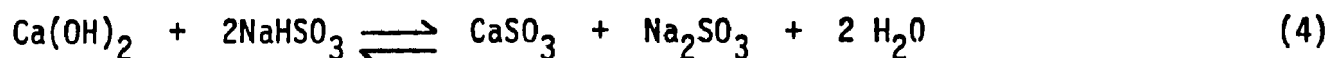
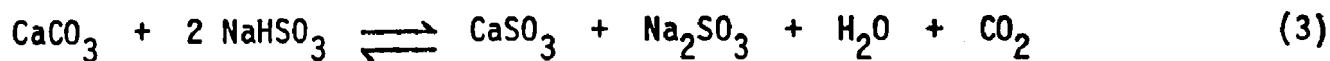
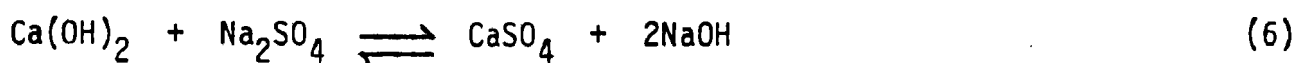
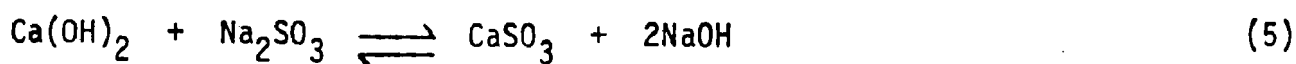


Figure 2. Distribution of aqueous sulfite species as a function of pH.



The EPA has performed batch laboratory experiments to characterize reactions 3 and 4 in simulated scrubber effluent solutions.⁽³⁾ The results of these experiments are consistent with laboratory and pilot plant results of other organizations involved in double alkali development programs. Hold times and utilizations using limestone and lime are mainly dependent on solution concentrations, temperature, agitation level and reactant stoichiometry. Generally, using limestone, hold times on the order of an hour or more are needed and utilizations on the order of 75-85% may be realized. Generally, using lime, hold times on the order of around 10 minutes may be used and utilizations of 90% or more may be realized. The benefits of using lime for the bisulfite/sulfite regeneration may be offset by higher chemical costs, slaking requirements, scaling potential and possible pH control problems.

In addition to the bisulfite/sulfite regeneration, lime may be used to react further with the sulfite and sulfate present in solution by reactions 5 and 6. The reaction between lime and sulfate is limited by the equilibrium hydroxide ion concentration of approximately 0.15M.⁽²⁾



Sulfite is the more active species and if more hydroxide is formed by reaction with sulfite (reaction 5) than the approximately 0.15M equilibrium value for reaction with sulfate (reaction 6), the reaction between lime and sulfate will not occur. The effective regeneration of sulfate using lime thus depends on the

sulfite ion concentration present and the hydroxide ion concentration formed from reaction 5. Batch scale laboratory experiments conducted by the Environmental Protection Agency have indicated that increased sodium sulfate concentrations tend to favor reaction with sulfate over sulfite when solutions are treated with an equilibrium amount of lime. With 1.78M (~ 20 wt%) sodium sulfate, roughly 50% of the final (3-hour batch reaction) hydroxide is from reaction with sulfate at 0.066M initial sulfite. With 0.67M (~10 wt%) sodium sulfate, roughly 50% of the final (3-hour batch reaction) hydroxide is from reaction with sulfate at less than .055M initial sulfite. Figure 3 shows the relative amount of reaction between lime and sulfite and sulfate in solution as a function of initial sulfite concentrations. Batch reactions were conducted at 52°C (125°F) with 1.78M (~ 20 wt%) sodium sulfate solutions and roughly equilibrium (0.078M/l) lime addition. This indicates that lime can be used to regenerate sulfate in the presence of dilute sulfite concentrations.

Oxidation and Sulfate Control

Oxidation of bisulfite and sulfite in the scrubber liquors occurs by reactions 7 and 8. The sulfate formed by oxidation must be removed from the system either as a solid product by regeneration or as soluble salts by a purge.



The effective removal of sulfate as a solid product is highly desirable from the standpoint of environmental acceptability. Completely closed loop operation is an ideal situation, while the opposite extreme would involve a balance between sulfate formed by oxidation and sulfate lost as soluble salts

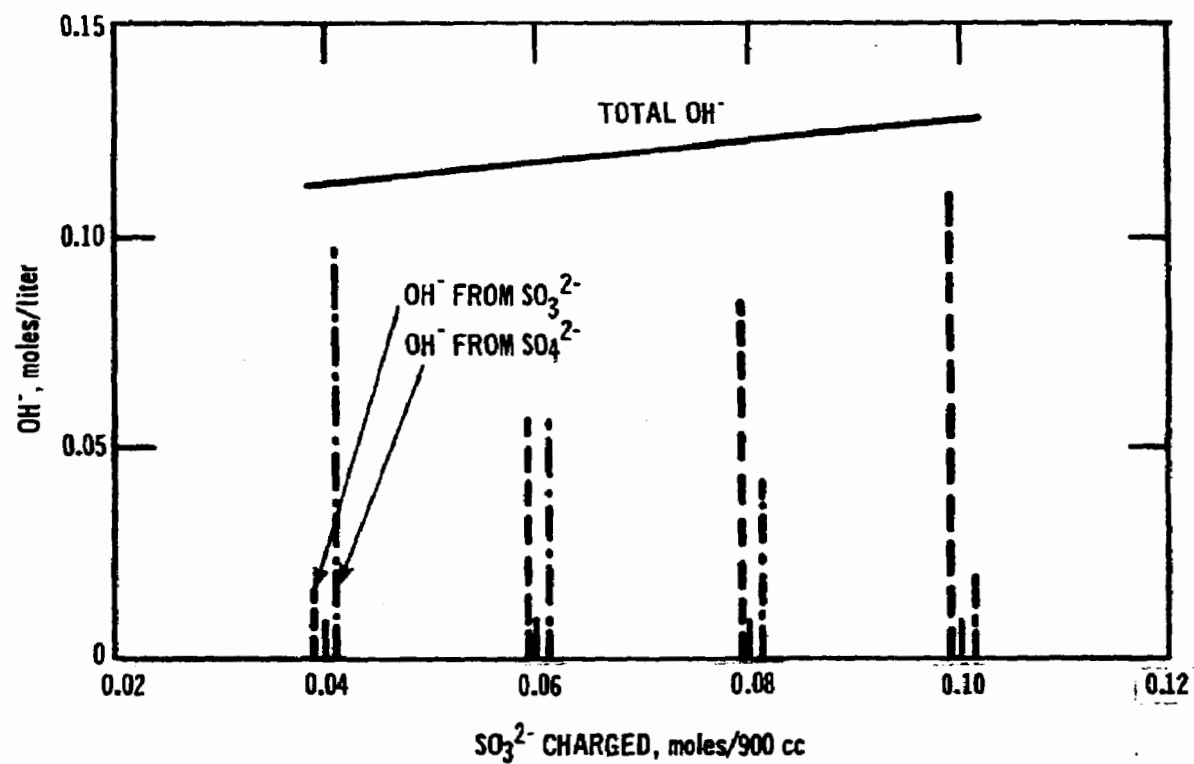


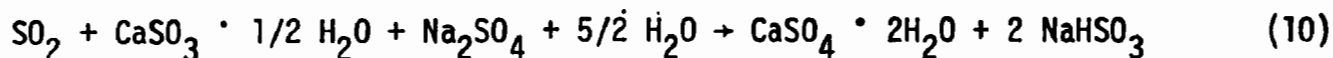
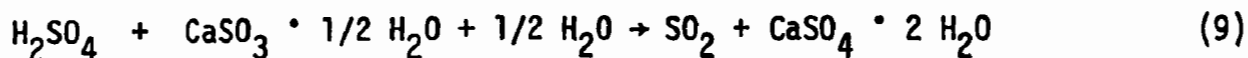
Figure 3. Batch reactions-- $\text{Ca}(\text{OH})_2/\text{Na}_2\text{SO}_3$, Na_2SO_4 [equilibrium OH^- , 1.60 moles/900 cc Na_2SO_4 @ 52°C (125°F)].

leaving the system with the solids or possibly as a simple purge. Considering the volume of sulfur removed and the fractional oxidation levels expected, the loss of all oxidized sulfur from the system as soluble salts represents a serious water pollution potential. Attempts must be made to regenerate the sulfate formed and remove it as an insoluble solid product.

Oxidation by reactions 7 and 8 is a function of solution concentration, oxygen mass transfer to the scrubbing solutions and probably a number of other factors such as traces of catalysts or inhibitors that may be present from sources such as fly ash. At least one oxidation inhibitor for this type of process is presently available.⁽⁴⁾ The oxidation reactions are not well defined or well understood. So far, most efforts have attempted to cope with oxidation problems without developing a complete understanding of the factors involved. The EPA recently funded a grant (No. 800303) with the University of Illinois to determine the mechanisms and kinetics of oxidation in soluble alkali scrubbing systems.

Sulfate regeneration with lime is possible in the presence of low sulfite ion concentrations ($<0.08M$) subject to the limitation of the equilibrium hydroxide ion concentration mentioned previously. The low sulfite ion concentrations necessary for effective sulfate regeneration using lime are a disadvantage because of the large volume of the dilute scrubbing liquor necessary for effective SO_2 removal. As an alternative to sulfate regeneration using lime, other sulfate removal techniques are under development which may be used with concentrated scrubbing liquors (sulfite concentrations of $\sim 0.5M$).

Sulfate removal would generally be carried out by treating a side stream from the scrubber liquor loop. An example of this approach is shown by the following reactions.⁽⁴⁾



A side stream from the scrubber discharge is mixed with calcium sulfite solids and sulfuric acid is added. The net effect is that sodium sulfate in the scrubbing liquor is converted to solid calcium sulfate and sodium bisulfite is generated for recycle to the main regeneration system. Additional limestone or lime is required to remove the sulfur added as sulfuric acid, i.e. the bisulfite generated by reaction 10. Roughly 125-150% of the theoretical sulfuric acid is required, based on the amount of sodium sulfate reacted. It is estimated that with 7% oxidation, roughly 9% of the solids produced would be derived from the sulfuric acid. This would add to the operating cost of a throwaway system.

Another alternative for sulfate removal being considered is the selective crystallization of sodium sulfate decahydrate by cooling of scrubbing liquors, in which the decahydrate will crystallize out at about 32°C (90°F). The crystals could then be separated and somehow treated to regenerate active sodium and precipitate a relatively insoluble solid product. Alternative methods of sulfate control are being considered.

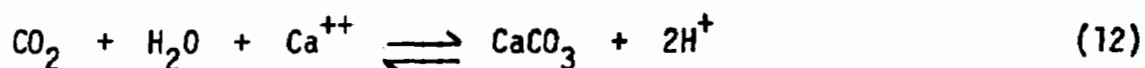
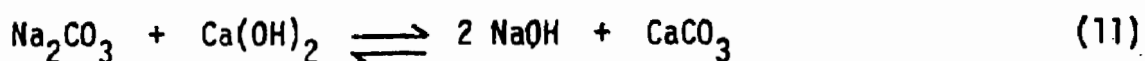
Scaling

Scaling may occur if conditions develop in the scrubber which cause supersaturation of calcium sulfate. The solubility product, K_{sp} , for calcium sulfite is roughly 2 orders of magnitude less than the K_{sp} value for calcium sulfate although steady state sulfite and sulfate concentrations may develop for which either solid may precipitate. Supersaturation and solids precipitation is desired

in the regeneration section but calcium ion concentrations must be controlled in the liquor returning to the scrubber to guard against supersaturation and precipitation in the scrubber. The relative solubilities of the various calcium compounds are shown in Figure 4.

The presence of solid calcium hydroxide and/or solid calcium sulfate at equilibrium with the liquid in the regeneration system produces high calcium ion concentrations on the order of 300-400 ppm. These high calcium ion concentrations must be reduced considerably to guard against calcium sulfate supersaturation and scaling in the scrubber.

Calcium ion concentrations may be controlled by "softening" reactions 11 and 12.



Treatment of scrubbing liquor with sodium carbonate (reaction 11) or carbon dioxide (reaction 12) before being sent to the scrubber leads to precipitation of calcium carbonate and thus removes calcium ions from solution. The reduction of calcium ion concentrations in this manner ensures against scaling in the scrubber. Addition of sodium carbonate has the advantage of both softening and replacing sodium losses from the system. Addition of Na_2CO_3 has the disadvantage of requiring a possible sodium purge if the amount required for softening exceeds the amount required to replace sodium losses.

Addition of carbon dioxide, which is acidic, also requires increased use of regeneration chemicals for neutralization. The net effect of adding either sodium carbonate or carbon dioxide is to reduce calcium ion concentrations

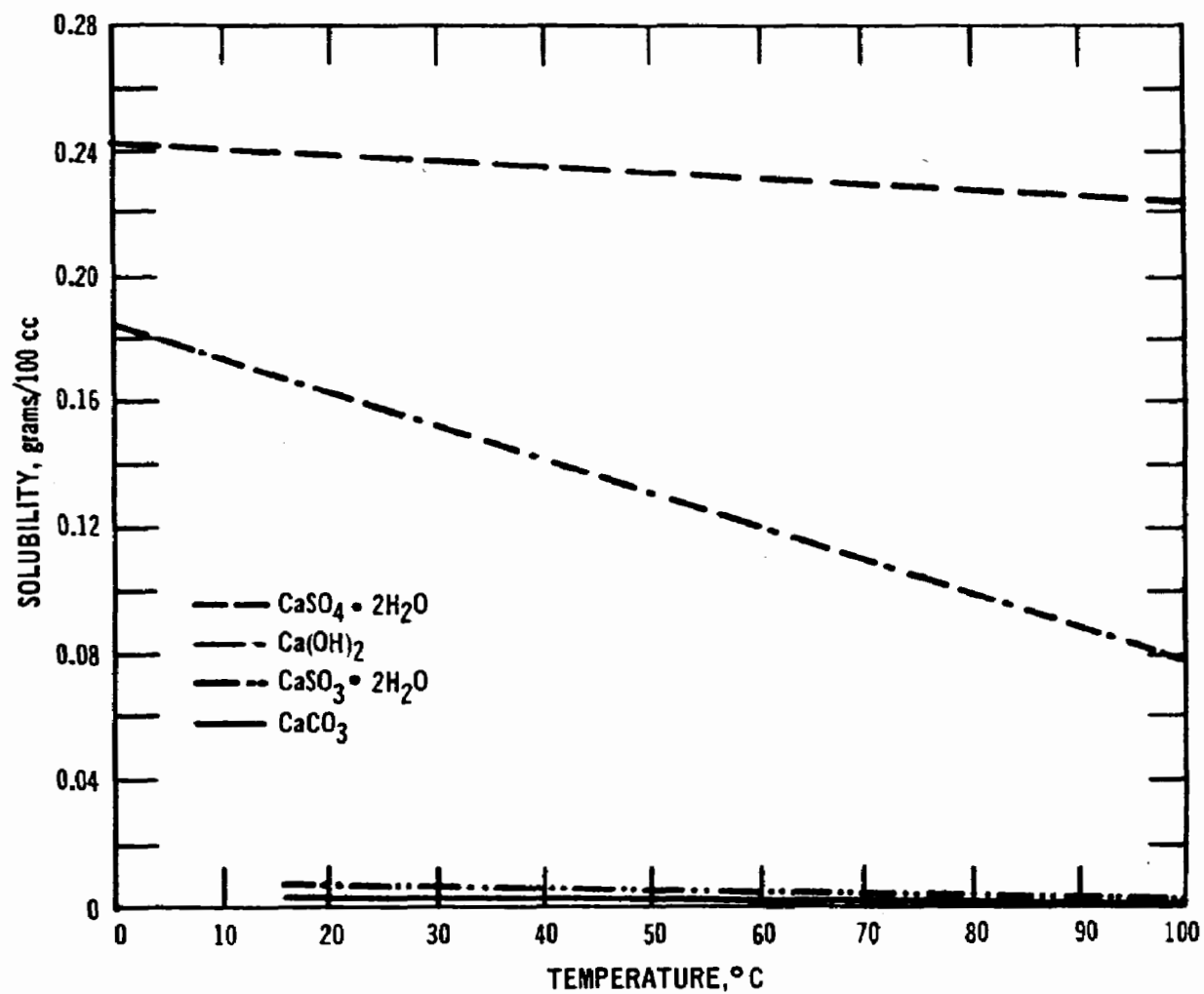


Figure 4. Relative solubilities of calcium compounds.

entering the scrubber to a level below the saturation value for calcium sulfate.

Process Chemistry--Summary

Before going on to discuss possible modes of operation for sodium-based double alkali systems, a brief summary of the process chemistry discussion will be made. Sulfur oxides are absorbed into a sulfite/bisulfite buffer solution. This absorption shifts the pH down and increases the bisulfite concentration. The liquor from the scrubber may then be treated with limestone to precipitate calcium sulfite and neutralize the bisulfite. The liquor from the scrubber or the limestone reaction vessel may be treated with lime to precipitate calcium sulfite and possibly calcium sulfate. Oxidation of absorbed sulfur requires the regeneration of sulfate; a few possible methods have been discussed. Calcium ion concentrations in the scrubber can be controlled by softening steps in the liquor loop.

DOUBLE ALKALI OPERATING SCHEMES

Five relatively distinct modes of operation have been identified for sodium/calcium double alkali scrubbing systems. These modes will be discussed very briefly with some advantages and disadvantages noted for each. More detailed discussion of these modes, with emphasis on commercial developments, is presented in Part II of this paper. The five operating schemes to be discussed are:

1. Limestone and lime regeneration, dilute active alkali, with sulfite softening.
2. Lime regeneration, dilute active alkali, with sulfite softening.
3. Lime regeneration, concentrated active alkali with side stream sulfate treatment (removal).
4. Limestone regeneration, concentrated active alkali with side stream sulfate treatment (removal).
5. Lime regeneration, dilute active alkali, with carbonate softening.

Limestone and Lime Regeneration, Dilute Active Alkali, with Sulfite Softening

The first mode identified is a double-loop (limestone/lime), dilute alkali system. Dilute alkali indicates that the sulfite or alkali concentration entering the scrubber will be less than approximately 0.08M. Dilute alkali scrubbing solutions allow sulfate regeneration with lime in this mode of operation. "Double loop" refers to the regeneration method. Spent scrubbing liquor is treated with limestone to neutralize the bisulfite and precipitate calcium sulfite. A stream from this limestone reaction vessel is then treated with lime to precipitate calcium sulfite and sulfate and generate sodium hydroxide.

The relative amount of reaction between lime and the sulfite and sulfate is determined mainly by sulfite and sulfate concentrations and lime stoichiometry. The liquor from the lime reaction vessel is returned to the limestone reaction vessel to ensure unsaturated calcium ion concentrations going to the scrubber. Desaturation is accomplished because of the presence of sulfite ion in the limestone reactor. The reduction of calcium ion concentrations by calcium sulfite precipitation is referred to as sulfite softening. Sodium carbonate may be added to provide additional softening and make up any sodium losses.

This scheme has the disadvantage of requiring relatively long hold times for the reaction with limestone, requiring two major reactors, and having to circulate large volumes of relatively dilute scrubbing liquor. The advantages appear to be the use of relatively inexpensive limestone and lime for regeneration of both bisulfite and sulfate, and relatively simple equipment requirements.

Lime Regeneration, Dilute Active Alkali, with Sulfite Softening

The second mode of operation is a double-loop (lime only), dilute alkali system. This system arrangement is very similar to the first system discussed. Spent scrubbing liquor is treated with lime to neutralize the bisulfite only. A stream from the lime/bisulfite reaction vessel is then treated with additional lime in a separate reaction vessel to react with sulfite and sulfate, forming calcium solids and sodium hydroxide. The liquor from this second reaction vessel is returned to the lime/bisulfite reaction vessel to ensure unsaturated calcium ion concentrations with respect to calcium sulfate by "sulfite" softening of the liquors before entering the scrubber.

This flow scheme has the disadvantage of difficult pH and calcium ion control in the regeneration loop because of the addition of a relatively concentrated

strong base (lime) to a dilute solution of a weak acid. The regeneration loop requires two reactors, and large volumes of relatively dilute scrubbing liquor must be circulated to the scrubber. The advantages of this system appear to be the relatively short hold times necessary for regeneration using lime and the relatively simple equipment requirements.

Lime Regeneration, Concentrated Active Alkali, with Side Stream Sulfate Treatment

The third mode of operation involves lime regeneration, concentrated alkali solutions and side stream treatment for sulfate removal and control. Lime is used for the bisulfite neutralization of the concentrated ($\sim 0.5M$) alkali scrubbing solutions. A side stream is taken from the liquor loop and treated specifically for sulfate removal. The major difference between dilute ($<0.08M$) and concentrated ($\sim 0.5M$) alkali systems is that lime cannot be used to regenerate sulfate in concentrated (greater than $\sim 0.08M$) sulfite solutions because of the equilibrium hydroxide ion concentration mentioned previously. Side stream treatment has been accomplished with proven technology (reactions 9 and 10)⁽³⁾ but sulfate removal and control is the subject of intense development efforts since proven technology is limited in this critical area.

This third flow scheme has the disadvantage of possible sulfate regeneration complications. The advantages of this flow scheme are: the relatively short hold times necessary for the bisulfite/sulfite regeneration with lime, high reactant utilizations, an advanced state of development and high SO_2 removal efficiencies with low flows of the concentrated alkali scrubbing liquors. This third mode of operation appears to be very promising but universal large-scale successful application depends on effective treatment for sulfate removal and control.

Limestone Regeneration, Concentrated Active Alkali, with Side Stream Sulfate Treatment

The fourth mode of operation involves limestone regeneration, concentrated alkali solutions and a side stream treatment for sulfate removal and control. Limestone is used for the bisulfite neutralization of the concentrated ($\sim 0.5M$) alkali scrubbing solutions. A side stream is taken from the liquor loop and treated specifically for sulfate removal. This scheme, like the previous one, has the possible disadvantage of sulfate regeneration complications. This scheme also has the disadvantage of requiring long hold times for the bisulfite/sulfite regeneration using limestone. Advantages of this flow scheme appear to be high SO_2 removal efficiencies with low liquor flow rates and high reactant utilizations. Successful large-scale application of this flow scheme also depends on effective treatment for sulfate removal and control.

Lime Regeneration, Dilute Active Alkali, with Carbonate Softening

The fifth mode of operation is lime regeneration, dilute alkali with carbonate softening for calcium ion (scaling) control. The spent scrubbing liquor is treated with lime to neutralize bisulfite and react with sulfite and sulfate. The dilute active alkali allows simultaneous reaction with both the sulfite and sulfate by reactions 6 and 7 even though the equilibrium hydroxide ion concentration for sulfate regeneration (reaction 7) limits the extent of the reactions. The calcium ion concentration in the liquor from the lime treatment tank would be high and represent serious scaling potential unless it is reduced considerably below saturation values for calcium sulfate and hydroxide. Carbon dioxide may be added to the system to precipitate calcium carbonate (reaction 12) and significantly reduce calcium ion concentrations in the liquor before entering the scrubber. Sodium carbonate may be used to soften (reaction 11) and make

up sodium losses. This scheme has the disadvantages of possible inadequate sulfate regeneration, possible scaling potential and having to circulate large volumes of relatively dilute scrubbing liquors. The advantages appear to be the ability to deal with high oxidation levels, relatively simple equipment requirements and an advanced state of development.

Modes 2 and 5 are very similar except the double-loop regeneration method of mode 2 would probably provide both sulfate regeneration and calcium ion control without a major softening step involving the addition of chemicals such as sodium carbonate or carbon dioxide. All advantages and disadvantages discussed serve mainly to compare these five modes relative to each other and not to other scrubbing systems. The advantages and disadvantages of these double alkali systems relative to other scrubber systems have been discussed in the introduction.

SUMMARY

The major process chemistry for sodium/calcium double alkali scrubbing of SO_x is well defined and reasonably well understood. A number of relatively distinct modes of operation have been identified and are at various stages of development. Development efforts are presently being directed at effective sulfate regeneration in concentrated sulfite solutions, control of scaling, and control and understanding of the oxidation reactions. Solids characteristics such as settleability, cake moisture and cake "fixing" are also being studied. Many minor variations are possible in the flow scheme configurations discussed; however, the description of these schemes was meant mainly to show the versatility of double alkali systems and the range of development efforts.

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AN EPA OVERVIEW OF SODIUM-BASED
DOUBLE ALKALI PROCESSES

PART II

STATUS OF TECHNOLOGY AND DESCRIPTION
OF ATTRACTIVE SCHEMES

by

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ABSTRACT

AN EPA OVERVIEW OF SODIUM-BASED DOUBLE ALKALI PROCESSES

PART II. STATUS OF TECHNOLOGY AND DESCRIPTION OF ATTRACTIVE SCHEMES

Important criteria for evaluation of double alkali schemes are given.

Flow sheets for potentially attractive schemes of operation are presented and described with emphasis on evaluation of each with respect to the criteria given.

A brief description of selected pilot plant and prototype experience and future plans for further development of double alkali systems is given. In addition, an effort is made to categorize each of the known commercially available double alkali systems presently being marketed, in accordance with the identified schemes.

The EPA/A. D. Little double alkali development program plan and general philosophy are described.

Double alkali technology, although less advanced, is presented as being potentially more reliable and less costly than lime/limestone technology.

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NOTES

1. Company Names and Products.

The mention of company names or products is not to be considered an endorsement or recommendation for use by the U. S. Environmental Protection Agency.

2. Units of Measure.

EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. Generally, this paper uses British units of measure.

For conversion to the Metric system, use the following equivalents:

<u>British</u>	<u>Metric</u>
5/9 (°F-32)	°C
1 ft	0.3048 meter
1 ft ²	0.0929 meters ²
1 ft ³	0.0283 meters ³
1 grain	0.0648 gram
1 in.	2.54 centimeters
1 in. ²	6.452 centimeters ²
1 in. ³	16.39 centimeters ³
1 lb (avoir.)	0.4536 kilogram
1 ton (long)	1.0160 metric tons
1 ton (short)	0.9072 metric tons
1 gal	3.7853 liters

INTRODUCTION AND BACKGROUND

Based on presently known firm commitments of utilities, the prevalent method of stack gas cleaning for reduction of sulfur oxide emissions from fossil fueled power plants is the wet lime/limestone scrubbing process.⁽¹⁾ Unfortunately, this method of control is not the perfect solution to the problem. Problems have been identified with wet lime/limestone scrubbing of flue gas which are mainly due to the fact that the absorbent and the products of the absorption reaction are present in the scrubbing equipment in the form of a slurry which has a tendency to cause solids build-up, scaling and erosion in the equipment; these can reduce the overall reliability of the system.

In order to circumvent the problems inherent with the use of an absorbent slurry, scrubbing with a soluble alkali is a logical first consideration; however, by itself, this method is not satisfactory since it would necessitate the disposal of large quantities of liquid containing dissolved sulfur compounds, thus creating a water pollution problem. The "Double Alkali" process, on the other hand, combines the advantages of wet lime/limestone scrubbing with those of soluble alkali scrubbing by scrubbing with soluble alkali and following with regeneration of the soluble alkali and precipitation of the absorbed sulfur oxides as insoluble calcium salts. The regeneration reaction involving the use of calcium compounds, which are considered to be potentially scale producing, is caused to occur outside the scrubber system where scaling tendencies can be more adequately controlled. In addition--whereas with lime/limestone systems, SO₂ removal is limited by solids dissolution rate--no such limitation is inherent with soluble alkali scrubbing systems. The net effect of the use of a double alkali process is the same as that of a wet lime/limestone process in that limestone and/or lime is consumed and calcium sulfite and sulfate are generated as a disposable waste product. An important exception to the previous statement is the fact that the disposable waste may be moderately contaminated with soluble salts which can potentially cause a water pollution problem.

The term "double alkali" is used generally to describe systems which employ a soluble aqueous alkali (e.g., Na⁺, K⁺, NH₄⁺ based) to scrub acidic sulfur oxides from flue gas and then produce an insoluble throwaway product by reacting the scrubber effluent with limestone and/or lime. This paper will address only sodium-calcium systems as these are the prevalent schemes under study and commercially available in the United States. An overview of these systems is presented with only some reference to the chemical complexities associated with them. The chemistry of these systems has been discussed in detail in part I of this paper; in summary, however, the principal scrubbing reaction in the many variations of the double alkali process discussed involves the absorption of sulfur dioxide by an aqueous solution of sodium sulfite, converting the sulfite to bisulfite.

IMPORTANT CONSIDERATIONS

In the discussion of various double alkali schemes, it is considered helpful to compare these in relation to lime/limestone scrubbing systems. The double alkali process has been considered a second generation version of the wet lime/limestone process and therefore comparison is considered reasonable.

Sulfate Removal

As in the operation of a lime/limestone system, some of the sulfur absorbed in double alkali processes appears in the system in the oxidized form as sulfate. In order to operate a double alkali system in a steady state continuous manner, provisions must be made to remove sulfate from the system at the rate at which it is formed in or absorbed into the system. This is not the case with lime/limestone systems since the oxidation product is insoluble gypsum. Failure to allow for sulfate removal in double alkali systems will ultimately result in precipitation of sodium sulfate somewhere in the system: quite possibly in the scrubber circuit. The known possible methods of removing sulfate from the system are:

1. purging a waste liquid stream containing dissolved sodium sulfate;
2. removing wet calcium sulfite/sulfate/flyash sludge containing dissolved sodium sulfate in the occluded water;
3. removing solid sodium sulfate from the system for sale or other disposal by selective crystallization or operation of another concentration process; and
4. precipitating the sulfate as insoluble calcium sulfate to be disposed of with the waste product sludge.

The first method is ecologically undesirable due to its contributing to water pollution by emission of dissolved sodium salts. In addition, depending on the concentration of active alkali (sulfite/bisulfite), the liquid discharge may have a high COD value.

The second method disposes of the sulfate in a more subtle manner than the first. Here a liquid stream is actually purged; however, it is much less obvious since the liquid is contained in the solid waste product, which appears to be relatively dry even when containing up to 40 percent moisture. The potential contribution to water pollution in this case is due to the leachability of the waste product sludge and water run-off from the sludge disposal area. A highly leachable sludge will result in slow contamination of the ground water table in the disposal area while water run-off would lead to contamination of surface water by soluble salts. An acceptable alternative to direct disposal of

wet solids as outlined above, would be disposal of a treated sludge which contains the required amount of soluble sulfates but in a "fixed" solid, unleachable, innocuous form. Although at present there is no demonstrated commercially available system to accomplish this, inclusion of double alkali sludge as part of a current program concerned with ecological treatment and disposal of lime/limestone wet scrubbing sludge is under consideration by EPA. (2)

The third method cited for sulfate removal involves the separation of sodium sulfate crystal from the scrubber liquor by a heating-cooling cycle or possibly by operation of a vapor compression cycle such as the system being marketed by Resources Conservation Corporation as a brine concentrator. To date, these methods have not been applied to double alkali systems and therefore more evaluation is necessary to determine their applicability. One possible problem created in removal of sodium sulfate crystal is the ultimate disposal of this soluble salt. Since the market for large quantities of sodium sulfate is sparse at best, dissolution and treatment with lime to produce insoluble calcium sulfate (gypsum) may be the acceptable short-term solution to the problem.

The fourth method, precipitating calcium sulfate directly from the scrubber liquor, can only be accomplished under carefully controlled conditions. Basically, calcium sulfate and sulfite will not be precipitated in appreciable quantities, simultaneously, in neutral or basic solution with lime treatment, unless the $[\text{SO}_4^{=}] / [\text{SO}_3^{=}]$ concentration ratio in solution is relatively high. A simple explanation for this is that CaSO_3 is much less soluble than CaSO_4 and thus is preferentially precipitated from solution. Since the concentration of sulfate is limited by the solubility of sodium sulfate (approximately 3 molar) the active alkali, sulfite, must be relatively dilute in order to maintain a high $[\text{SO}_4^{=}] / [\text{SO}_3^{=}]$ ratio and thus precipitate calcium sulfate upon treatment with lime. (See part I of this paper.)

A variation of the fourth cited method, precipitating calcium sulfate from the scrubber liquor, was developed by the Japanese. In this variation, a small portion of the scrubber liquor (a "slip stream") is treated with sulfuric acid and calcium sulfite to precipitate calcium sulfate. Adjustment of the pH with sulfuric acid allows the calcium sulfite to go into solution as soluble calcium bisulfate, thus increasing the calcium ion concentration in solution until the solubility of calcium sulfate is exceeded and calcium sulfate is precipitated from solution. The major advantage of this variation is that concentrated active alkali can be used in the scrubber loop. The obvious disadvantage is that sulfur is added to the system as sulfuric acid, procured from another source, and must be removed along with the sulfur in the flue gas.

Scale Prevention

One of the primary reasons, and probably the most important, for development of double alkali processes was to circumvent the scaling problems associated with lime/limestone wet scrubbing systems. Therefore, an obvious consideration in any double alkali system is the ability of the system to operate in a non-scaling manner.

In order to eliminate scaling tendencies, the calcium concentration in the scrubber liquor must be held to a minimum. Recirculation to the scrubber loop of supernatant liquor from a lime reaction vessel which is controlled to precipitate sulfite and sulfate is not acceptable. The calcium concentration of this liquor would be high enough to cause scaling problems since it is saturated with respect to calcium sulfate and calcium hydroxide. Figure 1 shows (with straight line interpolation between two data points) relative solubilities in water of the various calcium compounds present in a typical double alkali system. The figure shows that CaSO_4 and Ca(OH)_2 , although only slightly soluble, are about two orders of magnitude more soluble than CaCO_3 and CaSO_3 . In order to minimize the calcium concentration in the scrubber loop, the liquor returned to the scrubber from the regeneration process should be saturated with respect to CaSO_3 or CaCO_3 but not with respect to CaSO_4 or Ca(OH)_2 .

It should be noted that Figure 1 is not meant to specify the exact concentrations to be expected in double alkali systems but only to point out the direction to go in order to minimize scaling tendencies. The actual solubilities of these calcium species in real systems will be greatly affected by such important factors as pH, ionic strength and the presence of other chemical species.

In many cases scaling problems are not only due to high soluble calcium values related to saturated solutions of CaSO_4 and Ca(OH)_2 but are also possibly due to supersaturation with respect to any of the calcium compounds. In order to reduce scaling due to supersaturation, provisions to maintain high concentrations of suspended solids in the reaction zones of the regeneration equipment are necessary. This can be accomplished by recirculating precipitated solids to the reaction zones. This technique is stressed in the Envirotech system which is described under "Status of Technology" later in this paper. It has also been referred to as a crystal seeding.

In general, efforts to minimize scaling rely upon:

1. carbonate softening (i.e., reduction of soluble calcium),
2. sulfite softening, and
3. crystal seeding techniques.

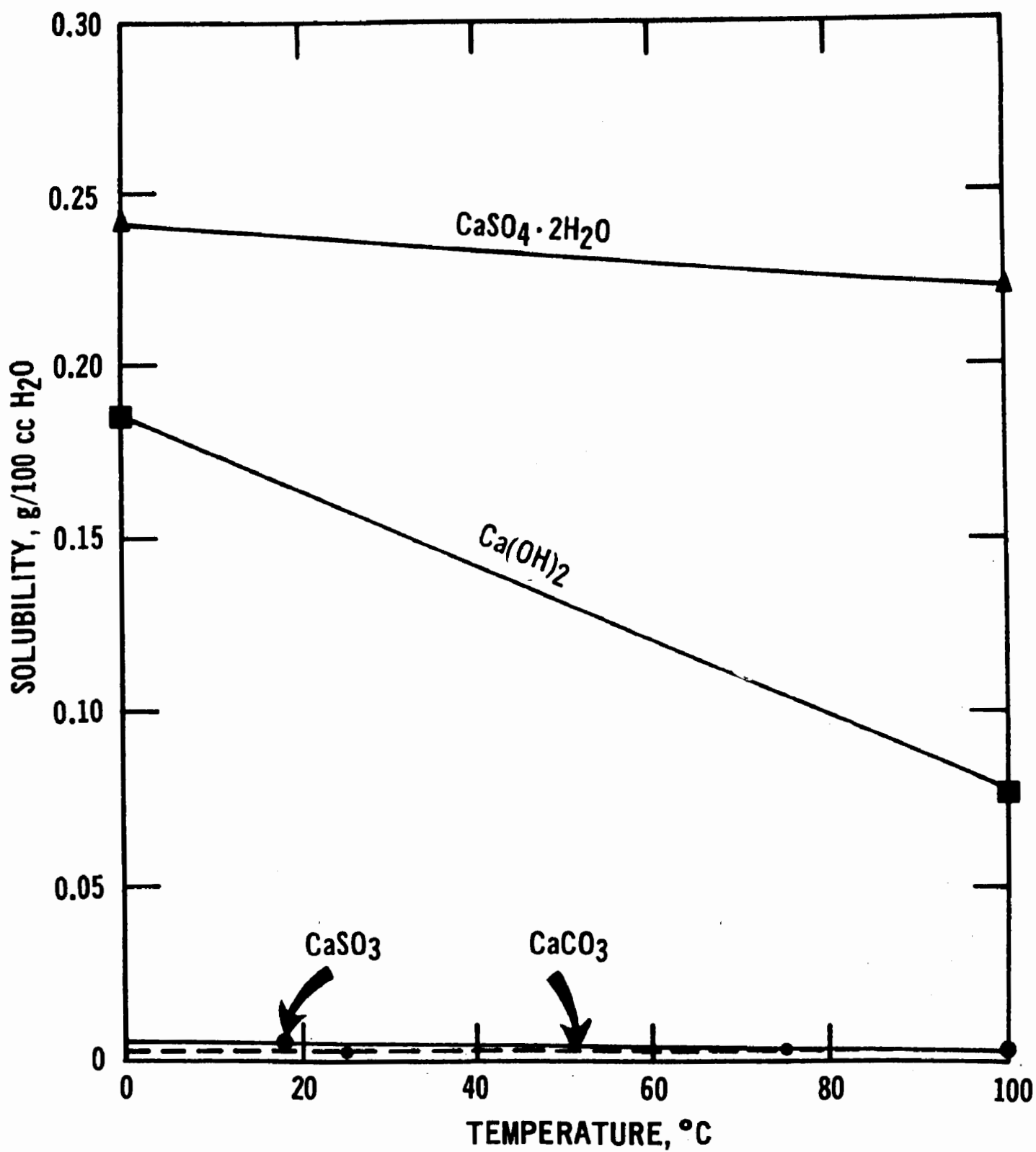


Figure 1. Solubility of calcium compounds.

Water Balance

In order to operate a closed system to avoid potential water pollution problems, system water balance is a primary concern. Water cannot be added to the system at a rate greater than the normal water losses from the system.

Generally there is a tendency to add fresh water to a scrubbing system to serve many purposes. These include:

1. saturation of flue gas,
2. pump seal needs,
3. demister washing needs,
4. slurry make-up needs, and
5. waste product washing.

On the other hand water should only leave the system in the following ways:

1. evaporation by the hot flue gas,
2. water occluded with solid waste product, and
3. water of crystallization in solid waste product.

Careful water management, part of which is the use of recycled rather than fresh water wherever possible, is necessary in order to operate a closed system.

Waste Product Washing

As previously indicated, disposal of wet solid waste containing soluble salts is ecologically undesirable. In addition, allowing active alkali or sodium salts to escape from the system is an important operating cost factor. Sodium make-up to double alkali systems is usually accomplished by adding soda ash (recently quoted at \$42 per ton) at some point in the system. Thus, both ecological and economic considerations dictate that waste product washing is desirable. With lime/limestone systems, there is no need to wash the solid waste product.

SO₂ Removal

Generally, the concentrated active alkali systems have a greater capability for SO₂ removal than the dilute systems. Based on pilot testing of concentrated systems in Japan, SO₂ removals of up to 98 percent

have been reported.⁽³⁾ With the dilute systems the range of SO₂ removal to be expected is probably in the 80-90 percent range. In general, SO₂ removal with double alkali systems is more efficient than with lime/limestone systems, since the active alkali is soluble.

Costs

Based on cursory design and cost analysis, with the assumption that a single scrubber device (e.g., a single stage venturi) can be used to remove particulates and SO₂ to the extent required to meet new source performance standards, the capital and operating costs of double alkali systems appear to be significantly less than those for a lime or limestone system designed for the same requirements.⁽⁴⁾

Generally, the dilute active alkali systems tend to be higher in capital costs than the concentrated systems since both equipment size and process flows are required to be larger to accomplish the same degree of desulfurization. Methods used for sulfate removal and for reduction of scaling tendencies will affect both capital and operating costs.

SCHEMES OF OPERATION

Five basic schemes of operation considered to be potentially attractive, based on design considerations discussed previously, are described below and illustrated with schematic diagrams. It should be noted that many variations on these five basic schemes can be produced by varying the many parameters associated with the systems such as:

1. concentration of active alkali;
2. water make-up addition points;
3. regeneration with lime, limestone or lime plus limestone;
4. sulfate removal method; and
5. method employed to reduce scaling tendency.

In addition, although the schematics shown are specific with respect to the type of equipment employed, this is done only for the sake of establishing the equipment function at a glance. Thus, the systems presented are not limited to the specific equipment shown, namely:

1. scrubber type,
2. solids separation equipment,
3. settling and thickening equipment, and
4. reaction vessel type.

Limestone and Lime Regeneration, Dilute Active Alkali with Sulfite Softening (Scheme 1)

This scheme of operation is typified by Figure 2. In this system sulfur dioxide is absorbed by the active alkali, aqueous sodium sulfite, in the scrubber to form sodium bisulfite. Limestone is used to regenerate sodium sulfite, by reacting with bisulfite and precipitating calcium sulfite in the limestone reaction vessel. Lime is used to precipitate sulfate as gypsum with regeneration of active hydroxide ion in the lime reaction vessel. The hydroxide is recirculated to the limestone reaction tank where it reacts with bisulfite to regenerate sulfite as does the limestone.

The product from the limestone reaction vessel is split into a clarified liquor stream for recirculation to the scrubber loop and a slurry stream to feed the lime reaction vessel for sulfate removal.

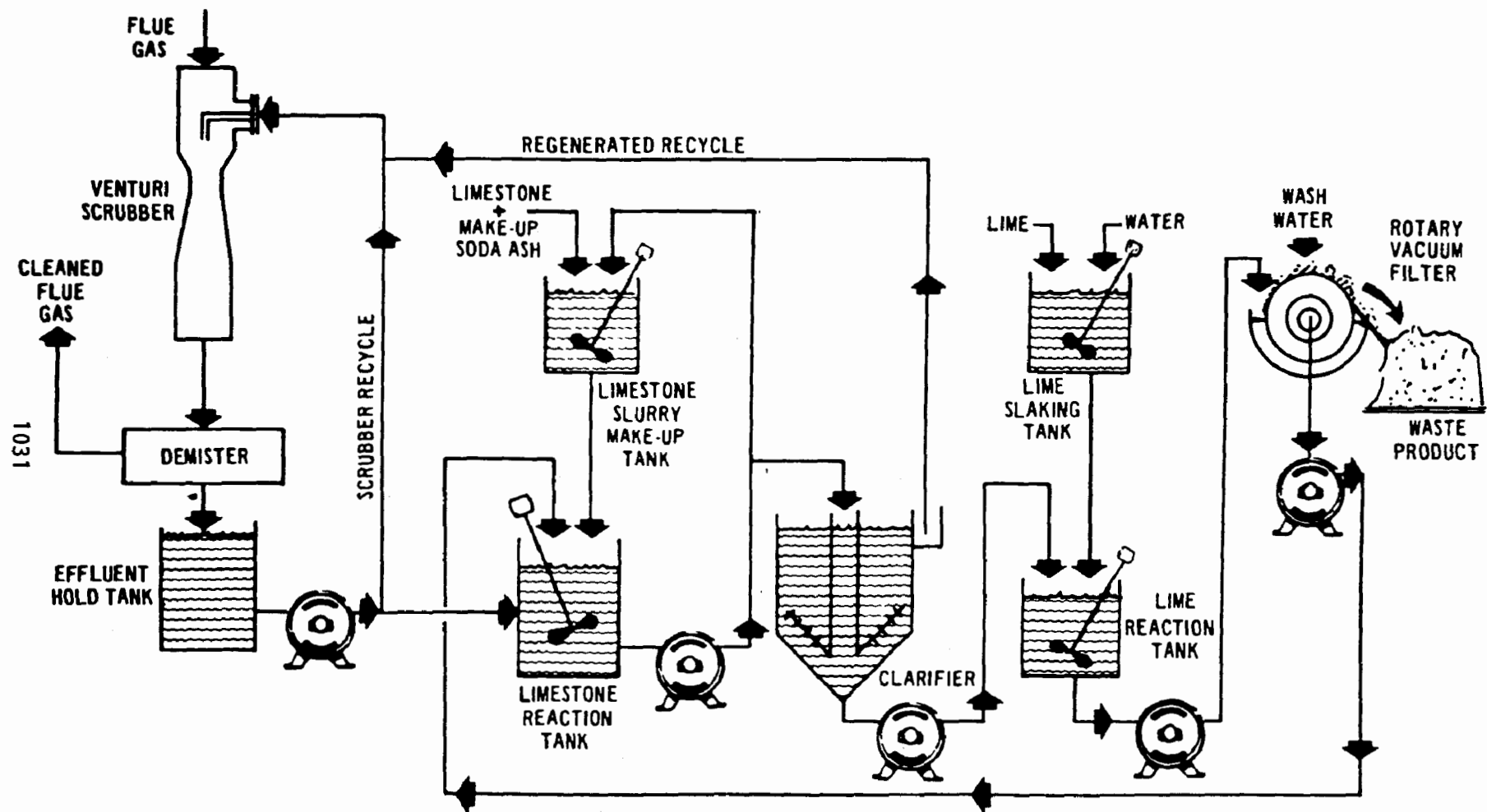


Figure 2. Limestone and lime regeneration, dilute, sulfite softening (Scheme 1).

Supernatant liquor (containing hydroxide ion) from the lime reaction vessel is recirculated to the limestone reaction vessel while the remaining slurry is processed to remove waste product solids from the system.

Sulfate is removed from the system as gypsum, by precipitation with lime; but in order to accomplish this, the system must be operated with dilute active alkali in order to maintain the needed high $[\text{SO}_4^{=}]/[\text{SO}_3^{=}]$ ratio. Dilute active alkali is somewhat of a disadvantage with double alkali systems in that higher liquor flow rates are needed and scrubbing efficiency is generally lower than with concentrated active alkali systems.

The scaling problem is minimized through the use of a sulfite softening technique. This is accomplished by recirculating (to the scrubber loop) only supernatant liquor which is unsaturated with respect to CaSO_4 and $\text{Ca}(\text{OH})_2$ from the limestone reaction system. Sulfite regenerated in the limestone reaction system tends to limit the calcium ion concentration to the low value established by the CaSO_3 solubility product. Sulfite softening is also advantageous when compared to carbonate softening in that a carbonate supplying compound (e.g., CO_2 or Na_2CO_3) need not be added to the system at additional cost (except as needed to make up for sodium losses).

Fresh water addition to the system is indicated only for:

1. lime slurry make-up, and
2. waste product washing.

Note that the limestone slurry is prepared with recycled water, and the gas is saturated in the venturi with recycled water. It has been reported⁽⁵⁾ that lime cannot be slaked successfully with recycled water containing high concentrations of sulfate ion.

Operating cost for this system may be lower than for some of the others to be discussed in that limestone, a very inexpensive calcium compound, is used as the major source of calcium. On the other hand, capital costs for this type of system may be higher than for some of the others since separate systems must be installed for handling lime and limestone. Limestone handling generally includes crushing and grinding equipment in addition. Also, regeneration with limestone, as opposed to that with lime, requires a much greater residence time to attain good utilization, usually on the order of 1-2 hours.⁽³⁾

It is anticipated that most of the water addition to this system will be done via a waste product wash step, thus reducing solubles in the solid waste product and conserving expensive sodium in the system.

It is interesting to note that the use of both lime and limestone for regeneration in this scheme is limited by the rate of sulfate formation (sometimes referred to as oxidation rate) in the system. At a 50 percent oxidation rate, no limestone would be consumed, since the hydroxide produced by the sulfate removal step will consume all of the bisulfite in the limestone reaction system. As a corollary, at oxidation rates greater than 50 percent, the system could be prone to scaling unless other provisions are made to reduce scaling tendencies. Obviously, if the expected oxidation rate is 40 percent or more, scaling could be a major problem and the advantages of using both limestone and lime are greatly diminished.

Lime Regeneration, Dilute Active Alkali with Sulfite Softening (Scheme 2)

This scheme of operation is illustrated in Figure 3. Basically, this scheme is the same as scheme 1 except that only lime is used for both regeneration of sulfite from bisulfite and for removing sulfate.

The sulfite softening is shown to take place in a reactor clarifier, a piece of equipment designed to combine the functions of a reaction vessel with those of a clarifier.

Comparison of this scheme with the previous one shows:

1. greater use of fresh water for lime slaking; and
2. an overall simpler system, probably leading to lower capital cost and possibly higher operating costs due to the use of lime only as opposed to lime and limestone.

Lime (Scheme 3) or Limestone (Scheme 4) Regeneration, Concentrated Active Alkali with Sulfuric Acid Sulfate Removal

These schemes of operation are illustrated in Figure 4. The schematic is taken from the flow sheets developed and pilot tested by two Japanese companies, Showa Denko K. K. and Kureha Chemical Industry Company.

Since there appears to be a good market for gypsum in Japan, the processes developed by the two Japanese companies include an oxidation step to convert all of the calcium sulfite to gypsum for sale. Limestone has been selected as the source of calcium by both Japanese companies.

In the United States, the market for gypsum is relatively smaller than in Japan. In addition, there is a tendency to avoid production of a salable sulfur waste product due to the inherent problems associated

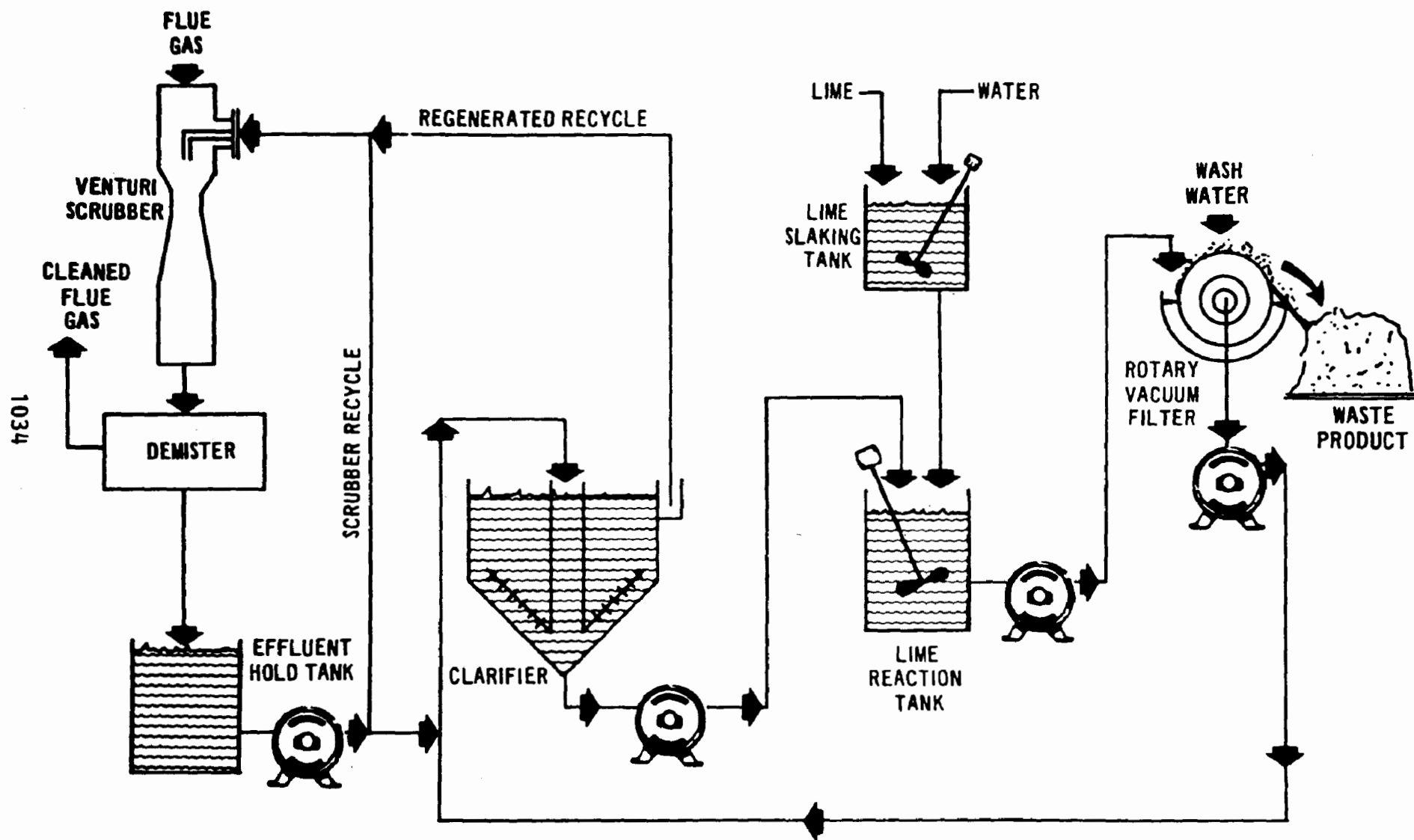


Figure 3. Lime regeneration, dilute, sulfite softening (Scheme 2).

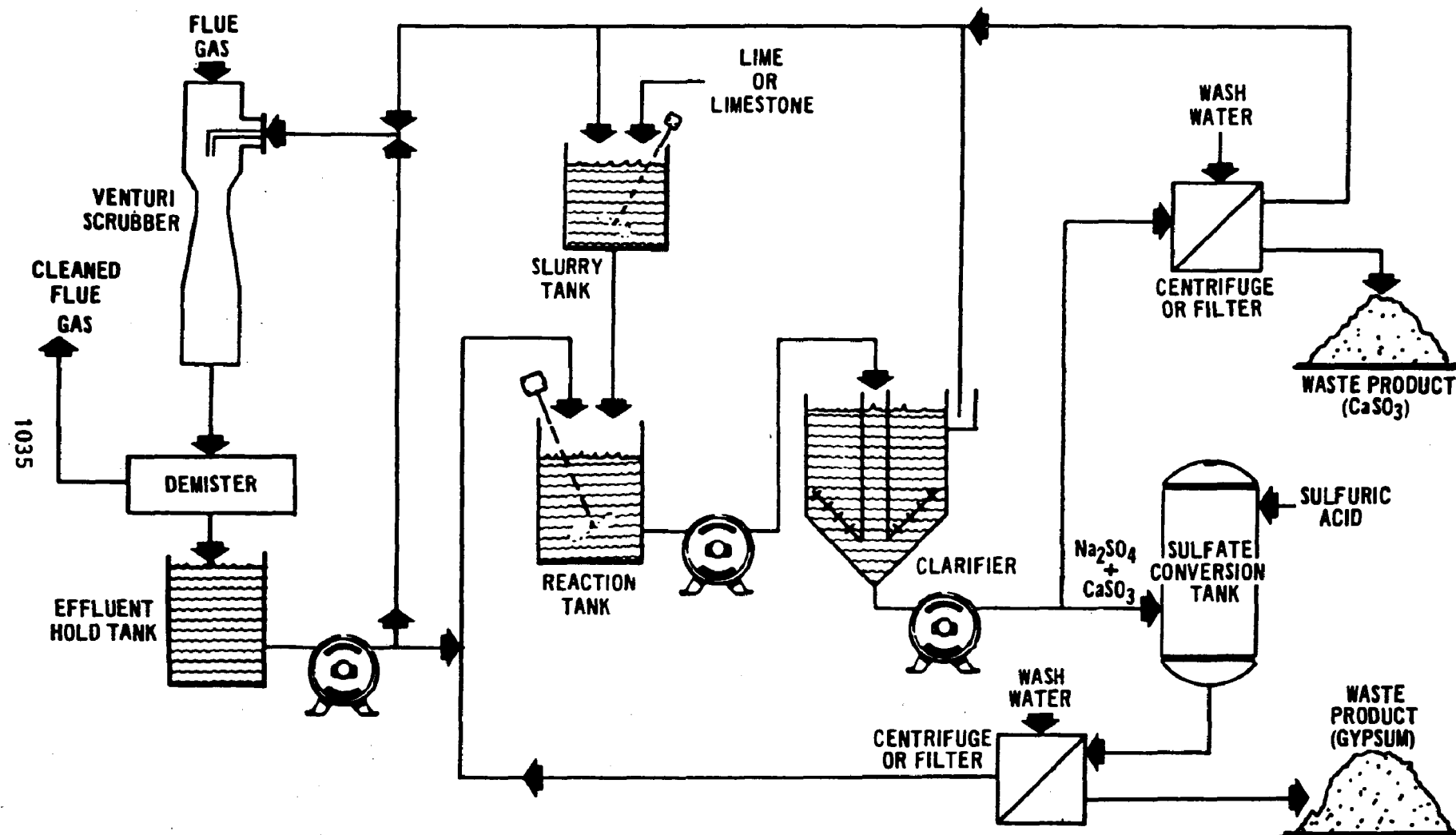
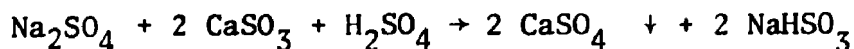


Figure 4. Lime (Scheme 3) or limestone (Scheme 4) regeneration, concentrated, H₂SO₄ sulfate removal.

with marketing a by-product. Due to these considerations, Figure 4 does not show the oxidation step designed for gypsum production.

In these schemes sulfate is removed by precipitation as gypsum from an acidic solution in which CaSO_3 is soluble. The overall sulfate removal reaction is represented as follows:



(water of hydration not shown)

The sulfuric acid used to acidify the reaction mixture must be procured from an outside source and added to the system. Scaling tendency is circumvented again in these schemes by sulfite softening. (There is excess sulfite present in solution in the liquor recycled to the scrubber circuit, thus maintaining a low calcium concentration.)

The fact that these systems can be operated with concentrated active alkali tends to reduce the capital costs. Liquor flows can be greatly reduced and most of the equipment can generally be smaller in size than that required by the dilute active alkali systems. On the other hand, anticipated operating costs for these systems would be higher than for dilute systems due to the cost of sulfuric acid and the additional cost of calcium required to remove the sulfur added by the sulfuric acid. In the United States, where there does not appear to be a large market for gypsum, these processes become prohibitively costly if the oxidation rate is high. Based on data from the Kureha pilot plant, however, only about 9 percent of the sulfur in the waste product is due to sulfuric acid added to the system. This figure is primarily affected by rate of oxidation in the system. It should be noted that the factors affecting oxidation rate in any double alkali system are not clearly defined and various systems have reported oxidation rates varying over a large range.

Lime Regeneration, Dilute Active Alkali with Carbonate Softening (Scheme 5)

This scheme is illustrated in Figure 5. Although this scheme is similar to schemes 1 and 2, there is a subtle difference. Here clarified liquor from the sulfate precipitation reaction is fed back to the scrubber loop, but only after its calcium content is significantly reduced by reaction with carbonate and after another clarification step. The carbonate is generally supplied to the system in the form of soda ash (Na_2CO_3) or carbon dioxide.

The advantage of using CO_2 is that no excess sodium is added to the system. A major disadvantage is the need to provide a complex system for adding the CO_2 , thus increasing capital cost and possibly leading to complications in the operation of the system (chance of CaCO_3 scaling).

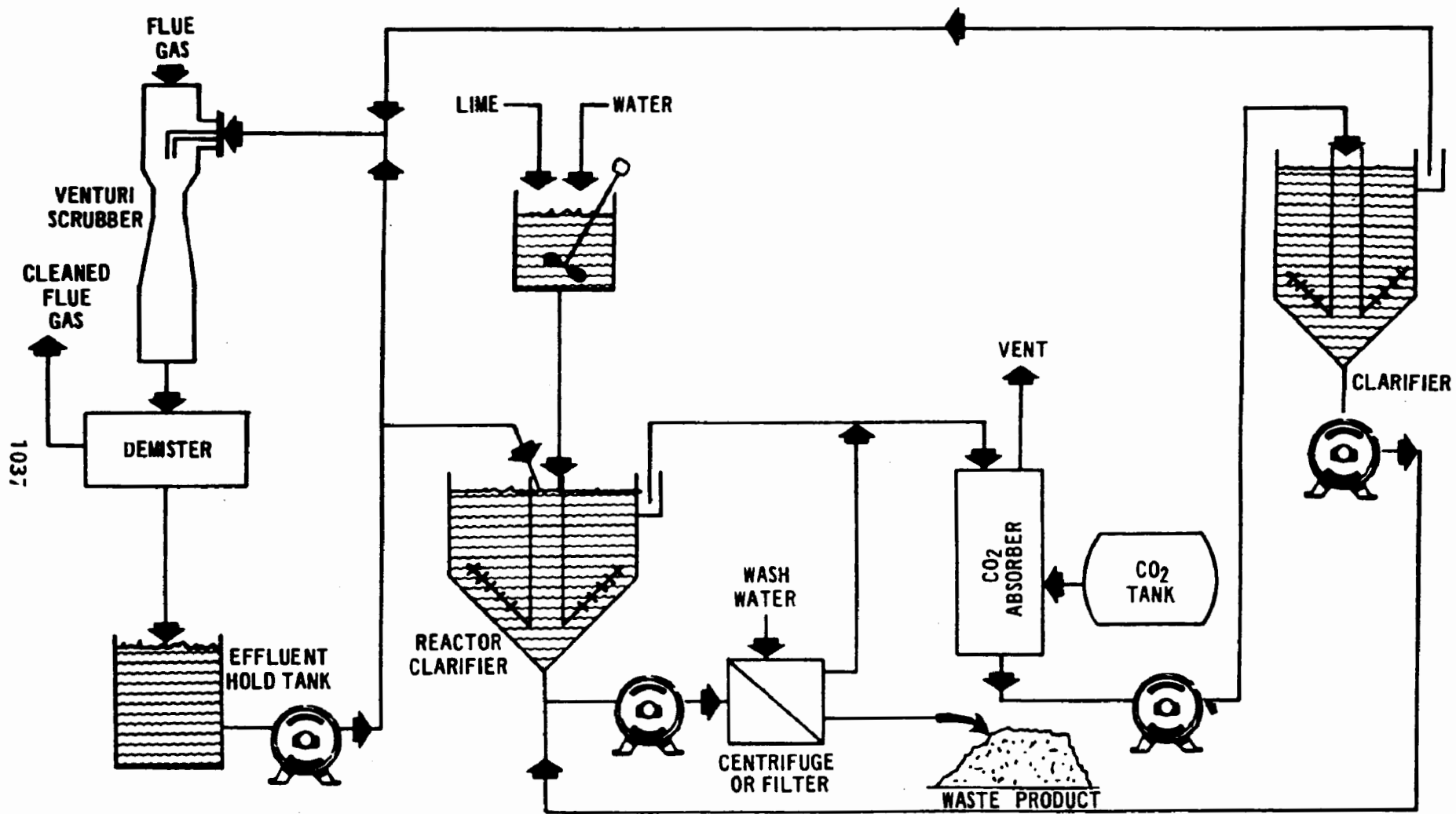


Figure 5. Lime regeneration, dilute, carbonate softening (Scheme 5).

Using soda ash, on the other hand, requires much simpler equipment and, therefore, would probably lead to lower capital cost. The potential problem, however, is that the amount of sodium carbonate added for softening purposes is in excess of that required as make-up for sodium losses. As a result, this excess sodium would have to be purged from the system, as sodium sulfate in order to establish steady state concentration. Obviously, a high purge rate is unacceptable from the standpoint of potential for water pollution by these emissions. A good compromise may be to use both CO_2 and soda ash, thus achieving the advantages of each.

The operating cost for this scheme would probably be slightly higher than for schemes 1 and 2 due to the additional cost of the carbonate-supplying reagent.

An advantage of this system over the other dilute systems discussed is that the active alkali recycled to the scrubber loop would be hydroxide rather than sulfite as is necessary in the systems employing sulfite softening. Feeding hydroxide rather than sulfite to the scrubber loop results in a higher scrubber liquor pH, and thus more efficient scrubbing.

Comparison of Schemes

Table 1 presents a qualitative comparison as a summary of the various double alkali schemes described. The ratings used are very subjective rather than absolute since some of the systems described are hypothetical. A comparison of actual systems would be greatly dependent on the specific equipment used.

Capital costs are shown to be higher for dilute systems only because it is assumed that the dilute systems will generally require larger size equipment and greater flow rates. Operating costs are shown to be higher or lower, based only on the need to supply additional calcium or other reagents exclusive of normal sodium make-up requirements.

Oxidation limitation of the systems, although tabulated as a specific oxidation rate, should only be taken to represent an attempt at quantification of this factor based on the chemistry of the system; this is commonly known as a "Guestimate."

Sulfur dioxide removal capability is relatively higher with the concentrated active alkali systems since more SO_2 can be removed per given volume of absorbent liquor than with dilute active alkali systems. In theory, however, both concentrated and dilute active alkali systems should be able to attain about the same SO_2 removal given the right conditions. In practice, cost becomes the controlling factor.

Additional reagents required is meant to include reagents in addition to those required to make up for minimal unavoidable sodium losses.

Table 1. COMPARISON OF ATTRACTIVE DOUBLE ALKALI SCHEMES

SCHEME	Ca ⁺⁺ CONTROL (SOFTENING)	ACTIVE ALKALI	SO ₄ ⁼ REMOVAL AGENT	CALCIUM SOURCE	ADDITIONAL REAGENTS REQUIRED	ESTIMATED OXIDATION LIMITATION	RELATIVE COST		RELATIVE SO ₂ REMOVAL CAPABILITY
							CAPITAL	OPERATING	
1	SULFITE	DILUTE	LIME	LIME AND LIMESTONE	NONE	40%	HIGHER	LOWER	LOWER
2	SULFITE	DILUTE	LIME	LIME	NONE	50%	HIGHER	LOWER	LOWER
3	SULFITE	CONC.	H ₂ SO ₄	LIME	H ₂ SO ₄	30%	LOWER	HIGHER	HIGHER
4	SULFITE	CONC.	H ₂ SO ₄	LIMESTONE	H ₂ SO ₄	30%	LOWER	HIGHER	HIGHER
5	CARBONATE	DILUTE	LIME	LIME	Na ₂ CO ₃ AND/OR CO ₂	NONE	HIGHER	HIGHER	MEDIUM

STATUS OF TECHNOLOGY

A number of organizations in the United States and abroad have studied and tested various double alkali schemes on systems ranging in size from the laboratory bench scale to 30,000 CFM. A summary of the status of development of these various systems will be presented in order to familiarize potential users of these systems with what is commercially available and what is planned for larger scale installation.

Every effort has been made to present a status report that is accurate. Information presented in an overview report of this type is necessarily "second hand," and obtained from a multiplicity of sources including process and equipment vendors, engineering companies and potential system users, all of whom did not always yield consistent and/or specific information due in part to the complexities and changing conditions associated with development programs.

FMC Corporation⁽⁶⁾

The requirement to control SO_2 emissions from large reduction kilns operated by FMC in Modesto, California, led to the development of a workable double alkali system. This full scale system has been in operation since December 1971. The double alkali system processes a combined 30,000 ACFM off-gas stream containing 5000-8000 ppm SO_2 and about 5-8 percent oxygen from two kilns. The scrubber at the Modesto plant consists of a vertical column packed with 9 feet of Intalox saddles. A wire mesh entrainment separator is used in series with the packed column. The absorbent liquor contains a high concentration of active alkali ($\text{Na}_2\text{SO}_3/\text{NaHSO}_3$) and sodium sulfate. Sulfate formed in the system as a result of oxidation is purged from the system, dissolved in the liquor adhering to the CaSO_3 waste product. A rotary vacuum filter effects the final solids separation and produces a waste product containing about 50 percent moisture, CaSO_3 , dissolved $\text{Na}_2\text{SO}_4/\text{Na}_2\text{SO}_3$ and kiln ash which is disposed of in an on-site pond.

The Modesto system is reported to operate continuously without scaling problems. The system is capable of attaining SO_2 removal in excess of 95 percent with simultaneous removal of kiln ash.

Figure 6 is a schematic representation of the FMC system. Comparing the FMC scheme to the five schemes previously presented, it is most closely related to scheme 3. The major difference is that the FMC scheme makes no provision for removal of sulfate as a solid innocuous waste product. Sulfate is removed from the system as a dissolved solid in the liquor entrained with the CaSO_3 waste product.

Although the FMC scheme makes no provisions for removal of sulfate as an insoluble solid, FMC reports⁽⁶⁾ that tests indicate a reduction in

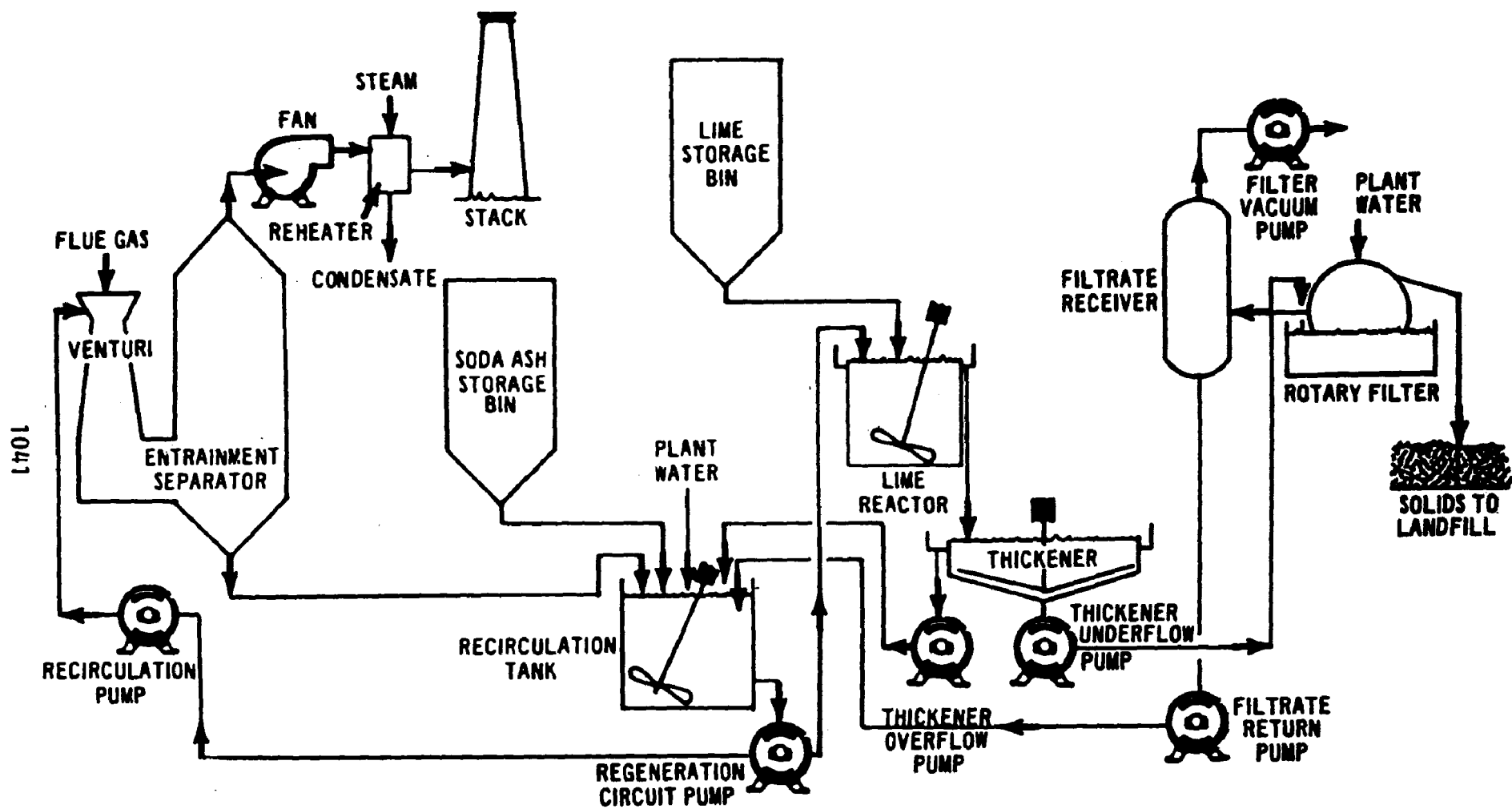


Figure 6. FMC schematic.

sulfate formation when the system is operated with high ionic strength absorbent liquor. As a result, provisions have been made for washing the solid waste product to the extent consistent with maintaining a steady state sulfate level.

In an effort to develop their system for application to industrial and utility boilers, FMC has continued testing their system at the pilot plant level.

A 2000 CFM pilot plant was operated at an FMC chemical plant in South Charleston, W. Va., for a period in excess of 6 months starting in June 1972. The flue gas supply was taken from an underfed stoker type steam boiler rated at 80,000 lb of steam per hour and burning 3.5 percent sulfur coal. The oxygen content of this flue gas was varied up to 13 percent in order to obtain conditions conducive to oxidation and to observe effects on the system.

FMC has also recently operated a 3,500 CFM pilot plant housed in a 40-foot trailer at the Mossville engine plant of the Caterpillar Tractor Company. The flue gas supply for this testing was taken from a steam boiler at the plant which burns typical high sulfur Illinois coal. This plant was equipped for filter cake washing to reduce sodium losses from the system. The waste product from this system contained about 40 percent moisture under optimum conditions and appeared to be relatively dry and easy to handle.

After initial testing in March 1972, in a 5,000 CFM unit at the Modesto Plant, all of the FMC pilot plant programs have employed the "FMC-Link Belt Dual Throat Variable Scrubber." This is a single stage venturi type scrubber coupled with a cyclonic type separator.

Typical operating parameters for the FMC system are:

SO ₂ removal efficiency	70-95%
Approximately alkali composition	15-20% Na ₂ SO ₄ 5-7% Na ₂ SO ₃ / NaHSO ₃
Ca:S stoichiometry	1.0
Scrubber pH range	6-7
Na ₂ CO ₃ requirements	8 moles Na ₂ CO ₃ /100 moles Ca(OH) ₂
Ca ⁺⁺ in scrubber liquor	< 5 ppm

Capital and operating costs for the FMC system are estimated by FMC to be:

	<u>Generating Capacity, MW</u>		
	8	20	200
Capital costs, \$/KW	184	100	30
Operating costs, \$/ton of coal	11	8	5

FMC is presently negotiating with a large industrial manufacturer in Illinois for a contract to install the FMC process to control SO_x and particulates from a system of steam boilers approximately equivalent in steam generating capacity to a 40 MW power plant. It is presently anticipated that this system will be in operation by June 1974.

Envirotech Corporation(5)

Envirotech has operated a 3,000 CFM double alkali pilot plant using various equipment arrangements for approximately a year, since early 1972. The pilot plant is located at the Gadsby station of Utah Power and Light.

After testing various equipment arrangements, and fighting the scaling problem with some, Envirotech developed the scheme shown in Figure 7. This scheme might be the typical scheme which would be proposed by Envirotech for control of SO_x and particulates from a utility or industrial boiler.

Examination of this flow sheet indicates that it is related to scheme 3 or 5, depending on the concentration of active alkali in the liquor. The concentration range of sulfite, bisulfite and sulfate in the liquor is considered by Envirotech to be proprietary information and, therefore, has not been disclosed. Operated with concentrated active alkali, this system is similar to scheme 3 without provisions for removal of sulfate (with sulfuric acid) as an insoluble solid. Operated with dilute active alkali, the system is similar to scheme 5, using soda ash for carbonate softening. In this case there is the necessity to purge from the system a certain amount of sodium dissolved in the liquor adhering to the waste product filter cake.

In the pilot plant, a perforated plate and an expanded metal tray were tested in the tray scrubber. The preferred arrangement was a 2-stage expanded metal tray scrubber. The pilot plant is reported to have operated in a scale-free manner for a period of 6 months with

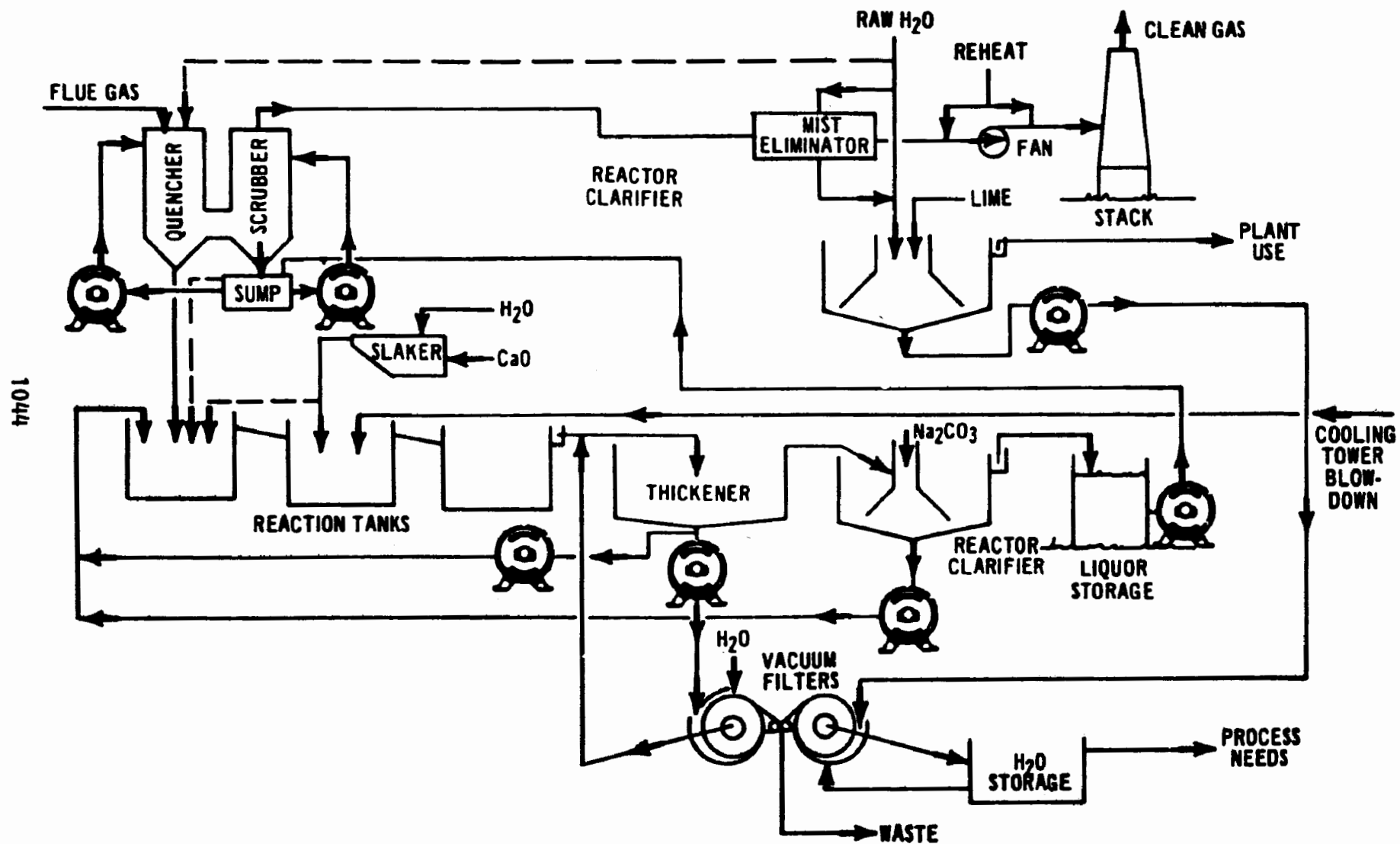


Figure 7. Envirotech schematic.

provisions for soda ash softening, inlet gas quenching with fresh water, and recycle of precipitated solids to the reaction tanks and reactor clarifiers. Quenching with fresh water, as pointed out previously, could lead to water balance problems and thus require purge. Use of cooling tower blowdown and sending demister wash water to plant use are examples of good water conservation attempts.

Envirotech lists the problems they consider significant in their operation of the system as follows (not necessarily in order):

1. scaling;
2. gas distribution at low pressure drop;
3. over-liming (relating to pH control);
4. mechanical problems - valves, pumps, piping;
5. flow regulation; and
6. inlet wet/dry interface accumulation.

A list of important process variables and their typical values from various pilot tests is given below:

SO ₂ in inlet flue gas	350-400 ppm
Scrubber pressure drop	4-9 in. H ₂ O
Calcium content of scrubber liquor	400 ppm
pH of scrubber liquor at exit	7
Scrubber L/G ratio	12 to 36 gal/ 1,000 ft ³
SO ₄ ⁼ /SO ₃ ⁼ concentration in scrubber liquor	not disclosed
SO ₂ removal efficiency	90%

Additional pilot plant testing, 24 hours/day, 5 days/week, for 2-3 months will be geared to investigate:

1. simultaneous removal of SO₂ and particulates; and
2. system operation at inlet SO₂ levels up to 1500 ppm.

Envirotech will attempt to demonstrate their system next at the 100-200 MW level.

General Motors (7,8)

The double alkali system developed by GM is schematically illustrated in Figure 8. After considering other possible alternatives, GM decided that a double alkali system was most practical for their SO₂ control requirements in that it fit the criteria of being relatively economical and uncomplex.

Pilot plant testing was conducted at the Cleveland Chevrolet plant using a 2,800 CFM cross-flow packed scrubber supplied and operated by Ceilcote for the joint development effort. Flue gas for testing was an isokinetic sample representing 10 percent of the total flue gas flow from a boiler having a steaming capacity of 80,000 lb/hour and burning 2 percent sulfur coal with 100 percent excess air.

In the pilot plant, it was found that a 1 molar sodium solution would give reasonably good SO₂ absorption, while also regenerating caustic and precipitating sulfate as gypsum. It was found that a maximum concentration of 0.1 M hydroxide could be regenerated in a 1 M sodium solution. Increasing the sodium ion concentration above 1 M did not give appreciable increase in regenerated hydroxide concentration. Lowering the sodium ion concentration, however, gave a decrease in regenerated hydroxide concentration.

Optimum lime utilization was found to occur with high speed mixing, using near stoichiometric quantities of lime. Eighty percent conversion of lime was attained in 5 minutes.

Early in the pilot plant program, GM ran into the calcium plugging problem; but later, using soda ash softening, they were able to alleviate it. Reportedly, using soda ash for sodium make-up, they were able to reduce the calcium content in the scrubber loop from 400 to 250 ppm.

A high degree of confidence in the double alkali system has prompted GM to construct a full-scale system at the Cleveland Chevrolet plant. The plant presently has four stoker-fired boilers, equivalent in steaming capacity to a 32 MW electric generating plant. The double alkali system, however, is designed to handle the flue gas equivalent of a 40 MW plant in order to accommodate possible future expansion. The system is being built at an approximate cost of \$3,000,000 and is scheduled to start up in December 1973.

The system in the full scale plant will consist of four parallel Koch tray (valve tray) scrubbers. Provisions for softening with soda ash and/or carbon dioxide will be included. Sodium make-up will be as sodium hydroxide and/or soda ash. The active alkali will be dilute to ensure removal of sulfate as insoluble gypsum by lime treatment. The anticipated sodium ion concentration will be in the range of 1-2 molar.

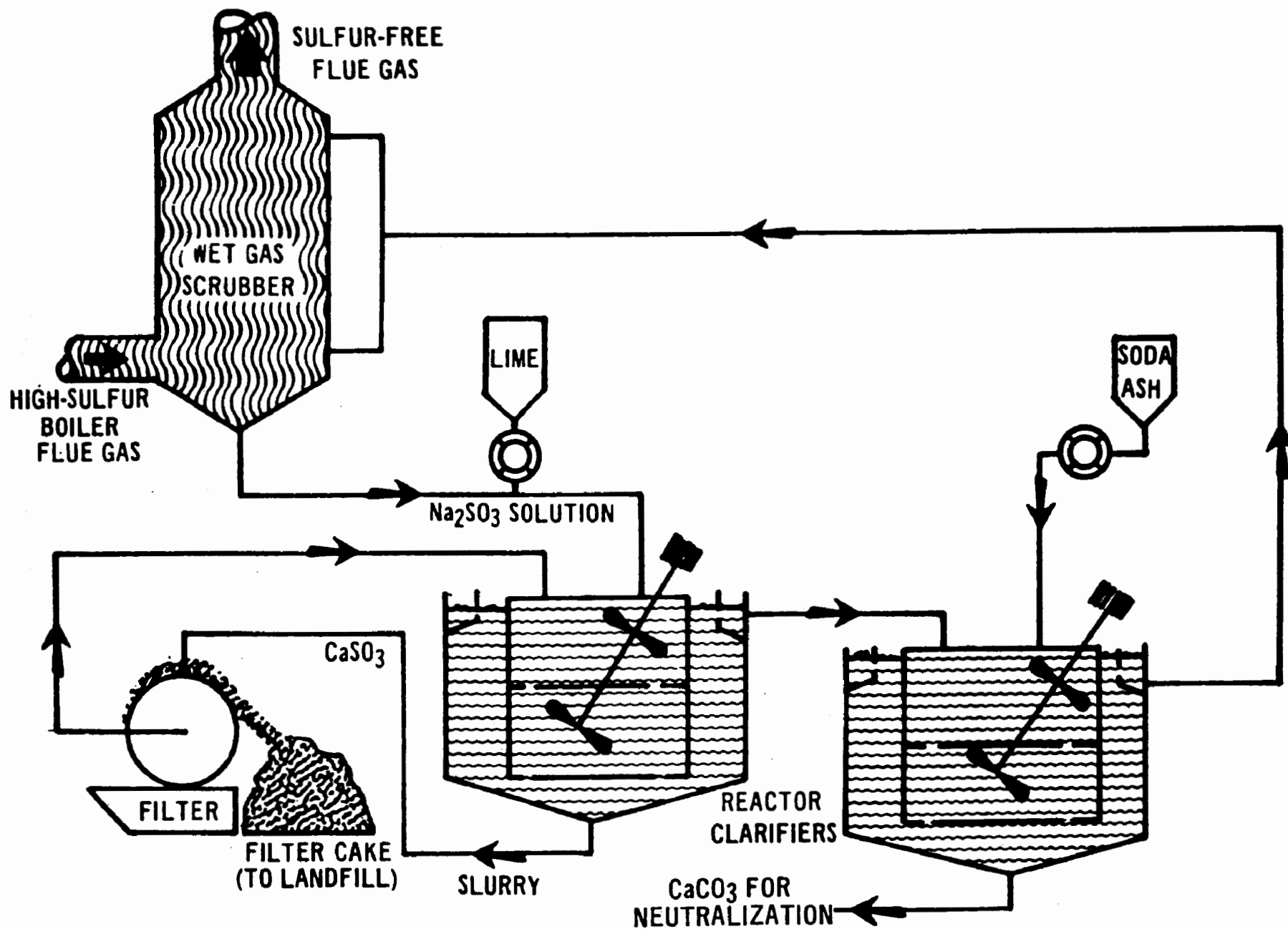


Figure 8. General Motors schematic.

Depending upon control of the operation, this system should be capable of producing an environmentally acceptable solid waste product, at least with respect to contamination by dissolved sodium salts.

This design is comparable to scheme 5, previously discussed.

Zurn Air Systems (9,10)

Zurn contracted with Southern Research Institute to conduct a laboratory study of the regeneration process for a lime/sodium, dilute double alkali system. The study, completed in 1972, basically confirmed the information reported by General Motors. This study was conducted in order to obtain a firmer basis for the design of a marketable double alkali system. Figure 9 is a schematic representation of the type system Zurn is prepared to market. This flow diagram is comparable to scheme 5, previously discussed, with soda ash softening.

The Zurn system would employ a "Dustraxtor" scrubber, briefly described as a multitube entrainment contactor capable of achieving high internal liquid/gas ratios.

It should be pointed out that the system would be capable of removing sulfate as insoluble gypsum by precipitation with lime; however, due to the lack of provisions for softening with carbon dioxide, a certain amount of sodium and sulfate would necessarily have to be purged from the system in the moisture associated with the waste product filter cake. Provisions for filter cake washing are shown. The system is anticipated to operate at a sodium concentration of 1-2 molar.

A Zurn operating cost estimate, exclusive of amortization of equipment, was given as \$4.86 per ton of coal burned. Zurn is presently negotiating with a large industrial manufacturer for a contract to install the equivalent of a 20 MW system on a coal-fired industrial boiler system.

Chemico (11)

Chemico tested a double alkali system in a 1,500 CFM pilot plant located at the Mitchell Power Station of Allegheny Power Service Company. Testing lasted approximately 6 weeks, and Chemico was able to operate the pilot unit in a scale-free manner, using either lime or limestone as the calcium source. Figure 10 is a schematic representation of that pilot plant, but not necessarily of the system which might be marketed by Chemico.

In the pilot plant, there were no waste product cake washing provisions, so dissolved solids were purged from the system in the moisture associated with the cake. In addition, since make-up sodium was added to the system as a mixture of sodium sulfite and bisulfite

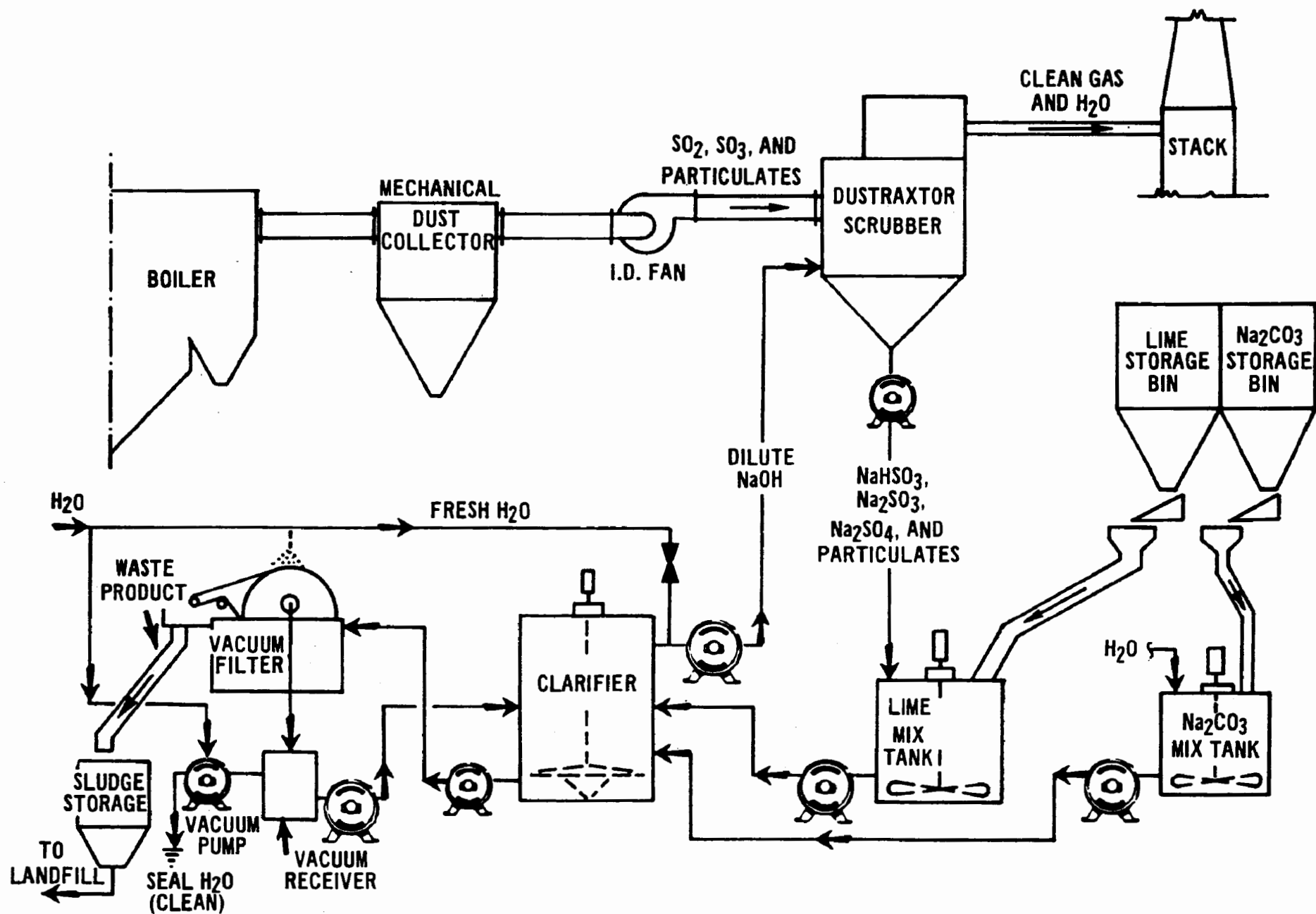


Figure 9. Zurn Air Systems schematic.

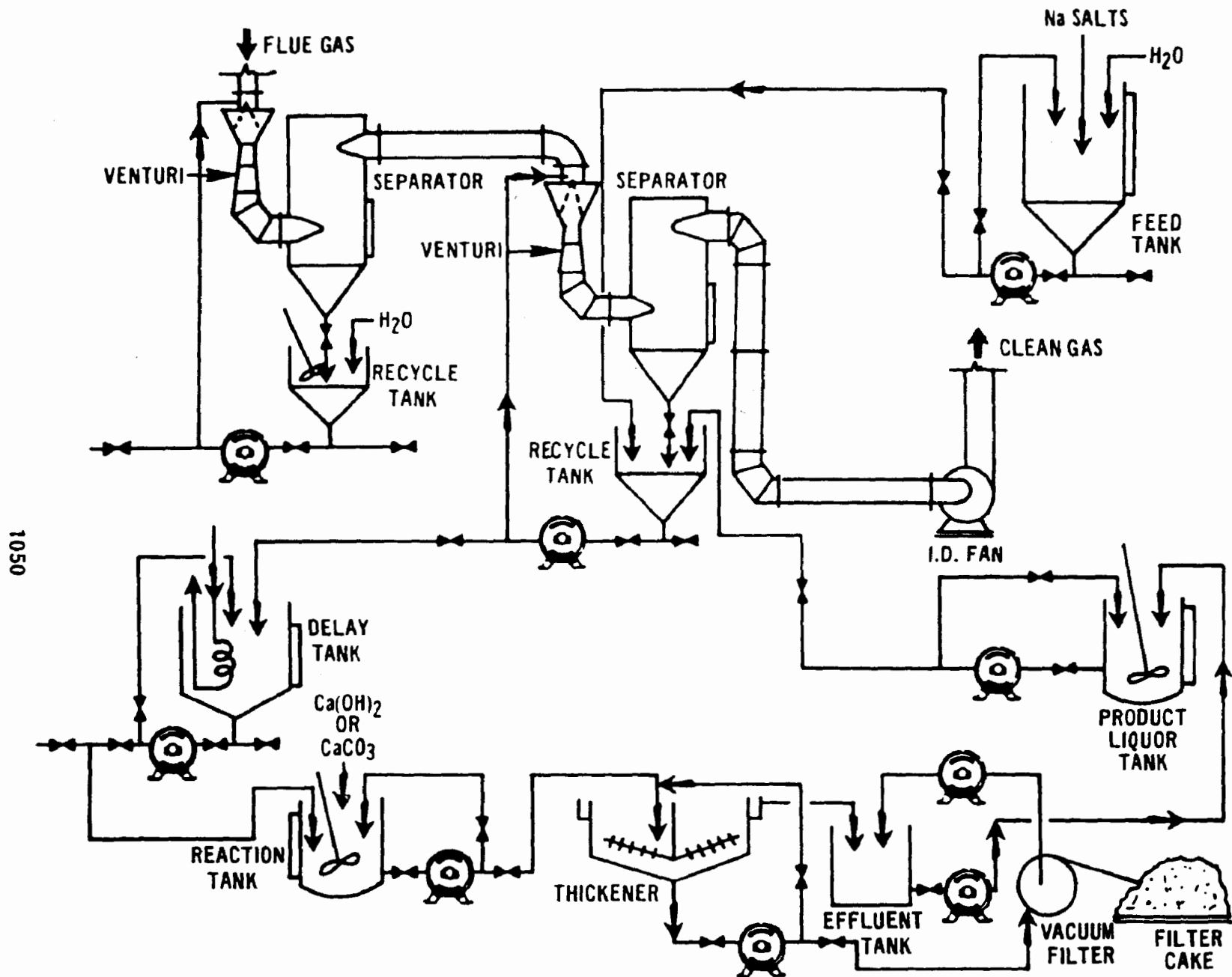


Figure 10. CHEMICO Pilot Plant schematic.

on a regular schedule, it necessarily follows that there must have been a significant purge from the system. Testing in this fashion was attributed by Chemico to be due to the fact that testing at such a small scale with separate pieces of equipment which were not sized to be consistent with each other tended to necessitate a somewhat open system. Typically, in small unit testing, leakage from the system is generally enough to simulate open system operation.

Based on testing in the pilot plant, however, Chemico developed other flow sheets for application to utility and other boiler systems which are apparently similar to schemes 1 and 2, previously discussed, provided that the systems are intended for operation with dilute active alkali. If these systems are operated with concentrated alkali, a purge of sulfate from the system in some form would be necessary.

Arthur D. Little/Combustion Equipment Associates⁽¹²⁾

ADL and CEA are involved, per a joint venture agreement, in developing and marketing double alkali systems. Generally speaking, CEA is an equipment and systems designer and manufacturer, and ADL participates in a developmental and engineering capacity, in the joint venture agreement.

A 2,000 CFM pilot plant has been in operation since January 1973, testing various double alkali configurations at the ADL facility in Cambridge, Massachusetts. The pilot plant unit was built by CEA for testing in connection with any of the ADL/CEA joint ventures. This pilot unit is supplied with flue gas generated by combustion of natural gas. There are provisions for addition of SO_2 , flyash and excess air. The scrubber system consists of a variable throat venturi, tray separator and radial vane demister. The solids handling facilities include a circular clarifier or settling tank with revolving bottom rake arm mechanism and a rotary vacuum filter with provisions for filter cake washing and drying. The plant is equipped with seven miscellaneous tanks, four of which are provided with mechanical agitation. These tanks serve as scrubber recycle tanks and reaction vessels as necessary.

ADL/CEA have contracted with The Southern Company (a utility combine producing electricity in the southeastern states, consisting of Alabama Power Co., Georgia Power Co., Gulf Power Co., Mississippi Power Co., Southern Electric Generating Co. and Southern Services, Inc.) for installation of a 20 MW SO_2 and particulate scrubber prototype system.⁽¹³⁾ Flue gas supply for the prototype will be half the flue gas produced from the Unit No. 1 boiler of the Scholz plant operated by Gulf Power Company. The scrubber systems to be tested will be various combinations of a venturi, spray tower, tray tower and packed tower. The system will be designed to test double alkali operation with lime only or lime and limestone.⁽¹⁴⁾ In addition, the system is designed to test lime and limestone slurry scrubbing. The exact plans for operation of this system

with respect to alkali concentration are not known; however, in order to produce an environmentally acceptable waste product, the system would probably have to operate, as previously described, by schemes 1, 2, or 5, since no provisions for sulfuric acid addition were revealed, as would be required for operation as depicted by schemes 3 and 4.

It is anticipated that construction of this prototype facility will be initiated in late 1973, and that the system will be in operation in June 1974, or earlier.

Kureha Chemical Industry Co. (Japan)⁽³⁾

Kureha has recently developed a sodium/calcium double alkali system which operates in a manner similar to that described by scheme 4, previously discussed. After testing in a small pilot plant, a larger pilot plant (3,000 SCFM) was built in a joint development effort with Kawasaki Heavy Industries and has been in operation since July 1972. Two commercial plants using this scheme of operation will be completed in 1974 to treat flue gas from oil-fired boilers at two different electric power plants each having a 150 MW generating capacity.

The proposed Kureha system consists of a venturi for particulate removal, followed by a grid-packed scrubber for SO₂ removal. The SO₂ absorber operates in the pH range 6.0 - 6.5. With an inlet concentration of 1,500 ppm SO₂, 98 percent removal is achieved. The scrubber liquid/gas ratio is 7 gal/1,000 ft³ of gas.

The limestone reactor operates at a temperature somewhat higher than the scrubber temperature and is designed to provide a 2-hour residence time. Centrifuges are used for the solids separation steps.

Composition of the absorber feed and discharge liquor is reported below:

Absorber feed -

Sodium sulfite	20-25%
Calcium	30 ppm
pH	7-8

Absorber discharge -

Sodium sulfite	10%
Sodium bisulfite	10%
Sodium sulfate	2-5%

Since there is a good market for gypsum in Japan, an oxidation step is added to the process described previously by scheme 4. Calcium sulfite is reacted with air at atmospheric pressure in an oxidizer developed by Kureha. The product gypsum, removed by centrifuge from the oxidizer liquor, is suitable for use in wallboard and cement.

Operating costs associated with this process include additional costs for sulfuric acid and the incremental cost for additional limestone required for precipitation of the sulfur added in the form of sulfuric acid. The cost penalty is aggravated if gypsum cannot be sold. As pointed out previously, the sulfuric acid requirement for decomposition of the sulfate is 125 percent of the theoretical amount; thus, about 9 percent of the product gypsum is derived from sulfuric acid.

Capital costs for this process can be split as follows:

Absorption system	30%
Limestone reaction system	30%
Sulfate removal	10%
Oxidation	30%
	<u>100%</u>

The system is reported to operate reliably with no scaling problem, while removing sulfate in an environmentally acceptable manner.

Showa Denko K. K. (Japan)⁽³⁾

The Showa Denko process is very similar to the process described for Kureha and again comparable to scheme 4 with the additional provision for oxidation of all the CaSO_3 to gypsum (for sale) in a separate oxidation step. This company uses a vertical cone type absorber which operates with liquid/gas ratios ranging from 7-14 gal/1,000 ft³ and with a pressure drop range from 8-15 inches of water.

Showa Denko has operated a 5,900 SCFM pilot plant using this process since 1971 to desulfurize flue gas from an oil-fired boiler. A commercial plant is currently under construction and expected to be in operation in June 1973. This plant (Chiba plant of Showa Denko) will treat flue gas equivalent to that emitted by a 34 MW electric generating plant.

Summary of Commercial Systems

A comparison of the double alkali systems developed by the various organizations discussed in this paper is presented in Table 2. The systems described by the table generally represent the systems developed,

Table 2. COMPARISON OF COMMERCIAL DOUBLE ALKALI SYSTEMS

COMMERCIAL SYSTEM	ACTIVE ALKALI	SULFATE REMOVAL	CALCIUM CONTROL	CALCIUM SOURCE	ADDITIONAL REAGENTS	LARGEST UNIT TESTED, cfm	PLANNED INSTALLATIONS	
							SIZE	DATE
FMC	CONC.	PURGE WITH WASTE	SO_3^-	L	Na_2CO_3	30,000	40 MW	7/74
ENVIROTECH	UNKNOWN	PURGE WITH WASTE	CO_3^-	L	Na_2CO_3	3,000	-	-
GENERAL MOTORS	DILUTE	LIME	CO_3^-	L	CO_2 AND/OR Na_2CO_3	2,800	40 MW	12/73
ZURN AIR SYSTEMS	DILUTE	LIME TREATMENT, SOME PURGE	CO_3^-	L	Na_2CO_3	LAB SCALE	20 MW	?
CHEMICO	UNKNOWN	LIME OR PURGE	SO_3^-	L AND/OR LS	DEPENDENT ON OPERATION	1,500	-	-
A.D. LITTLE/ COMBUSTION EQUIPMENT ASSOCIATES	DILUTE	LIME OR OTHER	SO_3^- OR CO_3^-	L AND/OR LS	DEPENDENT ON OPERATION	2,000	20 MW	6/74
SHOWA DENKO K.K.	CONC.	H_2SO_4	SO_3^-	LS	H_2SO_4	3,000	34 MW	6/73
KUREHA	CONC.	H_2SO_4	SO_3^-	LS	H_2SO_4	5,900	150 MW 150 MW	1974 1974

tested and/or available for marketing by each of the listed companies. In some cases several systems are implied. The reason for this is that most of the companies have tested several double alkali schemes during their development efforts. In some cases, the schemes tested are not necessarily the ones which would be marketed by the company. Information is presented in the table to allow the reader to identify each of the commercially developed systems with the attractive schemes of operation previously discussed in detail.

THE EPA DOUBLE ALKALI DEVELOPMENT PROGRAM

In an effort to more fully test and characterize double alkali systems, EPA has contracted with Arthur D. Little, Inc., (contract value approximately \$500,000) to conduct a two-task study. The proposed study is entitled, "A Laboratory and Pilot Plant Study of the Dual Alkali Process for SO₂ Control." Technical administration for this study will be split between the Research Laboratory and the Development Engineering Branches of the Control Systems Laboratory for administration, respectively, of the laboratory and pilot plant tasks. The test program and study are anticipated to last for 15 months. One of the main objectives of the program will be to develop several methods of producing environmentally acceptable waste while operating in a reliable trouble-free manner.

An outline of the program by task is given below:

Task 1 - Laboratory Study

1. A comprehensive literature survey will be performed stressing kinetics and thermodynamics of regeneration chemistry, SO₂ absorption, and solids separation operations related to calcium/sulfur compounds.
2. A laboratory study of the regeneration chemistry will be conducted, using lime and/or limestone.
3. A complete laboratory bench scale simulation of the absorption and regeneration systems will be constructed and tested in various attractive configurations to investigate SO₂ removal, scaling problems, residence times, optimum solution concentrations and solids settling and filtration rates.

Task 2 - Pilot Plant Study

1. Attractive schemes of operation will be tested at the ADL/CEA 2,000 CFM pilot plant in Cambridge.
2. A 9,000 CFM pilot plant at the Reid-Gardner station of Nevada Power Company will be modified to accommodate testing of attractive schemes of operation. (This pilot plant was formerly used to test once-through sodium carbonate scrubbing to firm up the design of a 250 MW desulfurization system now under construction at the Reid-Gardner plant by CEA and anticipated to start up in mid-1973.) The scrubber system in this pilot plant is the same as in the 2,000 CFM system located at the ADL facility.

3. Attractive schemes will be tested at the 9,000 CFM pilot level.
4. Data from the pilot plant operations will be assembled to provide input for an economic study to estimate capital and operating costs for various full scale systems.
5. Particular emphasis will be given to the important considerations previously discussed:
 - Sulfate removal methods
 - Scale prevention
 - Water balance
 - Waste product washing
 - SO₂ removal
 - Costs

Figure 11 is a simplified schematic of the "Double Alkali" process which is used by ADL to illustrate the system in a very general way. It should be noted that sulfate treatment is shown in a general manner, illustrating the possible application of any of a number of techniques to be tested to cope with the problem of removing sulfate in an environmentally acceptable way. There is additional significance to the general philosophy of treating for sulfate removal in a slip stream off the main liquor regeneration loop: methods developed to handle this problem would be applicable to other double alkali systems.

Conduct of the Test Program and Objectives

Testing will be conducted at three successive levels:

1. laboratory bench scale,
2. 2,000 CFM pilot plant, and
3. 9,000 CFM pilot plant.

The successive levels of testing will be used to screen and select the most attractive schemes from the many initially showing potential. Testing in this manner should allow testing of many schemes at the bench scale level, fewer at the 2,000 CFM pilot level and still fewer at the 9,000 CFM level where long-term, reliable, closed-loop operation will be stressed. Equipment at each level of testing will be designed with maximum flexibility consistent with budgetary constraints of the program.

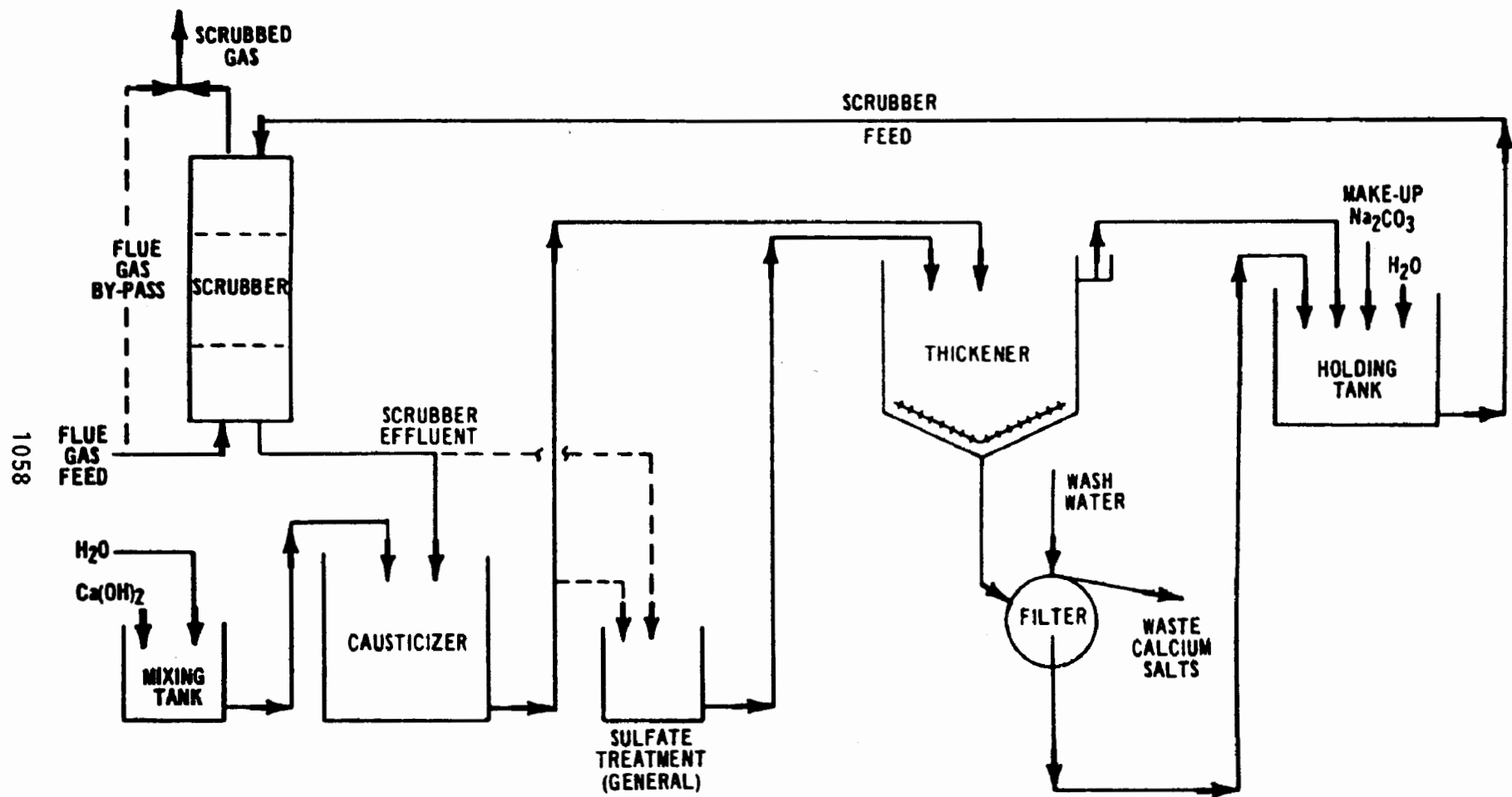


Figure 11. Arthur D. Little general schematic.

Pilot plant capabilities will include provisions for:

1. solid waste product washing,
2. control of SO_2 content of the inlet flue gas,
3. flyash addition,
4. sodium make-up as sodium sulfate,
5. recirculation of precipitated solids,
6. flue gas quenching, and
7. testing of at least five attractive schemes.

Following is a list of important program objectives:

1. demonstrate reliable system operation,
2. demonstrate high SO_2 removal, 95 percent desirable,
3. demonstrate high particulate removal,
4. demonstrate environmentally acceptable sulfate removal schemes,
5. minimize disposal of soluble material,
6. demonstrate closed-loop operation (or close approach to this ideal), and
7. obtain complete material balances.

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STONE & WEBSTER/IONICS
SO₂ REMOVAL AND RECOVERY PROCESS

by

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1. INTRODUCTION

The Stone & Webster/Ionics SO₂ Removal and Recovery Process is based on the absorption of sulfur dioxide in a caustic solution which then is regenerated using Ionics' electrolytic cells (electrolyzers), the key component of the process. This patented process is applicable to gaseous effluents from stationary power plants burning fuels containing sulfur and to tail gases from sulfur recovery plants, smelters and sulfuric acid plants.

The process consists of three essential steps arranged in a closed loop:

1. Sulfur dioxide (SO₂) is absorbed from flue gas in a solution of caustic soda (NaOH) in water to produce a solution of sodium bisulfite (NaHSO₃) containing some sodium sulfite (Na₂SO₃).
2. The sulfite-bisulfite solution is mixed with sulfuric acid (H₂SO₄), causing release of SO₂ from the solution. The SO₂ is recovered for sale as such, or converted to sulfur or sulfuric acid. The solution is converted to sodium sulfate (Na₂SO₄).
3. The sulfate solution is converted by an electrolyzer into two solutions, one containing caustic, and the other sulfuric acid. The caustic solution is recycled for use in step 1; the sulfuric acid solution is recycled for use in step 2.

Under a joint program co-sponsored by the Environmental Protection Agency and Wisconsin Electric Power Company, the process will be tested at Wisconsin Electric's Valley Station in Milwaukee. Phase I of the potential three-phase demonstration program is currently underway and consists of design, installation and operation of an integrated pilot plant, development of prototype scale electrolyzer system, preliminary design of a prototype system and development of test programs and operating schedules. Phases II and III of the program would involve the design, procurement and installation of a prototype facility treating the flue gas from one of the four 75 MW coal fired boilers at the station, and its start-up and long-term operation, respectively.

2. HISTORY OF THE PROCESS

Several years ago, Stone & Webster, because of its involvement in the design and construction of power plants, undertook to examine the various suggestions which had been advanced for SO₂ removal from flue gas and came to the early conclusion that scrubbing with an alkali solution was a promising and probably enconomic approach, provided that appropriate methods could be developed for regenerating and reusing the solution without excessive cost and without the production of additional pollutants. The advantages of electrolytic regeneration as proposed by Ionics, Incorporated of Watertown, Massachusetts, appeared particularly interesting.

Joint activity by Stone & Webster and Ionics commenced in 1966, and has been directed toward the engineering development of an economic system for an electric generating plant to remove SO_2 from flue gas by absorption in a caustic solution, the caustic being electrically regenerated and reused in a closed circuit. A major commercial installation of an electrolyzer system employing technology similar to that practiced in the Stone & Webster/Ionics SO_2 Recovery System was installed in a plant of Monsanto Textile Corporation in Decatur, Alabama, in 1967, for the reduction of acrylonitrile to adiponitrile, an intermediate in nylon manufacture.

An SO_2 removal pilot plant was installed at the Gannon Station of Tampa Electric Company in Florida in 1967 and was operated for approximately 6 months. It treated approximately 200 cfm of flue gas from a boiler operating on pulverized coal. The flue gas contained about 0.25 vol percent sulfur dioxide. The pilot equipment included a flue gas quench which cooled the gas to about 120°F and removed most of the fly ash. This was followed by an absorber for removal of the sulfur dioxide, and an electrolyzer system for regeneration of the caustic. The pilot program confirmed the soundness and operability of the process, and pointed the way toward further development of both the electrolyzer and the flue gas absorber.

As result of the pilot work, electrolyzer materials of construction were revised by Ionics to improve reliability and to reduce costs. In addition some design modifications were introduced to reduce electrical energy requirements. Subsequently, the electrolyzer was scaled to its full commercial height, and a six month test period of operation was carried out in a second electrolyte pilot plant at Ionics' Watertown Laboratory using this "tall cell model." A third pilot plant has been built and successfully operated in Japan. Its purpose is to demonstrate the regeneration of caustic for removal of SO_2 from the flue gas of oil fired boiler under Japanese conditions.

Following the Tampa pilot work and recognizing that considerable effort had to be expended on the design of absorbers for large steam plant installations, the National Air Pollution Control Administration (NAPCA) engaged Stone & Webster to make a study of existing absorber concepts. The study was based on removing sulfur dioxide from flue gas produced in a coal-fired power station rated at 1,200 MW and consisting of four boilers, with special emphasis on minimizing the oxidation of sulfites to sulfate in the absorption system. It was concluded that a packed tower was best suited to the Stone & Webster/Ionics Process.

Having carried through the laboratory experiments at Ionics, scale-up engineering and semi-commercial studies for the various system components within the process, the next logical step would be to undertake a demonstration program of the entire process using each significant component in

its presently developed state. However, considering the small size (200 CFM) of the Tampa Pilot Plant and the large thruput of even a modest sized prototype plant, say 75 MW, which would have stack gas volume of about 225,000 CFM, it was decided to install an intermediate sized pilot plant of 2,000 or 3,000 ACFM. This should provide data less subject to gross error than a scale up from 200 to 225,000 CFM.

Such a program is now under way at Wisconsin Electric's Valley Station in Milwaukee.

3. PROCESS DESCRIPTION⁽¹⁾

3.1 General

The process involves three basic steps. These are:

1. Absorption
2. Sulfur Dioxide Recovery
3. Absorbent Regeneration and Oxidation Product Rejection

The flow scheme is shown on Figs. 1-1 and 1-2.

3.1.1 Absorption

The flue gas is first cooled by direct water quench in the bottom of the absorber tower, after which it is contacted with a dilute (8%) caustic solution containing sodium sulfate. At the top of the tower, the flue gas, with most of the SO₂ removed, is reheated if necessary and returned to the stack. The absorbing solution is converted to a sodium bisulfite-sodium sulfite-sodium sulfate mixture which contains the SO₂ and SO₃ removed from the flue gas.

3.1.2 Sulfur Dioxide Recovery

The bisulfite-sulfite mixture is reacted with a dilute mixture of sulfuric acid and sodium sulfate recycled from the electrolytic cells (electrolyzers). This reaction forms sodium sulfate, SO₂ and water, and is carried out prior to entering a stripping tower. In the latter, SO₂ is removed as the overhead, leaving as tower bottoms a solution of sodium sulfate.

3.1.3 Absorbent Regeneration and Oxidation Product Rejection

The sodium sulfate solution is sent to two types of electrolyzers which are described in detail later in this section. In both electrolyzers, sodium hydroxide (caustic) containing sodium sulfate is generated. This caustic is recycled to the absorption tower for reuse as the absorbing medium. Also in both electrolyzers a mixture of sodium sulfate and sulfuric acid is generated and recycled as the dilute acidic solution required in the Sulfur Dioxide Recovery step mentioned above.

- (1) Description is general but relates more specifically to prototype plant rather than pilot plant.

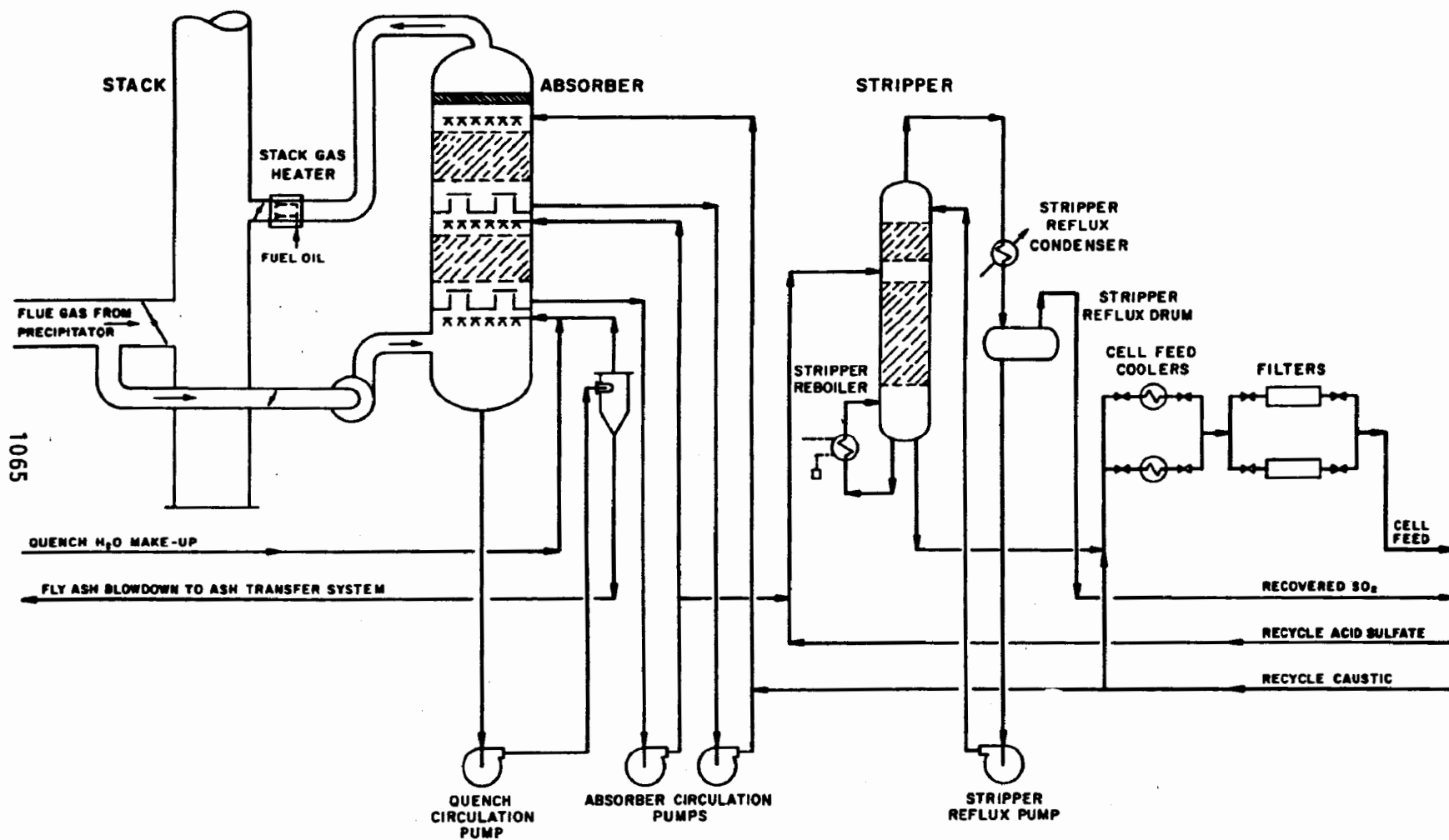


FIGURE 1-1
SO₂ REMOVAL SECTION
 STONE & WEBSTER / IONICS SO₂ REMOVAL & RECOVERY PROCESS

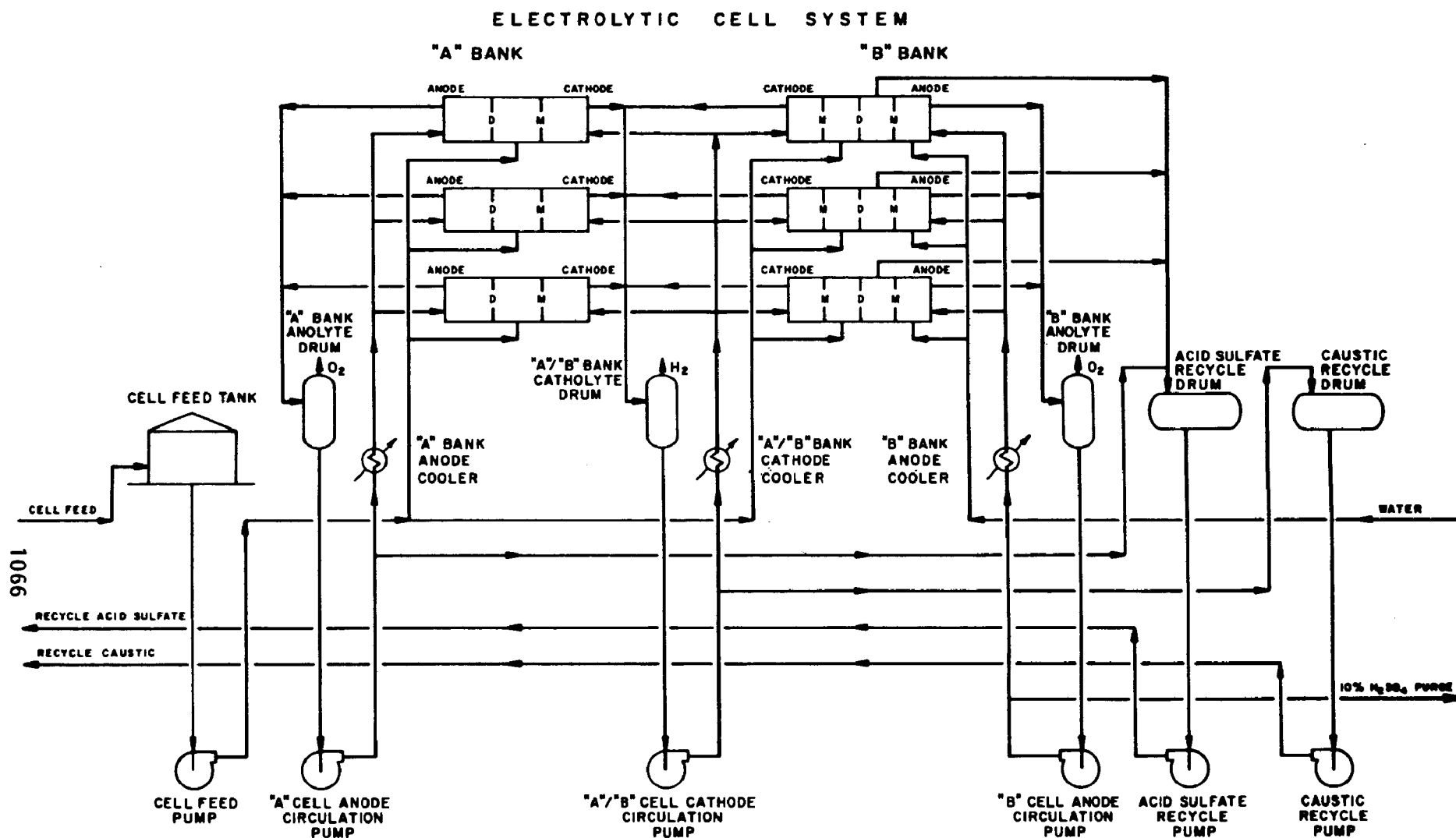


FIGURE 1-2
REGENERATION SECTION
 STONE & WEBSTER / IONICS SO₂ REMOVAL & RECOVERY PROCESS

Oxygen is generated at the electrolyzer anodes as a pure gas. Hydrogen is generated at the cathodes as a pure gas. If not recovered as byproducts, the hydrogen is burned and the oxygen is vented to the atmosphere.

In the four compartment electrolyzers, and anode product is dilute H_2SO_4 equivalent to about 6 to 8 percent of the SO_2 absorbed. Being commercially pure, it is withdrawn from the system for marketing, or other disposal. The sulfate ion so removed as dilute acid represents the method by which SO_3 contained in the flue gas from the boiler plus the SO_2 oxidized in the absorber to SO_3 are removed from the system. The total amount of SO_3 determines the required number of four compartment electrolyzers and the amount of dilute acid produced.

3.2 Technical Considerations

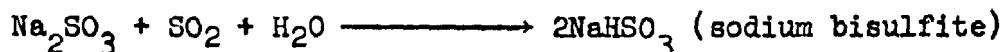
3.2.1 Absorption

In the absorption step, capital investment and operating cost are influenced by caustic utilization and by sulfite oxidation. The following sections explain and describe the influence of each.

A. Caustic Utilization

The first important process variable is the caustic utilization in the absorption system, that is, the mols of SO_2 reacted per mol of caustic ($NaOH$). The 8 percent caustic at the top of the absorber will first react with the CO_2 in the flue gas to form sodium carbonate. The latter will then react with the SO_2 in the flue gas to form sodium sulfite (Na_2SO_3). The partial pressure of SO_2 above a solution containing sodium sulfite is essentially zero, so it is possible to absorb virtually all of the SO_2 from the flue gas.

In the lower part of the absorber, the entering flue gas reacts with the sodium sulfite as follows:



As the conversion of sodium sulfite to sodium bisulfite occurs, the absorption work accomplished by each mol of caustic fed to the absorber increases. For example, if the fluid removed from the tower is a solution of sodium sulfite in water (neglecting the sodium sulfate recirculated and any formed in the tower), one mol of SO_2 can be removed from the flue gas for each two mols of caustic entering the tower. If all of the sodium sulfite is converted to sodium bisulfite, one mol of SO_2 can be removed from the flue gas for each mol of caustic entering the tower.

There is, however, an inherent constraint that limits the extent to which sodium sulfite may be converted to sodium bisulfite in a practical situation; it is that the partial pressure of SO_2 in the flue gas entering the absorber must exceed the equilibrium partial pressure of SO_2 exerted by the sodium

bisulfite solution. The partial pressure of SO₂ in the flue gas entering the absorber depends on the sulfur content of the boiler fuel and the amount of excess air fired. The equilibrium partial pressure of SO₂ exerted by the sodium bisulfite solution depends on the concentration of bisulfite in the solution and the absorption temperature, both of which variables can be influenced by the engineer designing the system. Additionally, the design of the absorber tower, which the engineer controls, influences the rate of transfer of SO₂ from the flue gas to the solution.

Accordingly, the absorption system can be designed to optimize the production of sodium bisulfite, taking into consideration absorber capital investment, solution recirculation expense, and electrolyzer system investment and operating cost.

B. Oxidation

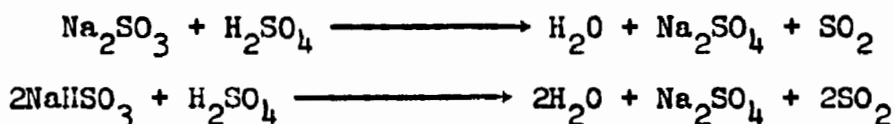
The second major consideration in the absorber design is the extent of oxidation of sulfite to sulfate by oxygen absorbed from the flue gas in the absorber. SO₂ in the sulfate form cannot be released by neutralization with recycled dilute acid solution. Sulfate generated by oxidation in the absorber poses no technical problem but imposes some economic penalty, reflected in both the investment and operating costs of the entire process.

Operating costs are increased because more caustic is required to remove SO₂ as sulfate than as bisulfite. Capital investment also is increased by the need to include in the process a four compartment electrolyzer for rejecting the excess sulfate as dilute pure H₂SO₄. This four compartment electrolyzer, described in section 3.2.3, achieves rejection of sulfate without loss by the overall system of valuable sodium ion but with some additional sodium ion recirculation.

Since absorbed oxygen reacts slowly to form sulfate, the engineer's objective is to design an absorber that will not absorb much oxygen, but will rapidly absorb a substantial portion of the SO₂ as bisulfite. Based on performance data from packed tower in SO₂ removal service, a system removing SO₂ to the 150 to 300 ppm range should experience an oxidation to sulfate of approximately 6 to 8 percent of the SO₂ transferred from the flue gas to the liquid.

3.2.2 Sulfur Dioxide Recovery

The liquid effluent from the absorber is mixed with a recycled dilute acid solution before entering the stripper. The following reactions take place:



The SO₂ is taken overhead from the stripper, sufficient trays being provided to insure that 99.5 percent of the SO₂ generated in the above reactions is removed from the liquid.

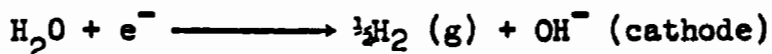
The stripped sodium sulfate solution is cooled, adjusted in pH, filtered, and fed to the electrolyzers. It is desirable to maintain the feed slightly alkaline in order to keep the cation membrane resistance at a minimum. Therefore, the pH of the stripped sodium sulfate solution is adjusted with caustic. Addition of the caustic causes heavy metal ions (leached out of fly ash in the absorber) to precipitate from solution as hydroxides, which are removed by filtration and ion exchange.

Absorber output varies with plant load, and average electrolyzer operation is a function of average caustic production. In a plant with a large peak demand, it is possible to shut off cell power during the peak and run at a slightly higher rate when off peak. This can be done by providing storage for sodium sulfate solution, caustic and acid, thus allowing absorber and stripper operation to follow power plant loading, and the electrolyzers to operate on the spinning reserve power available from the generators during off-peak periods.

3.2.3 Absorbent Regeneration and Oxidation Product Rejection

The unique feature of the Stone & Webster/Ionics Process is the electrolyzer system in which the caustic is continuously regenerated. Reference has been made above to the use of two different designs, a three compartment electrolyzer and a four compartment electrolyzer. The former is the basic design which converts sodium sulfate into two streams, sulfuric acid and caustic soda. The four compartment design represents a further refinement and is the means by which excess sulfate is removed from the recirculating liquid system as dilute, pure sulfuric acid.

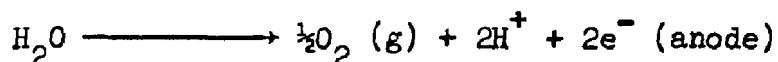
A schematic diagram of the three compartment (Type A) electrolyzer is presented on Figure 2-1. The main components are an anode, a microporous diaphragm, a cation-transfer membrane, and a cathode. These components are separated from each other by flow directing spacers which also provide the required gasketing. The sodium sulfate is fed to the central compartment at a concentration of about 20 wt percent. Sodium ions migrate through the cation-transfer membrane toward the cathode under the influence of a direct current voltage impressed across the electrolyzer. At the cathode, water is electrolyzed to hydrogen gas and hydroxide ion as follows:



The hydroxide ions are electrically balanced by sodium ions entering the cathode compartment through the cation-transfer membrane. Thus, the catholyte effluent consists of NaOH plus Na₂SO₄ which, after disengaging hydrogen, is sent to the caustic storage tank and then to the absorption tower.

The function of the cation-transfer membrane is to prevent physical mixing of the catholyte and center compartment feed streams. Essentially, only sodium ions from the center compartment pass through the membrane to combine with hydroxide ions produced at the cathode. In industrial applications other than SO₂ removal by the Stone & Webster/Ionics Process water may be fed to the catholyte compartment in sufficient quantity to produce 8 to 10 percent caustic. However, the Stone & Webster/Ionics Process is an essentially closed system. Therefore, to maintain water balance in the system it will generally be necessary to feed recycled sodium solution to the catholyte compartment instead. This procedure does not introduce any problems.

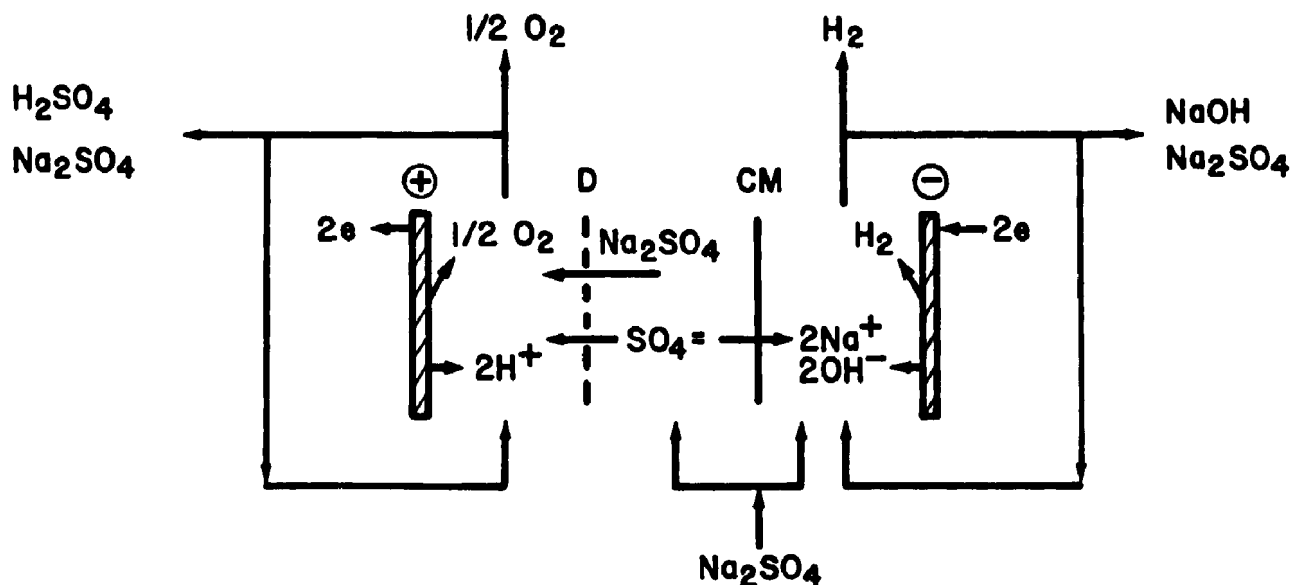
The center compartment feed stream passes through the microporous diaphragm, into the anode compartment. At the anode, water is electrolyzed to hydrogen ions and oxygen gas:



The hydrogen ions combine with sulfate ions to form sulfuric acid. The diaphragm flow is designed to prevent hydrogen ions from migrating across the cation-transfer membrane. Such flow must give enough linear velocity through the diaphragm to sweep hydrogen ions back into the anolyte compartment. The diaphragm should have an hydraulic resistance adequate to insure that such flow is substantially uniform over the entire surface. A flow which is sufficient to sweep back most of the hydrogen ions carries with it about half of the sodium in the center compartment. Thus at the anode, only part of the sodium sulfate in the feed stream is electrolyzed to sulfuric acid. The anode product is therefore a mixed solution containing both sulfuric acid and sodium sulfate. This product is the dilute acid solution that is recycled to release SO₂ in the stripper.

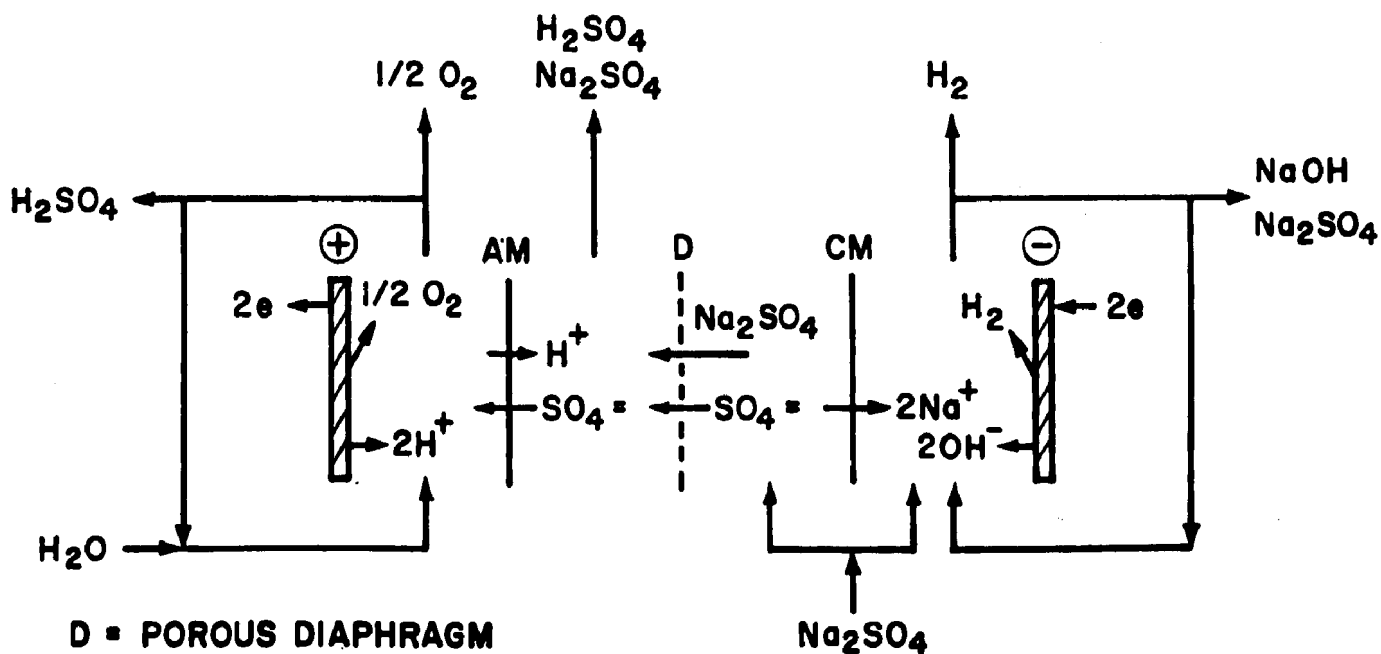
In the four compartment (Type B) electrolyzer, a schematic diagram of which is presented on Figure 2-2, the reactions and operation of the catholyte compartment are exactly those described for the three compartment electrolyzer. The catholyte effluents from both electrolyzer types are combined before being pumped to the absorber. The center compartment feed flows through the porous diaphragm, into the "mid-anolyte compartment," from whence most is discharged from the electrolyzer. This stream contains some sulfuric acid due to the inability of the membrane to exclude completely the hydrogen ion. It is combined with the anolyte stream from the three compartment electrolyzers.

The important reactions of the four compartment electrolyzer occur at the anode, where water is electrolyzed to hydrogen ions and gaseous oxygen. These hydrogen ions combine with sulfate ions entering the anode compartment to form a sulfuric acid anolyte. The function of the anion-transfer membrane is to exclude sodium from the anode compartment while allowing sulfate to enter. It also, to a large extent, prevents hydrogen ions from leaving the anode compartment. Thus, the anode reactions permit removing sulfate ions without losing sodium.



D = POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE

FIGURE 2-1
SCHEMATIC DIAGRAM OF "A" ELECTROLYTIC CELL



D = POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE
AM = ANION SELECTIVE MEMBRANE

FIGURE 2-2
SCHEMATIC DIAGRAM OF "B" ELECTROLYTIC CELL

A large number of materials of construction have been tested in order to optimize the life and performance of the electrolyzer components. Anodes are a lead alloy; cathodes are steel. The microporous diaphragms and ion transfer membranes are polymeric organic materials.

Each electrolyzer consists of an anode, a cathode, at least one membrane, and one diaphragm with appropriate separators and internal flow distributors. A second membrane is placed between the diaphragm and the anode in the Type B electrolyzers. Fluid is internally manifolded and is in parallel. The electrolyzers are arranged into a number of modules within a single structural frame. The electrolyzers within a module are in parallel electrically and the modules are in series. In order to conserve space and minimize field piping, three frames are arranged in a vertical array to form a bank. The internal fluid manifolding is brought to headers in the frames. The headers are provided with quick disconnect fittings to the electrolyzer fluid distribution and collection mains. Typical arrangements of modules, frames and banks are shown schematically in Figures 3-1 and 3-2.

3.2.4 Electrolyzer System Auxiliaries

Hydrogen produced by the cathodes is gathered in standpipes and passed to gas collection mains. Caustic is collected from the bases of the standpipes and pumped to the caustic surge tank. Oxygen is similarly collected from anode fluids.

Since Ohmic losses must be dissipated from the electrolyzers, heat exchangers are provided for the recirculating anolyte and catholyte streams. The anolyte coolers have Karbate tubes and the catholyte coolers carbon steel tubes. The pure, dilute acid, produced in the Type B electrolyzers, will be approximately 9 percent acid.

3.2.5 Potential Problems and Process Limitations

A number of problem areas have been identified and potential solutions postulated. These include:

1. Oxidation of SO_2 to SO_3 ; amount and affect on economics.
2. Effect of oxidation inhibitors if used, on system and cells.
3. Effect of NO_x on system and cells.
4. Effect of fly ash on system; which minerals, if any, affect oxidation, absorption, filtration, cell performance and cell life.
5. Effectiveness of quench section and absorption section in removing fly ash.

6. Effectiveness of ion exchange in removing heavy metals from solution.
7. Deleterious impurities in recovered SO₂; nature, amount, and effect.
8. Efficiency of absorption, stripping, and electrolysis.
9. Materials of construction.
10. Disposal of weak acid from "B" cells.

None of the above problem areas appear to be without a reasonable solution.

The potential process limitations mainly lie in the area of efficiency in absorption, stripping, minimization of cell power, and the ability of the system to produce a high bisulfite to sulfite ratio.

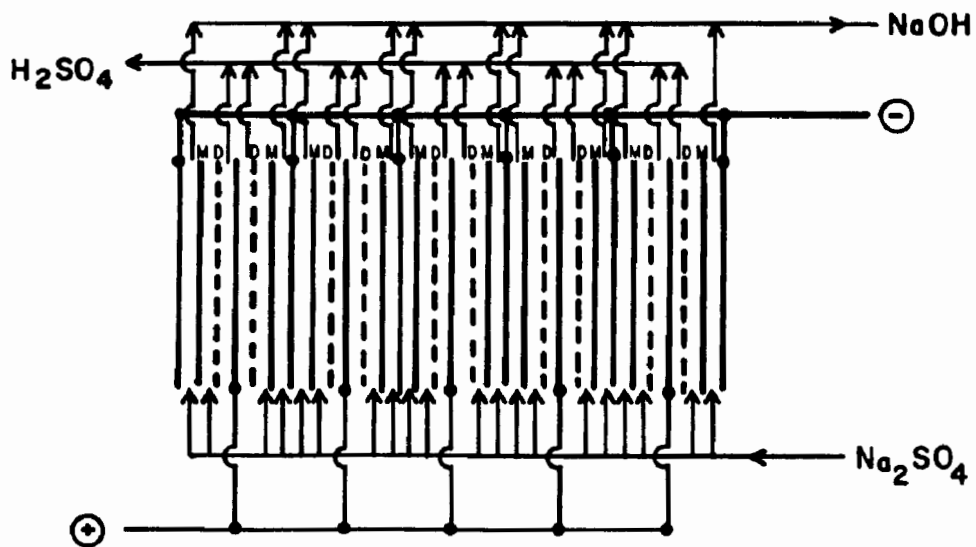
Pilot plant work in Tampa and at Watertown has given indications of what may be expected but long run testing on commercial sized equipment will be required to give reliable answers to many of these areas. Corrosion test coupons that are being installed in the WEPCO pilot plant will aid in selection of materials for the prototype plant.

4. PILOT PLANT

The pilot plant at Wisconsin Electric is being installed primarily to verify operability of the Stone & Webster/Ionics process in an integrated operation under Wisconsin Electric conditions, and to confirm the process design of the 75 MW prototype plant. The pilot plant will process a slip stream of about 2,900 ACFM of flue gas at 300 F containing about 1,000 ppm of sulfur dioxide from a coal fired boiler. It is designed to remove a maximum 95 percent of the SO₂.

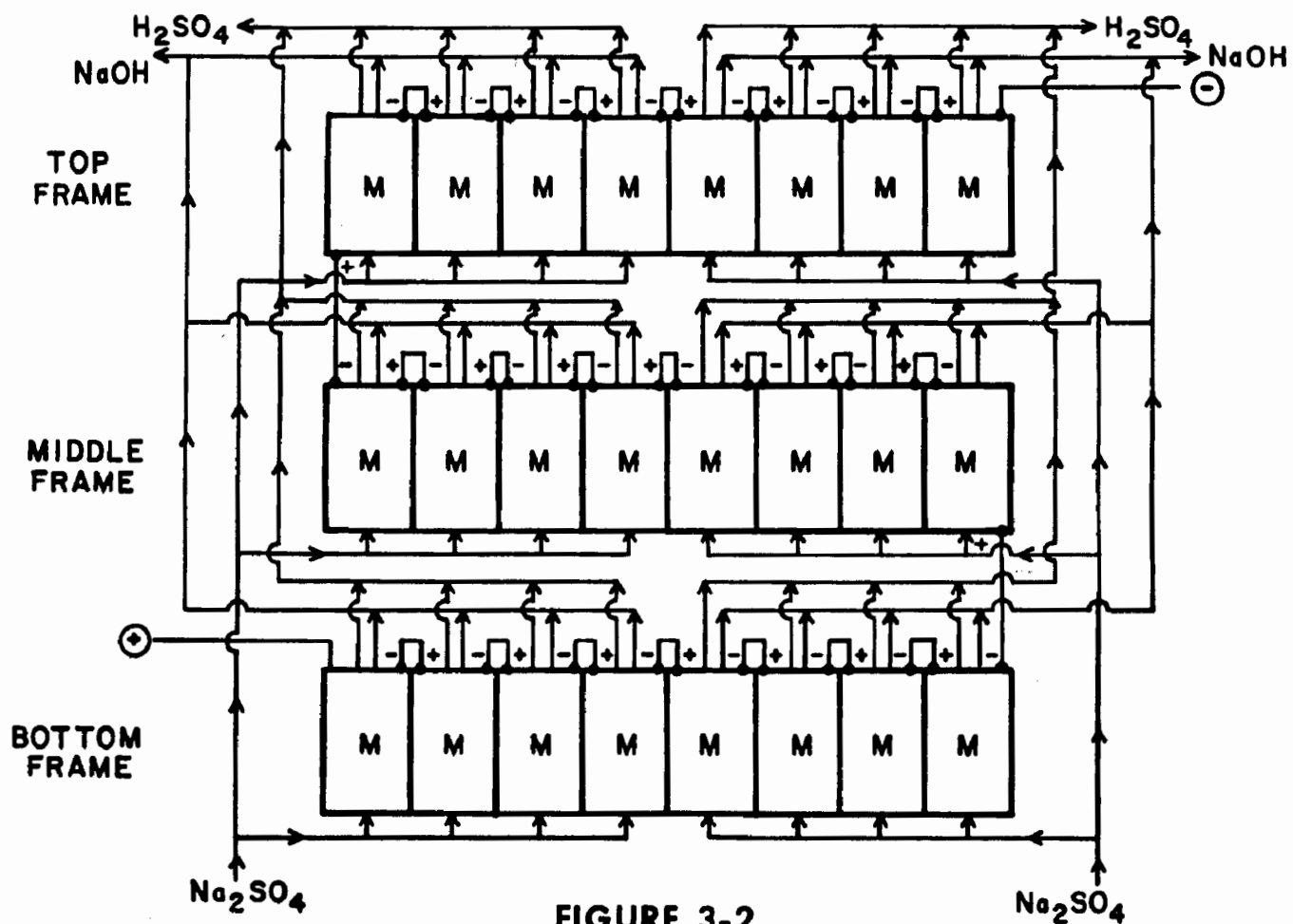
As in any coal fired boiler, it is to be expected that the sulfur content in the flue gas will vary with the quality of the coal. At Wisconsin, the amount of sulfur is known to vary from as low as 1/2 percent to as high as 5 percent. Since it is desirable to operate the pilot plant at reasonably uniform conditions during any one test, a by-pass from the discharge of the absorber to the suction of the forced draft fan has been installed to permit adjusting the SO₂ content of the flue gas to a fixed value for each test.

The absorber contains three stages of contact with provision to operate on two only if desired.



**FIGURE 3-1
MODULE**

M = MEMBRANE
D = DIAPHRAGM



**FIGURE 3-2
BANK**

M = MODULE

The pilot plant contains all the elements that present knowledge indicates will be required in the 75 MW prototype plant. The equipment, in so far as possible, is of a type that can be obtained for the larger plant. Materials of construction have been selected based on previous experience to be suitable for commercial operation. In addition, test coupons of various materials are installed at strategic locations so as to provide information on alternate materials of construction.

The testing program is expected to begin in May 1973 and extend for about six months. Data will be obtained on:

- a. Mass transfer coefficients in the absorber and stripper;
- b. Extent of SO_2 oxidation to SO_3 ;
- c. Effect of operating variables on SO_2 removal and on sulfite-bisulfite ratio in the rich liquor;
- d. Performance data on electrolyzers, including power consumption for both types of electrolyzers under field conditions and over a range of operating variables.

Concurrent with the pilot plant testing, prototype electrolyzer modules similar in design to that intended for installation in commercial plants, will be operated at Ionics' Watertown facility to obtain data for the design of the full-sized electrolytic cell system.

5. 75 MW DEMONSTRATION (PROTOTYPE) FACILITY

Following successful demonstration of the pilot plant, Stone & Webster will proceed with design and installation of the 75 MW Demonstration Facility, assuming that the estimated costs of the system are acceptable.

5.1 Basis of Design

The basis of design is:

1. Process all the flue gas from one 75 MW boiler at 100% load factor; approximately 225,000 ACFM at 300°F
2. Average sulfur content at 2.5 wt % in the coal.
3. Flue gas to be desulfurized to 200 ppm or lower.
4. Oxidation of SO_2 to be a maximum of 10 percent.
5. Minimum ratio of mols SO_2 absorbed per atom of recirculated sodium equal to 0.87.

Figs. 1-1 and 1-2, referred to earlier, show the major equipment and flow schemes for the 75 MW unit.

The Facility will be designed to remove a minimum of 90 percent of the SO_2 from the stack gas. A minimum of 90 percent of the absorbed SO_2 will be recovered as SO_2 and the balance removed as dilute sulfuric acid.

Anticipated pressure drop across the absorber, including duct losses, is eight inches of water.

The recovered SO_2 will be dried, compressed, and liquefied for sale. It is believed that during the test program an outlet can be found for the 9 wt % sulfuric acid purge stream, amounting to about five tons per day as 100% H_2SO_4 .

5.2 Operating Program

The primary purpose of the prototype plant is to provide information on the operating and maintenance characteristics of the process, and to develop conclusions with respect to its technical and economic feasibility. The program includes:

1. Systematically varying the primary process variables over the practical operating ranges, and collecting the data required to characterize the process;
2. Developing correlations to assist with scale-up of the process equipment and estimating performance under a variety of operating conditions;
3. Determining the electric power consumption of the electrolyzers;
4. Evaluation of the operator work load and maintenance in the electrolyzer and non-electrolyzer sections.
5. Evaluating the effects of corrosion, to serve as a basis for selecting materials of construction for future installations.

6. PROCESS ECONOMICS

Since many large boilers supplying steam for power generation are in the 400 to 500 MW range, we have developed process economics for this paper for a 400 MW unit instead of the smaller 75 MW unit planned for Wisconsin. We believe this will be more representative of the average power plant installation. Cost of utilities do not necessarily reflect WEPCO costs but are those generally used in assessing costs of competitive processes.

An operating load factor of 80 percent for the 400 MW unit has been used for the utility and a 4 percent sulfur coal has been assumed. Credit taken for the byproduct sulfuric acid is deemed to be reasonable for the sale of the acid by the utility. Fuel value only is assumed for the hydrogen even though there may be particular locations at which hydrogen could be sold at a much higher value. No credit is taken for the byproduct oxygen.

Approximate installed costs and operating costs for Stone & Webster/Ionics SO₂ removal unit for a 400 Mw coal fired steam generating unit are given in Table 1. Included is the cost of facilities to convert the SO₂ to commercial grade sulfuric acid. Alternatively, the SO₂ could be dried and sold as liquid product or could be converted to sulfur.

The fixed charge rate assumes 100 percent financing by industrial revenue bonds at 6 percent interest, straight line pay backs of principal, accelerated depreciation under IRS Section 169, and a 7 percent discount rate for all cash flows. Such industrial revenue bonds and accelerated depreciation have become very popular for financing pollution control plants. It is assumed that these provisions will remain in effect. They permit a fixed charge rate of 7.1 percent per annum after taxes on the 20 year life assumed for this project.

The indicated annual cost of about \$2 million for SO₂ removal is influenced by the rate the station charges for power used in the electrolyzers and by the credit assigned to the by-product sulfuric acid. As shown in the footnote of Table 1, the net annual cost of the plant may be defrayed by (a) an average increase of 0.73 mills in the price of sold power; (b) an increase of \$15.00 per ton in the price of sold sulfuric acid; (c) a decrease of 9 mills in the station service electric rate; (d) a decrease of \$1.88 in the price of purchased coal; or (e) any combination of these. Each of these alternatives includes a provision for income taxes of 50 percent. As indicated by the footnote, the trade-off point between SO₂ removal and the purchase of low sulfur coal is a premium of \$1.88 per ton for the latter.

The energy consumption of the electrolyzers is a unique type of station service account. The absorption section must process flue gases as generated, but the sulfur dioxide recovery and the absorbent regeneration and oxidation product rejection may be decoupled from a real-time, operational standpoint. (They may be geographically removed as well, connected with the absorption section by relatively small, liquid-handling pipelines.) Electrolyzers, when on line, can be instantly interrupted without damage, either in blocks or all at once at the sole control of the utility dispatch center. Power pool agreements as well as plant operating principles provide for spinning reserve capacity which can be made available from generators which are spinning and generating power at a rate less than nameplate ratings. Such reserve is usually sufficient to cover a predetermined per-

centage of total system load or a percentage of the load on the largest generator in the system. If the generator capacity represented by this reserve is under the sole control of the utility dispatch center, there should be no bar to using this reserve for performance of useful work.

Such an interruptible station service account is instantly available in comparison with the usual "interruptible" customer and should be regarded as loaded spinning reserve. It therefore seems reasonable to charge the removal system only for the marginal cost of fuel, labor, and maintenance materials without capital charges. If this approach is followed and the electrolyzers are operated on spinning reserve power, the SO₂ removal cost might be reduced by about 0.3 mills per kwhr.

The regeneration subsystem is amenable to evolutionary development. Significant reductions in energy and maintenance costs of the electrolyzers may be confidently predicted, based on pilot plant results to date. Such improvements should result in the electrolyzer characteristics shown in Table 2. The 1975 components should result in 15 to 20 percent saving in electrical energy consumption.

APPROXIMATE ANNUAL OPERATING COST
STONE & WEBSTER/IONICS SO₂ REMOVAL PROCESS

Basis = 400 Mw Station Burning 4.0 Wt % S Coal
80% Operating Load Factor

Installed Cost

SO ₂ Removal Unit	\$14,000,000
Sulfuric Acid Unit	2,500,000
	<u>\$16,500,000</u>

Annual Cost

	<u>Unit Cost</u>	<u>Quantity</u>	<u>Annual Cost</u>
Fixed Charges after Taxes	7.1% per annum		\$1,174,000
Operating Cost - SO ₂ Removal Unit			
Steam	\$0.60 per 1,000 lb	70,000 lb per hr	313,000
Electricity (cells, pumps, blowers & lighting)	\$0.007 per kwhr	31,900 kw	1,570,000
Cooling Water	\$0.02 per 1,000 gal	8,500 gpm	76,000
Process Water	\$0.05 per 1,000 gal	650 gpm	14,000
Deionized Water	\$1.00 per 1,000 gal	40 gpm	18,000
Operating Labor	\$10.00 per hr(1)	2 oper/shift	175,000
Maintenance	4% per annum		<u>560,000</u>
Subtotal			\$2,726,000
Operating Cost - H ₂ SO ₄ Unit(2)	\$2.00 per ton	465 tons per day	<u>271,000</u>
			4,171,000
Credits			
Sulfuric Acid	\$15.00 per ton	465 tons per day	(2,035,000)
Hydrogen	\$0.60 per MM Btu (LHV)	24.7 MM Btu per hr	<u>(104,000)</u>
Subtotal			(2,139,000)
Total Annual Cost			\$2,032,000

Notes

Equivalent Cost per Sold Kwhr	0.73 mills or
Equivalent Increase in Sold Sulfuric Acid Price	\$15.00/ton or
Equivalent Decrease in Station Service Rate	\$0.009/Kwhr or
Equivalent Decrease in Cost of Purchased Coal (1,083,000 ton)	\$1.88/ton

(1) Includes overhead, and supervision

(2) All costs including maintenance are represented.

ELECTROLYZER CHARACTERISTICSSTONE & WEBSTER/IONICS SO₂ REMOVAL PROCESS

Basis: Plant of Table I

<u>Electrolyzer Type</u>	<u>Voltage</u>	<u>Current Efficiency (%)</u>	<u>Kilowatts AC</u>
1973 "A"	4.6	95	24,400
1973 "B"	4.9	95/40 ⁽¹⁾	<u>4,500</u>
Total 1973			28,900 ⁽²⁾
1975 "A"	3.8	95	21,300
1975 "B"	4.2	95/60 ⁽¹⁾	<u>2,600</u>
Total 1975			23,900

(1) First number is overall current efficiency.
 Second number is current efficiency for the pure H₂SO₄.

(2) Cell requirement only. Added 3,000 kw in Table 1 for
 pumps, blowers, etc.

**FW-BF DRY ABSORPTION SYSTEM
FOR
FLUE GAS CLEAN UP**

by

**W. F. Bischoff
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Livingston, New Jersey**

ABSTRACT

The information contained in this paper is directed to those individuals in private industry and governmental agencies concerned with the reduction of SO₂ in flue gas emissions. It is intended to serve as a means of presenting information on the history of the dry adsorption process developed by Bergbau-Forschung, GmbH, process description, technical details, pilot plant experience, demonstration plant design and economic factors.

FW-BF Dry Adsorption System
for
Flue Gas Clean Up
by
W. F. Bischoff
Foster Wheeler Corporation

I. Introduction

Foster Wheeler is a major manufacturer of steam generation equipment and also a major process plants contractor. In both of these roles we have been actively concerned with pollution problems and their proper solutions. To this end the Corporation has participated in considerable research and development work in order to solve the pollution problems of our customers.

Our research program has included, in part, the extensive technical and economic evaluation of various pollution control systems. One of the systems on which we have expended considerable time is the subject of this paper.

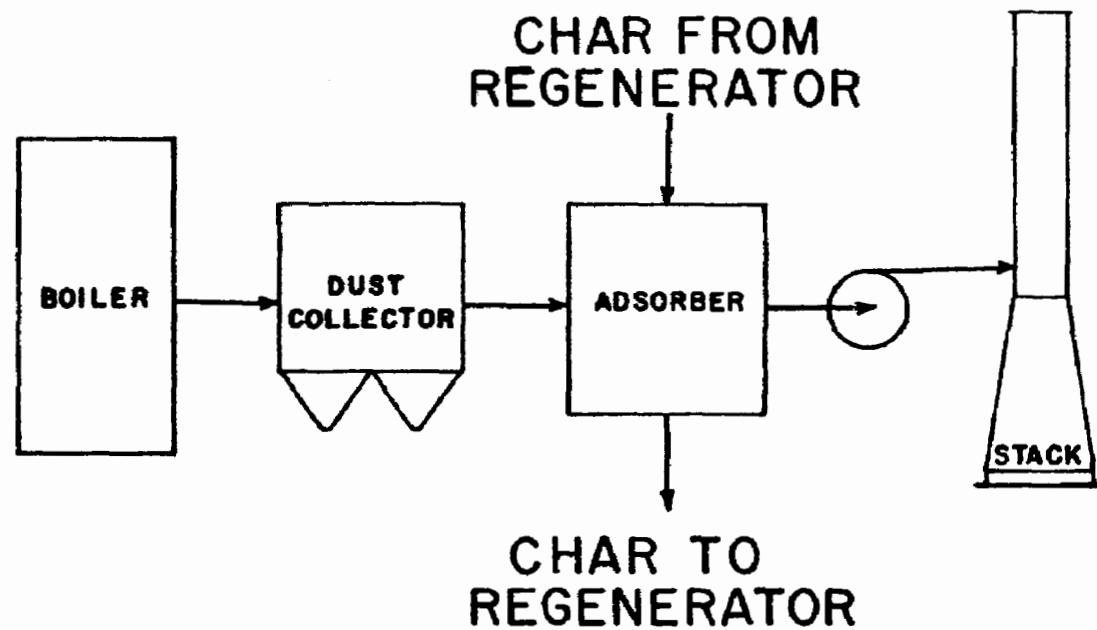
II. Background of Bergbau-Forschung, GmbH

Bergbau-Forschung, GmbH, (BF) is the central research institute for the German coal mining industry. They are industry supported and therefore analagous to our own Bituminous Coal Research Institute..

In 1963 Bergbau became interested in the application of chars produced from coal to remove sulfur dioxide from stack gases. The chemical reactions involved for adsorption were well known but, the means for doing it successfully on a continuous basis were not. Bergbau therefore determined to produce a char from non-coking coals which would meet the system requirements they had conceived. The char had to have the following characteristics:

1. High mechanical strength
2. High SO₂ adsorption capability
3. High ignition point
4. Low pressure drop when put in a travelling bed reactor

BLOCK DIAGRAM



FW-131-004

Fig. 1

Bergbau was successful in this endeavor and then built a laboratory scale pilot unit to test their system. After the successful operation of the laboratory unit Bergbau built a pilot plant of about 1.5 MW equivalent which was operated in a slip stream from a coal fired utility boiler. The gas flow through the pilot plant was 3000 m³/hr. (105,000 SCFH). This pilot unit was run continuously for two years during which time all of the correlations developed during the laboratory work were confirmed. Although the system was basically developed for removing SO₂, it was discovered in the pilot plant work that the system also has capability to significantly reduce NO_x and particulates in the flue gas stream.

As a result of the work done by Bergbau as well as our own development efforts on the system Foster Wheeler is convinced that the Bergbau system is the most feasible for application to a wide variety of boiler flue gas pollution problems. Because of this conviction Foster Wheeler has become fully licensed under the Bergbau technology and patents.

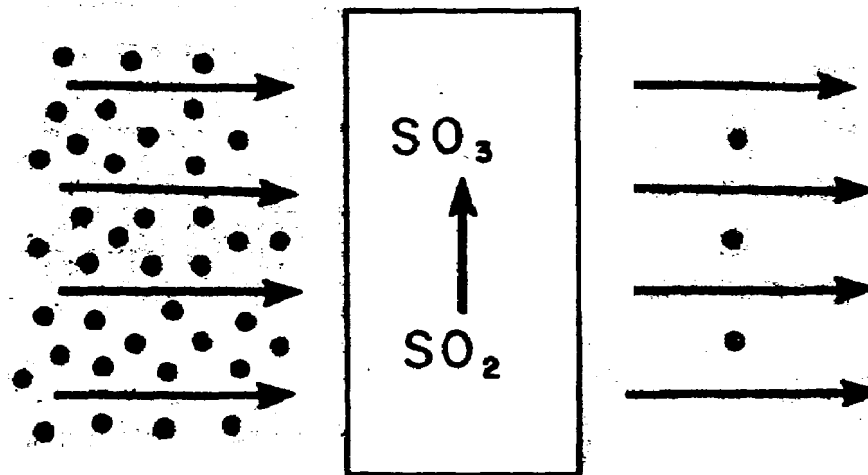
During the period that Foster Wheeler has been licensed for the process, development work has continued both in Germany and in the United States. The development work has resulted in what is known as the FW-BF Dry Adsorption System.

III. Process Description

Figure 1 shows how the FW-BF System fits into a typical utility boiler system. The adsorber is the key to this system. It consists of parallel louvre beds which support and contain the char during the adsorption phase. The char moves slowly downward in plug flow while the pollutant laden gases pass through the adsorber bed in a cross flow. The fan indicated at the gas discharge of the adsorber is utilized to make up the pressure losses which occur during the passage of the gas through the adsorber bed. Clean gases

REACTIONS

FLUE GAS (250-300 °F)



CHAR PELLET
3/8" DIA. X 3/4" LG.

FW-131-005

Fig. 2

leaving the fan are directed to the stack for disposal. Once the char has progressed through the adsorber it is taken off and sent to the regeneration section. Once regenerated the char is recycled to the top of the adsorber. This process scheme allows for the continuous adsorption of pollutants and the continuous on site regeneration of the adsorbent media.

The reactions that are taking place in the adsorber are shown in part in Figure 2. The rectangular block represents a single char pellet which is approximately $3/8$ " in diameter x $3/8$ " - $5/8$ " long. Boiler flue gases containing SO_2 , NO_x , water vapor and particulate matter come into contact with the char pellet. The SO_2 , oxygen and water vapor are adsorbed into the char pellet. Once in the char pellet the SO_2 is oxidized to SO_3 and subsequently catalytically converted to sulfuric acid which is firmly held in the interior pore system of each char pellet.

Nitrous oxides are likewise adsorbed in the char pellet and held until regeneration occurs. Particulate matter is collected on the surface of the char pellets.

The reactions in the adsorber are designed to take place through a range of temperatures above 250°F . The lower limit of 250°F is specified because of dew point considerations. The relationships between adsorber size, adsorption efficiency and operating temperatures indicate that optimum efficiency is achieved at temperatures around 275° to 300°F range.

As a result of the adsorption phenomena and the dust collection capabilities of the system, it is possible to reduce pollution emission levels as indicated below:

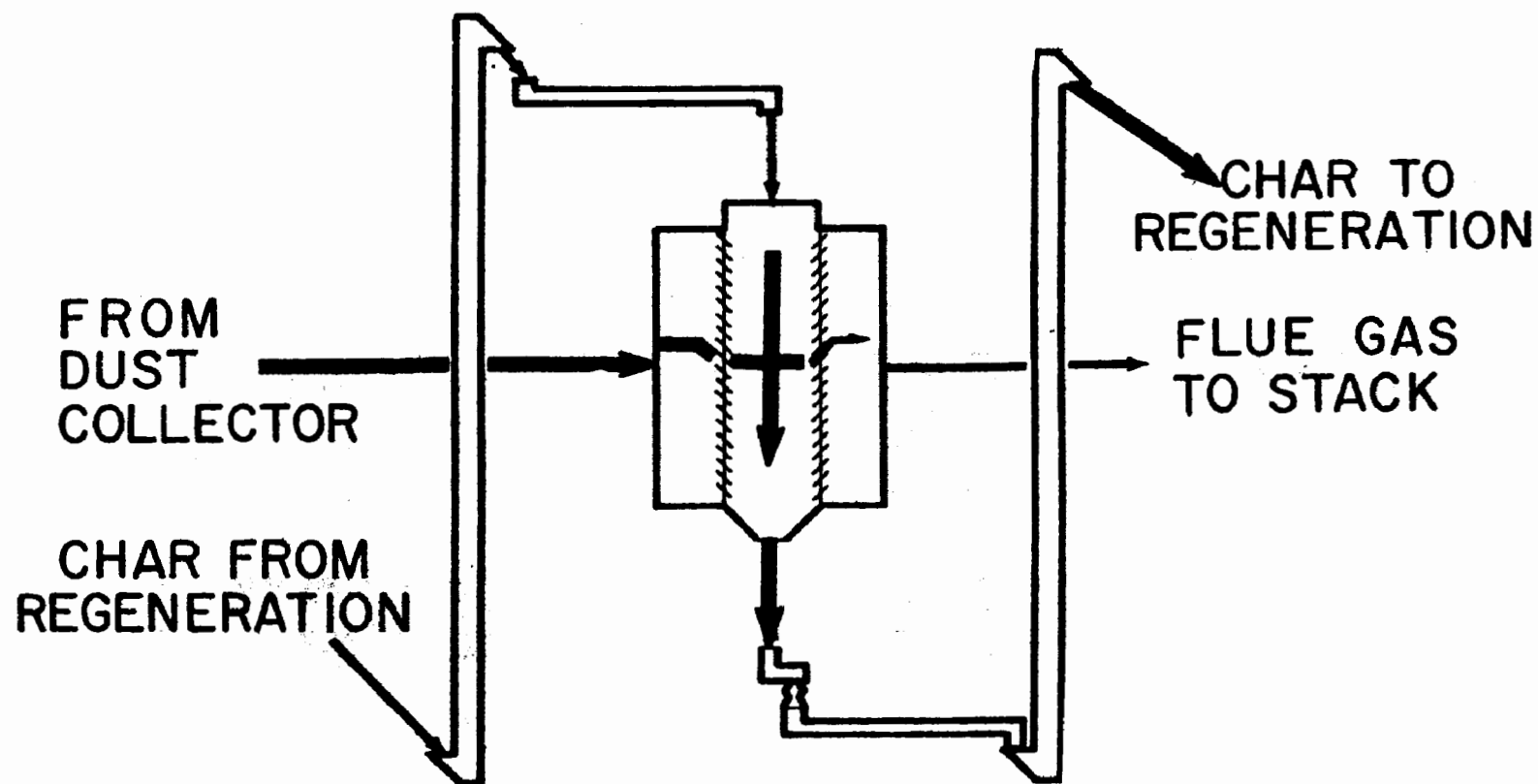
<u>Pollutants</u>	<u>Removal Efficiency</u>
SO ₂	80-95%
NO _x	40-60%
Particulate matter	90-95%

The SO₂ removal efficiency is listed as a range to indicate flexibility of design. In some cases, dependent on the sulfur in the fuel, it may not be required to achieve a 95% removal efficiency to be in accordance with the required codes. Therefore economies in the design can be realized by virtue of the lower removal efficiency requirement. NO_x efficiencies are indicated as a range for the same reasons. The particulate removal efficiency shown above is meant to indicate that the system is capable of removing from 90 to 95% of the particulate matter received in the inlet of the adsorber after prior treatment with high efficiency electrostatic precipitators.

The regeneration of the saturated char can be accomplished by washing (wet regeneration) or by contacting it with hot sand (thermal regeneration). Wet regeneration produces dilute sulfuric acid (18% by weight) as a by-product material. Because of the limited use for this material thermal regeneration is the more practical method of regeneration.

In thermal regeneration an enclosed refractory lined vessel is utilized to contact the saturated char pellets with hot sand which has been heated to approximately 1500°F. Regeneration is a function of vessel size, retention time, sand to char ratio, and sand temperature. As the char pellets become heated the reactions that took place in the adsorber are reversed producing a concentrated stream of SO₂, H₂O, CO₂, and N₂. In other words the H₂SO₄ produced in adsorption is converted to H₂O + SO₃. The SO₃ is reduced to SO₂ in the presence of the hot char and produces CO₂ by the combination of the liberated oxygen with the carbon in the char. In a like manner the oxides

ADSORPTION



FW-131-008

Fig. 3

of nitrogen are reduced to N_2 with the resultant production of additional CO_2 .

The concentrated stream of off-gas is then directed to a proprietary Foster Wheeler OGT system for conversion of the SO_2 to elemental sulfur.

IV. Technical Details

The FW-BF System consists of three basic sections:

1. Adsorption
2. Regeneration
3. Off Gas Treatment

The adsorption and regeneration sections of the system are those which were developed and designed originally by Bergbau. The Off Gas Treatment section is a proprietary FW design for which we have made patent application.

A. Adsorption

The adsorption section, as stated previously, is the heart of the system. It is here that the reduction of pollutants take place. As can be seen in Figure 3 the adsorber is a vertical bed in which the char moves slowly downward at a rate of from 0.5 to 1.0 ft.per hour. This slow but variable movement allows for operational flexibility as well as guaranteeing low abrasion rates in the adsorber. The louvres are designed to not only support and contain the moving char bed but also to give direction to the incoming and outgoing flue gases. Flow distribution of the gases across the bed is maintained by means of adequate pressure drop. The pressure drops that have been measured for these types of adsorber beds vary from 4" H_2O to 14" H_2O depending upon the adsorber configuration.

The adsorber has been designed based on the information generated during pilot plant operation. During this pilot plant operation several different bed cross sectional areas were utilized varying from 0.5 meter x 0.5 meter

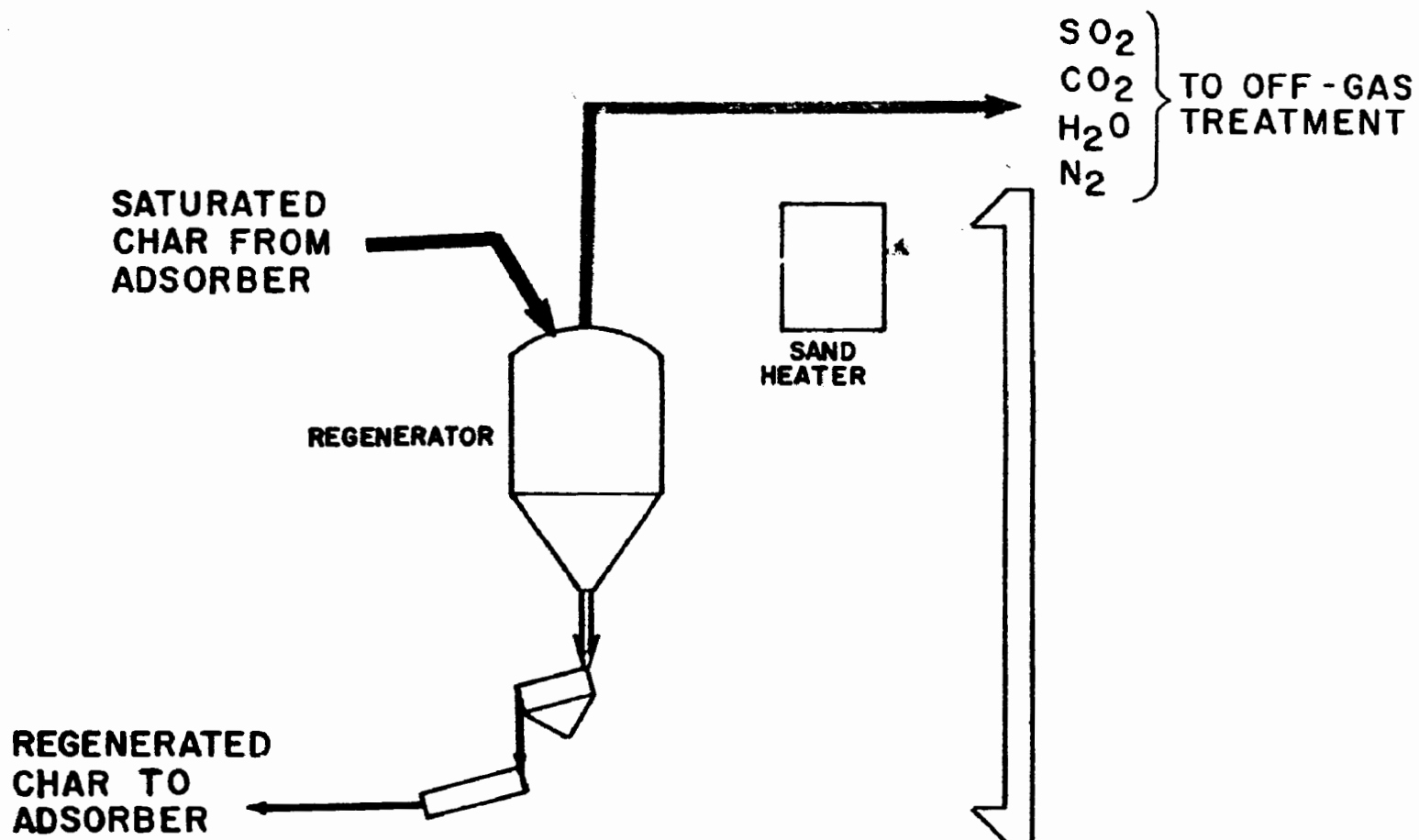
to 1 meter x 1 meter. Commercially sized beds vary from 4' x 4' to 6' x 6' thus keeping the scale-up factor for adsorption beds within reasonable limits. The height of adsorber beds is varied to achieve the necessary frontal bed surface area to bed volume ratio. For large gas flows a series of beds are operated in parallel so as to achieve the desired removal efficiency. By designing large adsorbers as a series of modules it allows for maximization of shop fabrication and minimizes field erection.

The flow of char through the adsorber beds is controlled at the bottom of each bed by a vibratory feeder which is controlled as a function of the amount of SO_2 entering the adsorber. This mode of operation gives flexibility to the system not only from the standpoint of variations in load but also variations in the percent of sulfur in the fuel. As load decreases the amount of SO_2 entering the adsorber also decreases and therefore it is possible to reduce the flow rate of char so as to maintain a consistent removal efficiency. The reduction of char flow then results in a lowering of operating costs for the unit. For a given boiler load with an increasing percent sulfur in the fuel the char flow rate can be increased so as to achieve a reduction efficiency comparable with the fuel being fired.

Upon leaving the feeder at the bottom of each adsorber bed section the char is discharged onto a natural frequency or oscillating type conveying system. The end of this conveyor is fitted with a screening section which screens off the majority of the fly ash collected in the adsorber. The fly ash removed is in a dry form. In order to eliminate fly ash losses from the system the entire system is totally enclosed. Once the char and fly ash have been separated the char is elevated by means of an enclosed bucket elevator and sent to the regeneration section. Upon completion of regeneration the char is returned to the adsorber section, elevated in an enclosed bucket elevator and distributed evenly across the top of the adsorber beds.

The entire adsorber and its associated distribution system is

REGENERATION



1092

FW-131-009

Fig. 4

enclosed so as to provide a sealed system and eliminate any possible secondary pollution sources.

B. Regeneration

In Figure 4 the saturated char from the adsorber enters the regenerator vessel where it is mixed with hot sand. The char temperature is raised as a result of this contact to a level where the reactions that have occurred in the adsorber are reversed as previously discussed.

Sand is utilized as an inert heat transfer media and as such does not take part in the reactions occurring within the regenerator. Its sole function is to supply heat so that the reactions may take place.

The mixture of hot sand and hot char pellets flow slowly downward through the regenerator and their flow is controlled at the discharge of the regenerator by a char-sand feeder and separator. This feeder-separator not only controls the flow rate of the materials through the regenerator but also acts to separate these two materials after regeneration has taken place. The char pellets, being considerably larger than the sand, flow overhead on the char-sand separator and are subsequently cooled and are then returned to the adsorber for reuse. The sand passes through the screen section and is returned via an enclosed hot bucket elevator to a fluidized bed sand heater. The fluidized bed sand heater restores the heat lost to the char and recycles the reheated sand to the top of the regenerator.

The production of CO_2 in the regenerator results in a chemical consumption of the char pellets which accounts for approximately 90% of the char makeup requirement. The remaining 10% char makeup is as a result of mechanical or abrasion losses. As the char is consumed chemically or reduced in size mechanically it eventually becomes too small to pass over the top of the screening section in the char-sand separator. At this point the small quantity of small char particles enter the hot sand side of the cycle and

make their way to the fluidized bed sand heater. There, in the presence of excess oxygen, they are consumed as a fuel. However, the quantity of these particles represent a negligible savings to the fuel requirement for the sand heater.

The hot flue gases emanating from the top of the sand heater contain SO_2 as a result of fuel combustion and also contain a source of recoverable heat. These hot gases are piped back to the inlet of the boiler air preheater where they are mixed with the boiler flue gases. The heat in this stream is utilized in the air preheater to preheat incoming boiler air. The additional SO_2 is now a part of the incoming flue gases to the adsorber and is adsorbed in the same manner as the SO_2 from the boiler flue gases.

That portion of the fly ash which was not removed by screening at the discharge of the adsorber is removed from the char in the regenerator by the gentle interaction of the sand with the char. This material passes through the char sand separator and enters the hot sand loop where it too acts as a heat transfer media. The quantities of fly ash removed in this manner are extremely small but eventually constitute a buildup in the inventory of material in the sand loop. It is therefore necessary to periodically remove a portion of the sand fly ash mixture and replace it with a smaller quantity of new sand.

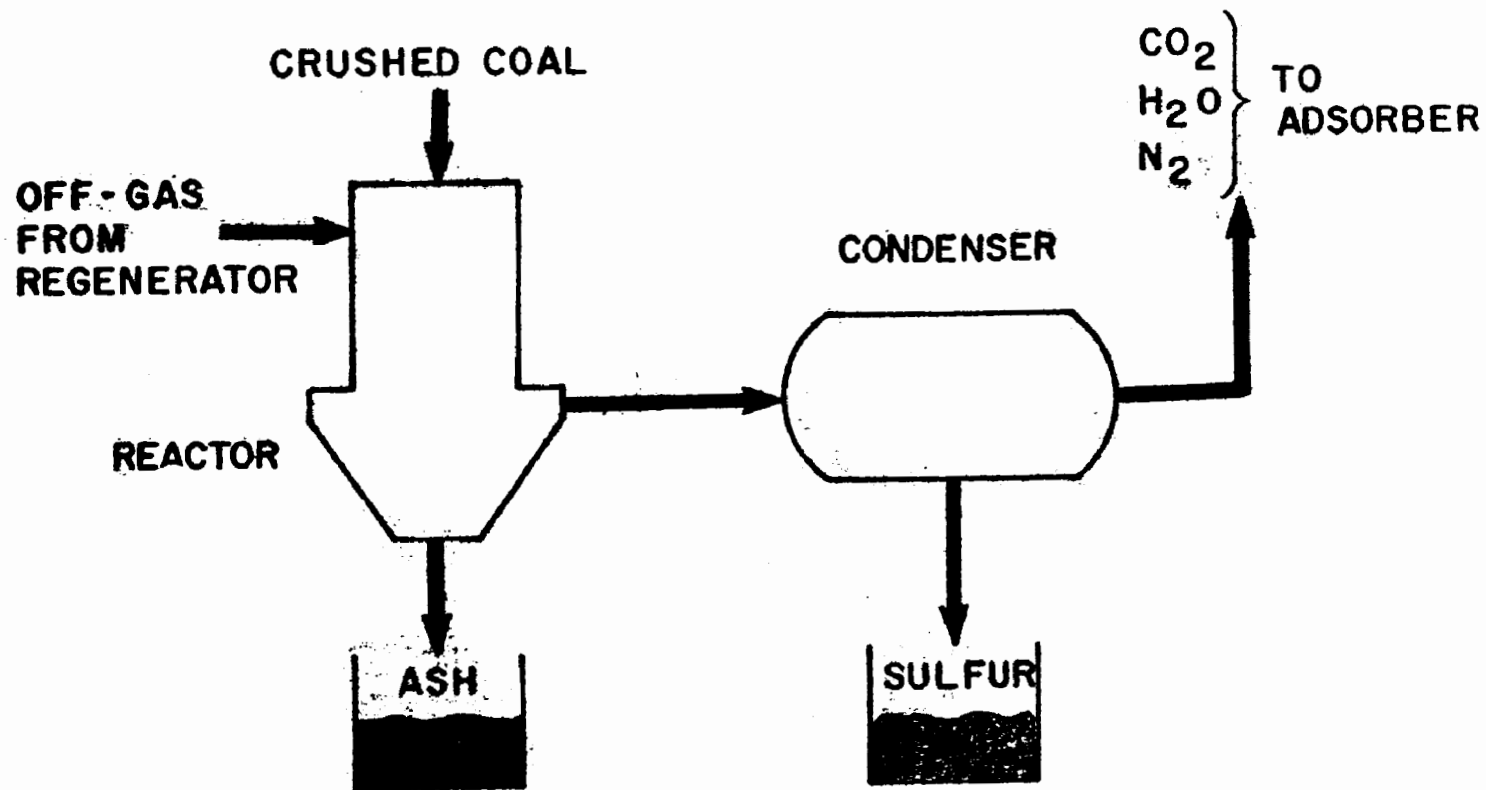
The regenerator vessel utilized in this section is identical to a vessel utilized in the production of the adsorbent char. This regenerator has been in operation for five years in a commercially sized char production facility in Germany. Therefore the problems associated with its design and operation have already been solved.

The fluidized sand bed heater utilized in the regeneration section, while unfamiliar to many in the utility field, has been used for many years by the process industries in applications identical to those contemplated here.

C. Off-Gas Treatment Section

Figure 5 schematically illustrates Foster Wheeler's proprietary

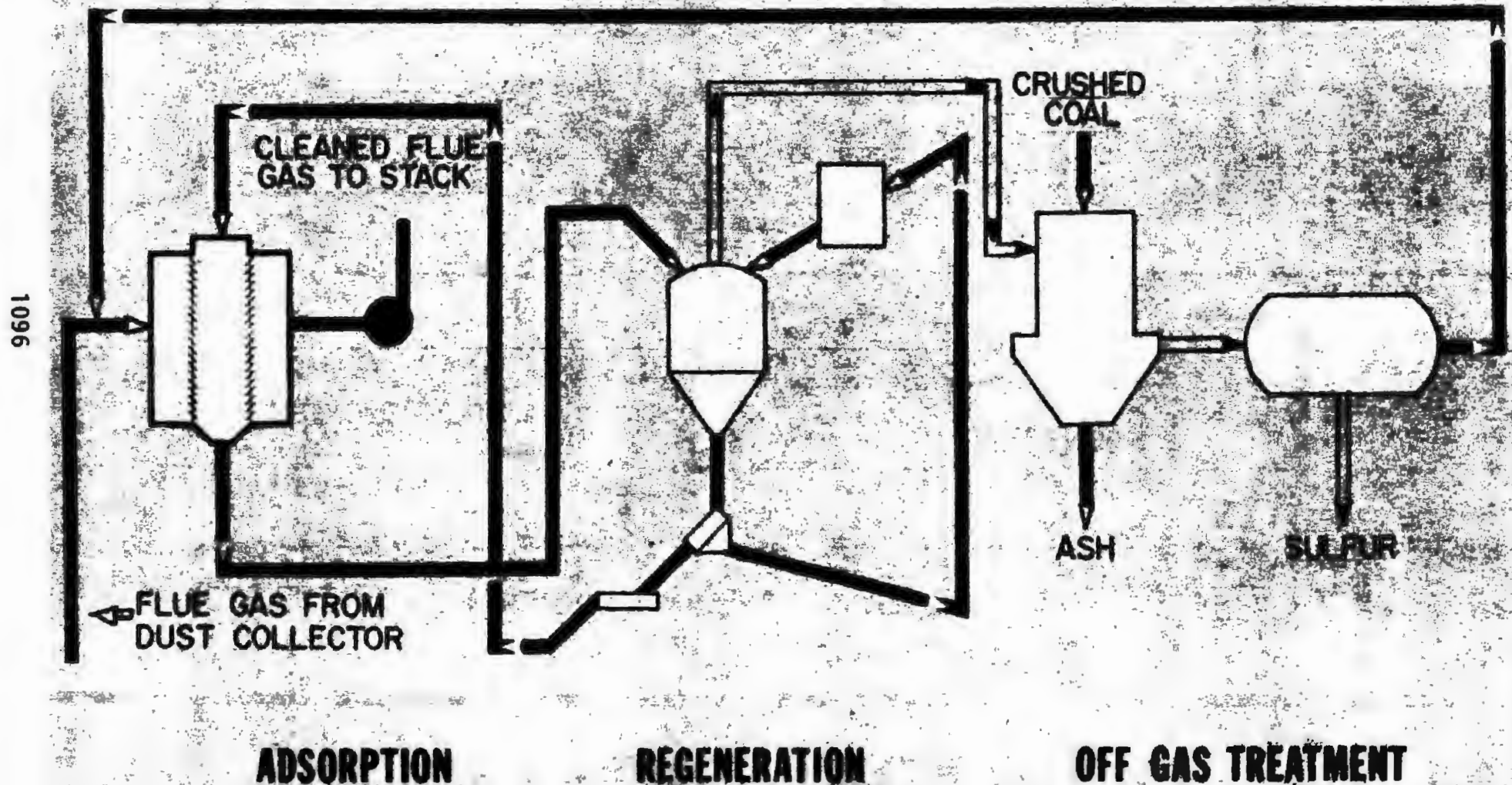
OFF-GAS TREATMENT



FW-131-010

Fig. 5

FW-BF SYSTEM



FW 131-015

Fig. 6

design for the off-gas treatment section. In this section concentrated off-gas, rich in SO_2 , is received from the regenerator and converted to elemental sulfur. The reaction takes place in a reactor vessel which is filled with crushed coal. The SO_2 stream is reduced to gaseous elemental sulfur and the liberated oxygen combines with a portion of the coal to form carbon dioxide. The gases leaving the reactor enter a sulfur condenser where the sulfur is condensed and carried off as molten elemental sulfur. The sulfur is collected and stored in an insulated tank which is equipped with steam heating to make up for heat losses through the insulation system and thereby maintaining the sulfur in a molten form pending shipment via heated tank car or heated truck. These two methods of sulfur transfer are common in the sulfur industry and have been utilized for many years. As an alternative the sulfur could be pumped to cooling pits and allowed to harden for shipment as a dry solid.

The gases leaving the condenser consist of carbon dioxide, water vapor, elemental nitrogen and those remaining sulfur values not converted to elemental sulfur in the Off-Gas Treatment section. These gases are recycled to the front of the adsorber where the sulfur values are adsorbed on the char. The CO_2 , H_2O and N_2 are non-reactive materials at 350°F and therefore pass through the adsorber bed and enter the atmosphere as non-polluting gases.

D. System Recap

The three sections of the FW-BF Dry Adsorption System are shown together in Figure 6. As can be seen the system is composed of a series of closed loops which allows only cleaned gases or by-product materials to leave the system.

The requirements of the system are relatively simple. Cooling water is required to cool the char and also condense the sulfur. The major portion of this water is recoverable and recycleable. In addition to cooling water the system requires char, sand, crushed plant coal and auxiliary power.

V. Major Areas of Application

The FW-BF system is applicable to all fossil fuel fired utility applications. Primary application would be in the area of large coal fired control station utility boilers because of the system's inherent ability to handle all three of the pollutants associated with coal fired boilers. Size is another factor. It is felt at least for the present that applications above 150 MW size range will show superior economic advantages. Of course it is possible to apply the system to smaller units which could be connected in parallel to a single FW-BF unit thereby achieving the economics of larger sized units.

Similar units in refinery or chemical process plants could also be handled provided that similar size considerations are taken into account.

Work is presently underway to determine application to metals smelting operation. Initial studies, particularly those involving wet regeneration, indicate good potential application in this area.

VI. Demonstration Plant Design

At the present time two demonstration plants for the system are in the design stages.

One contract is being executed in Germany which has been financed in part by the West German government. This contract involves the installation of a BF unit as a 35 MW equivalent slipstream off of a large central station boiler. The system will use the thermal regeneration scheme and will be ready for operation in fourth quarter of 1973.

At the same time Foster Wheeler is designing an FW-BF unit to be installed at a major southeastern utility. This unit is designed to meet State and EPA code for SO₂ removal when burning 3% S coal. The adsorber will be capable of handling a 50% slipstream from a nominal 40 MW coal fired boiler. The thermal regeneration and off-gas treatment sections are being sized for the full 40 MW flow. The combination of half sized front end and full sized

back-end will allow a comprehensive testing program utilizing fuels varying in ash and sulfur contents while minimizing capital expenditures during the demonstration program. At the completion of testing it is anticipated that a second 20 MW adsorber will be installed thereby converting the unit to a full sized 40 MW unit.

High efficiency electrostatic precipitators capable of meeting state codes for particulate emissions will be installed upstream of the FW-BF system. During the testing program sections of these precipitators will be selectively de-energized thereby imposing higher dust loadings on the FW-BF unit. Measurement of dust loadings will be taken at the inlet and outlet on the FW-BF unit to determine its actual efficiency as a particulate removal system. It is anticipated that the test work previously conducted by Bergbau-Forschung will be re-confirmed on this large scale test and that the particulate removal efficiency of the FW-BF unit will be firmly established.

VII Capital and Operating Costs

The capital and operating costs of the system vary as a function of the unit size (expressed as the MW rating of the boiler) and the sulfur content in the fuel. Capital costs represented as dollars per kilowatt can be plotted against the megawatt rating of the boiler and the percent sulfur in the fuel. This plotting will result in a family of curves which stabilize and become relatively level after a boiler size of 150 to 200 megawatts is reached. Beyond the 200 megawatt level relatively little decrease in the curves is witnessed. This indicates that the most economic application of the system is in a range of boiler sizes above 150 to 200 megawatts. Below this level the fixed engineering costs cause the curves to rise more sharply so that the cost for units below 50 megawatts are uneconomic. This uneconomic situation can be overcome, however, by the connection of several smaller boilers to a single treatment system which would then have a rating equivalent to the sum of the individual boilers connected to it.

The capital costs in the range above 200 megawatts vary from \$20 to \$40 depending on the percent sulfur in the fuel. \$20 per kilowatt represents a system utilizing .9% sulfur fuel and \$40 per kilowatt represents a system utilizing 4.3% sulfur fuel.

Operating costs vary from 80¢ per ton of fuel fired to \$2.60 per ton as a function of the sulfur content in the fuel and within the limits of those sulfur contents described above.

VIII. Conclusions

In conclusion we can say that the FW-BF Dry Adsorption System for Flue Gas Clean-up will:

1. Meet or exceed EPA and State codes for SO₂ removal
2. Significantly reduce NO_x emissions
3. Significantly reduce particulate emissions

Further we can summarize the advantages of the FW-BF Dry Adsorption System as follows:

1. No stack plume
2. No reheating of stack gases
3. Minimum water consumption
4. Low auxiliary power
5. Minimum waste disposal
6. No handling of wet material
7. Handles coals of variable ash and sulfur contents
8. High SO₂ removal efficiency and the ability to deal with SO₂, NO_x and particulates in one system
9. Low operating costs
10. Low capital costs

We therefore say that the FW-BF Dry Adsorption System is a second generation gas cleanup system of superior capability.

THE ATOMICS INTERNATIONAL MOLTEN CARBONATE
PROCESS FOR SO₂ REMOVAL FROM STACK GASES

by

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THE ATOMICS INTERNATIONAL MOLTEN CARBONATE PROCESS FOR SO₂ REMOVAL FROM STACK GASES

I. INTRODUCTION

The molten carbonate process (MCP) was invented at Atomics International in 1965, and has been under continuous development there since then. In the first phase of the process development program, emphasis was placed on process chemistry and materials corrosion studies and on bench scale engineering tests. This phase was completed in 1971; the results were encouraging, and the process was developed to the point where a pilot plant test under actual power plant operating conditions was both warranted and required for further progress. The initial process development work was funded by Rockwell International Corporation; subsequent first-phase work was done under contract to the U. S. Environmental Protection Agency.

Con Edison has undertaken to help finance the pilot plant program, in conjunction with Northeast Utility Services Company (Hartford, Connecticut) and Rockwell International Corporation, United Engineers and Constructors (Philadelphia, Pennsylvania) are construction managers for the pilot plant.

The pilot plant phase of the process development program is now underway. A pilot plant has been designed and is now being built at the Consolidated Edison Company's Arthur Kill Power Generating Station. This pilot plant will treat a side stream of 20,000 scfm of flue gas from an oil-fired steam generator (equivalent to about 10 mw of generating capacity). This paper describes the molten carbonate process in general and the pilot plant design in particular, and gives a status report on the pilot plant program.

II. PROCESS DESCRIPTION

A. BASIC PROCESS FEATURES

In the molten carbonate process, a molten eutectic mixture of lithium, sodium, and potassium carbonates is used to scrub the power plant gas stream. The sulfur oxides in the gas stream react with the molten carbonates to form sulfites and sulfates, which remain dissolved in an unreacted excess of carbonate melt. The molten carbonate (sulfite-sulfate) mixture is then regenerated chemically, converting the sulfite and sulfate back to carbonate and recovering the sulfur as hydrogen sulfide. The regenerated carbonate is recirculated to the scrubber to repeat the process cycle, and the hydrogen sulfide is converted to elemental sulfur in a Claus Plant.

The regeneration of the carbonate is done in two steps: first the sulfite and sulfate are reduced to sulfide, and then the sulfide is converted to carbonate plus hydrogen sulfide. The reduction is accomplished by reaction with a form of carbon, such as petroleum coke. The conversion of the sulfide to carbonate is accomplished by reacting the melt with steam and carbon dioxide.

The basic process fluid is the molten-eutectic mixture of 32 wt. % Li_2CO_3 , 33 wt. % Na_2CO_3 , and 35 wt. % K_2CO_3 . This mixture melts at 747°F (397°C) for form a clear, mobile, non-volatile liquid. At 800°F , the melt has the physical properties listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF MELT AT 800°F

Viscosity	12 cp
Specific Gravity	2.0
Specific Heat	0.40
Thermal Conductivity	$\simeq 0.3$ Btu/hr., ft., $^\circ\text{F}$ (estimated)

The melt can be pumped and sprayed just like any other liquid.

In the process, the melt composition (and freezing point) changes as sulfur compounds are formed and reacted. The process will be controlled so that melts with freezing points above 850°F are avoided. This limitation corresponds to melts containing about 30 wt. % sulfur compounds.

The freezing point limitation makes it necessary to keep the temperature above 850°F in all process equipment in which melt is handled, including the scrubber. The flue gas being treated must also be above 850°F when it enters the scrubber. The ramifications of this requirement are discussed further in the following sections of the paper.

B. PROCESS FLOW DIAGRAM

The basic process flow diagram is shown in Figure 1. Each step in the flow diagram is numbered, and discussed in the corresponding section below.

1. Gas Preparation

The gas to be treated is removed from the boiler at a temperature above 850°F, or else it is reheated to above 850°F. In a new plant designed for this process and in some retrofit situations, the gas will be removed from the boiler at the superheater or reheater outlet or economizer inlet at a nominal temperature of 850°F. If the boiler is burning coal, the flue gas will be passed through an 850°F, high-efficiency electrostatic precipitator where nearly all of the fly ash will be removed. Such electrostatic precipitators with efficiencies of greater than 99% are presently available. If hot gas cannot be removed from the boiler, or if the heat needed to reheat the flue gas can be used or recovered, the flue gas can be removed from the power plant air heater (or low temperature precipitator if coal is burned) and reheated to a nominal 850°F. The reheat can be done by direct firing with gas or oil, or by indirect heat exchange. In any case, the gas preparation step provides the flue gas stream at 850°F, with as much fly ash removed as possible.

2. Scrubbing

The flue gas stream then enters the scrubber, where it is contacted intimately with the molten salt. The sulfur oxides react chemically with the molten

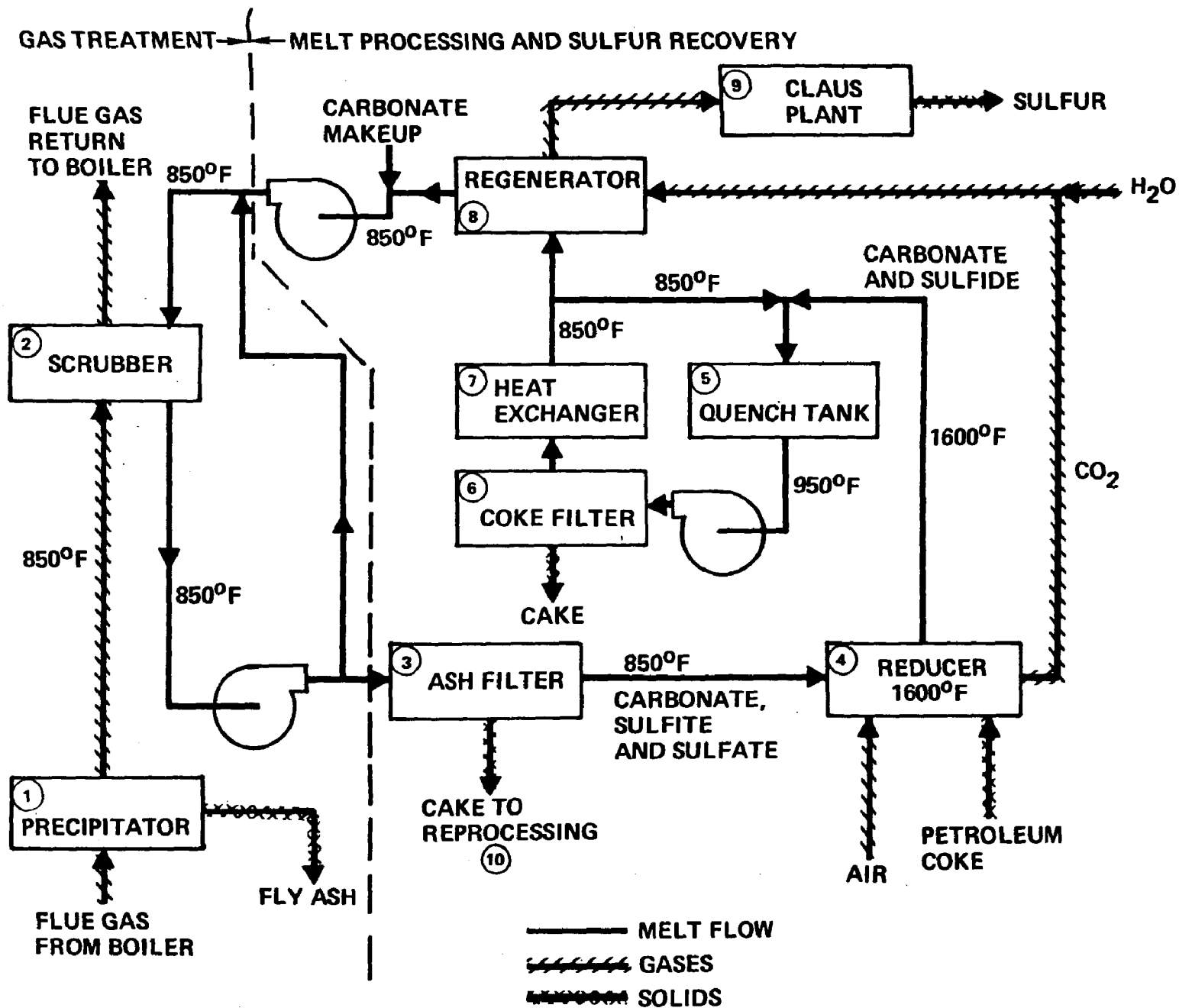
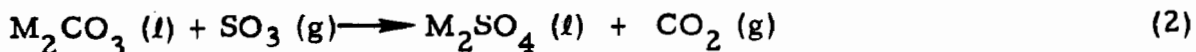
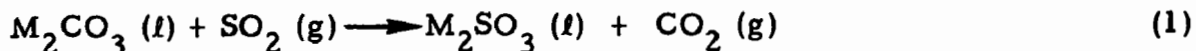


Fig. 1. Process Flow Diagram

carbonate to produce sulfur compounds and evolve carbon dioxide:



(where M = mixture of Li, Na, and K cations.)

This gas-liquid scrubbing removes 90 to 95% of the sulfur oxides and most of the remaining particulate matter from the gas stream. The cleaned gases are then returned to the boiler (or elsewhere) for further heat recovery, and eventually pass out the stack.

The molten salt stream entering the scrubber consists of recycle melt from the scrubber discharge (already containing sulfite and sulfate) plus fresh carbonate from the regeneration system and from make-up. The reactions in the scrubber increase the concentration of sulfite and sulfate, and the mixture then flows from the bottom of the scrubber to the scrubber pump inlet. The pump discharge melt stream is divided; a major portion of the melt is recycled to the scrubber inlet, and the rest is diverted to the melt processing and sulfur recovery side of the process. This side stream is balanced to remove as much sulfur from the scrubber as the incoming gas brings in; roughly 1 gpm for each 10,000 scfm of flue gas treated.

The reactions between sulfur oxides and carbonate to form sulfite and sulfate (1 and 2) are rapid, and strongly favored thermodynamically. This makes it possible to remove a high percentage of the sulfur oxides with a minimum number of transfer units. Spray scrubbers with multiple banks of spray nozzles will be used, since they are simple and impart a minimum pressure drop to the gas stream. Each scrubber will have a high-efficiency mist eliminator to prevent carryover of melt droplets.

3. Ash Filtration

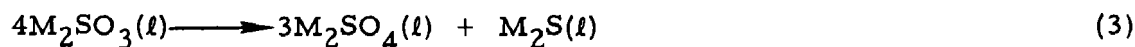
The ash and other particulate matter that enters the scrubber is picked up by the process melt. Since the melt is all recycled, this particulate matter must be removed so that it does not build up continuously. If the power plant is

burning coal, the ash is removed by filtering the side stream of melt being processed. If the power plant is burning oil, the particulate matter in the flue gas is mainly carbonaceous. In this case, it should be possible to eliminate the ash filter, since the carbon will be consumed in the reducer and the oil ash can be removed in the coke filter (see Figure 1). The need to filter oil particulates out of the melt upstream of the reducer will be determined in the pilot plant.

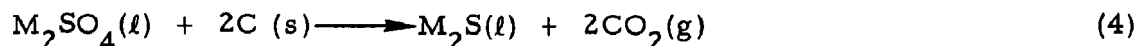
The ash filtration step is carried out in centrifugal basket-type filters, which produce a continuous "dry" cake discharge. A filter aid, such as petroleum coke particles, may be used to enhance the filtration. The filter cake is collected and treated to recover its lithium content, using a recovery process described below (Item 10).

4. Reduction

The melt next enters the reducer, where the sulfur compounds are reduced to sulfide with carbon. The sulfite disproportionates to sulfate and sulfide as the melt enters the reducer (or even before) according to the reaction:



The reduction reaction is thus actually that for sulfate only:



The melt temperature is raised from 850°F to about 1600°F to enhance the rate of reaction 4. The heat required for this, plus the endothermic heat of reaction, is obtained by re-oxidizing some of the product sulfite to sulfate with air:



The net result of the heat generation reaction is the sum of reactions 4 and 5:



The heat is thus actually generated by the indirect combustion of excess carbon.

In actual practice the reduction step will be carried out in a two-zone vessel, using petroleum coke as the reducing agent. The coke will be consumed in the first (reduction) zone, and air will be injected into the second (oxidation) zone to generate heat. Internal circulation will carry heat and reactants between the two zones. This is shown schematically in Figure 2. The vessel will be lined with corrosion resistant high-density alumina refractory, since the melt is very corrosive at these elevated temperatures.

The reducer produces a molten mixture of carbonate and sulfide, plus carbon dioxide. The carbon dioxide is sent to the regenerator (Step 8) where it is used as a reactant.

5. Quenching

The reducer produces a molten mixture of carbonate and sulfide, at about 1600°F. This mixture must be cooled back to about 900°F before it undergoes further reaction. The major part of this cooling is done by mixing the hot melt stream with a pool of cooler melt (about 900°F) in the quench tank. This procedure makes it possible to cool the melt to below 1000°F without using a direct-contact heat exchanger.

The quench tank is a large tank containing a melt pump; it is also used as a drain tank for melt storage during temporary shut-downs.

6. Coke Filtration

Cooled melt from the quench tank is filtered to remove coke ash and coke particles carried over from the reducer. Equipment similar to that described for ash filtration (Item 3) is used.

The filter cake from this step is combined with that from the ash filter (if one is used) and treated to recover its lithium content.

7. Cooling

The filtered melt is then cooled further, to about 850°F, in a heat exchanger. The cooled melt discharge stream from the heat exchanger is divided; about 90% is recycled to the quench tank to cool melt from the reducer, and the remainder goes to the regenerator.

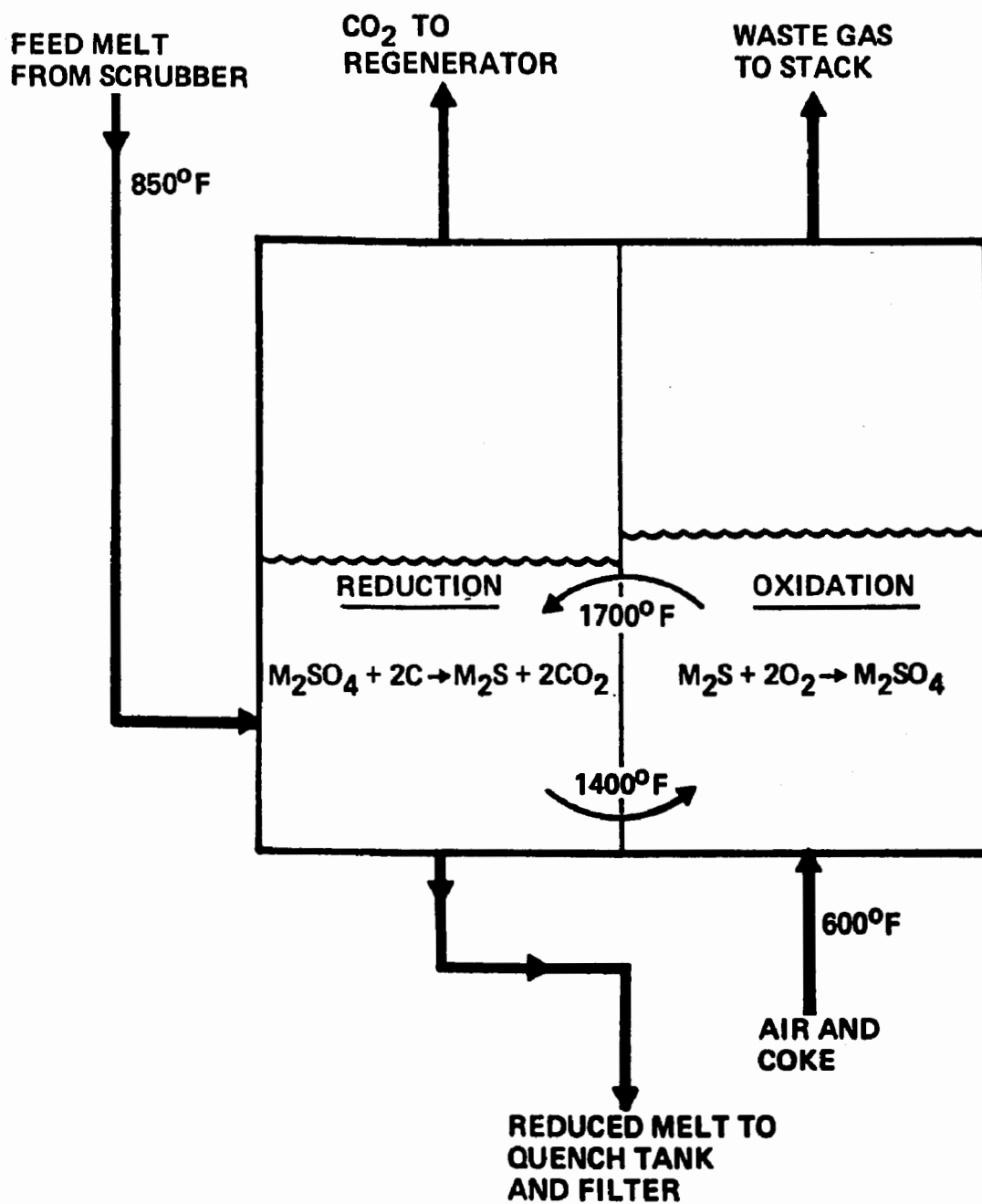
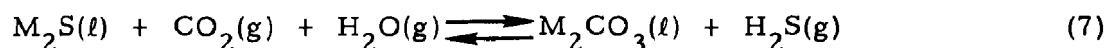


Fig. 2. Reducer Schematic

The heat exchanger is a shell and tube design, with melt on the tube side and air or water on the shell side. Provision must be made to prevent the melt from freezing, even under upset conditions.

8. Regeneration

In the regenerator, the sulfide-containing melt is reacted with a gaseous mixture of carbon dioxide (from the reducer) and steam. The reaction is



The reaction is exothermic, and reaches equilibrium rapidly, with the formation of hydrogen sulfide being favored by lower temperatures. To attain a high degree of regeneration, the reaction is carried out in a multi-stage countercurrent gas-liquid reactor, such as a tray column.

9. Sulfur Recovery

The hydrogen sulfide from the regenerator is sent to a Claus unit, where it is converted to elemental sulfur. A conventional Claus unit is suitable; however, the feed gas stream has a high water content, so it is sent to a condenser-cooler before undergoing the Claus reactions. The tail gas from the Claus plant is incinerated and ducted to the scrubber inlet and scrubbed along with the flue gas, so there is no Claus plant air pollution.

10. Lithium Recovery

The melt used in the process is relatively inexpensive except for lithium carbonate, which it is desirable to recover from the process filter cake. An aqueous process has been developed for this purpose. The filter cake is slurried with water and filtered, to extract the very soluble sodium and potassium carbonates; lithium carbonate remains with the ash since it is relative insoluble (1 wt. %) under these conditions. The ash-lithium carbonate cake is then re-slurried in water and the lithium is solubilized by treating it with carbon dioxide to convert it to the bicarbonate. The ash is removed by filtration and the soluble lithium bicarbonate in the filtrate is precipitated as the insoluble carbonate. The lithium carbonate is separated by filtration and returned to the process stream; the saturated lithium carbonate filtrate is recycled to conserve lithium. Laboratory tests have demonstrated that over 90% of the lithium can be recovered from fly ash filter cake by this technique.

C. PROCESS MATERIALS AND EQUIPMENT

1. Materials of Construction

Extensive testing has been done to determine the rate of corrosion of steels and other materials in the different process melts. The results of many tests, including one-year dynamic tests in rotating capsules under various conditions, have shown that the 300-series austenitic stainless steels are suitable up to temperatures of about 1000°F. Type 347 stainless steel is most corrosion-resistant, followed in order by 321, 304, and 316. Type 304 was chosen for the pilot plant, because of its availability and its well-known welding and fabricating technology.

The corrosion resistance of the 300-series stainless steels in the carbonate melts is due to a protective LiCrO_2 film which forms a compact, tenacious, and self-healing layer. This film forms in about 500 hours, and decreases the corrosion rate to a few mils per year below 1000°F. However, at temperatures of 1500 to 1600°F (corresponding to the reducer internals) the protective layer breaks down and steels are rapidly and severely attacked. At these temperatures, the only corrosion-resistant material available is dense, high-purity alumina.

Corrosion testing is continuing in a forced-circulation test loop which is in operation at Atomics International.

2. Pumps

Three pumps are required to circulate the process melt in the flow scheme of Figure 1. These pumps are vertical cantilever-shaft centrifugal pumps, designed to operate with no seals or bearings in contact with the melt. The design features of this type of pump are shown in Figure 3. One of these pumps has been operating satisfactorily for over 3200 hours in the test loop mentioned above.

3. Valves

Conventional stainless steel valves can be used, employing a corrosion-resistant stem packing material such as Union Carbide's "Grafoil". Both hand and pneumatically actuated valves have been tested successfully in the test loop.

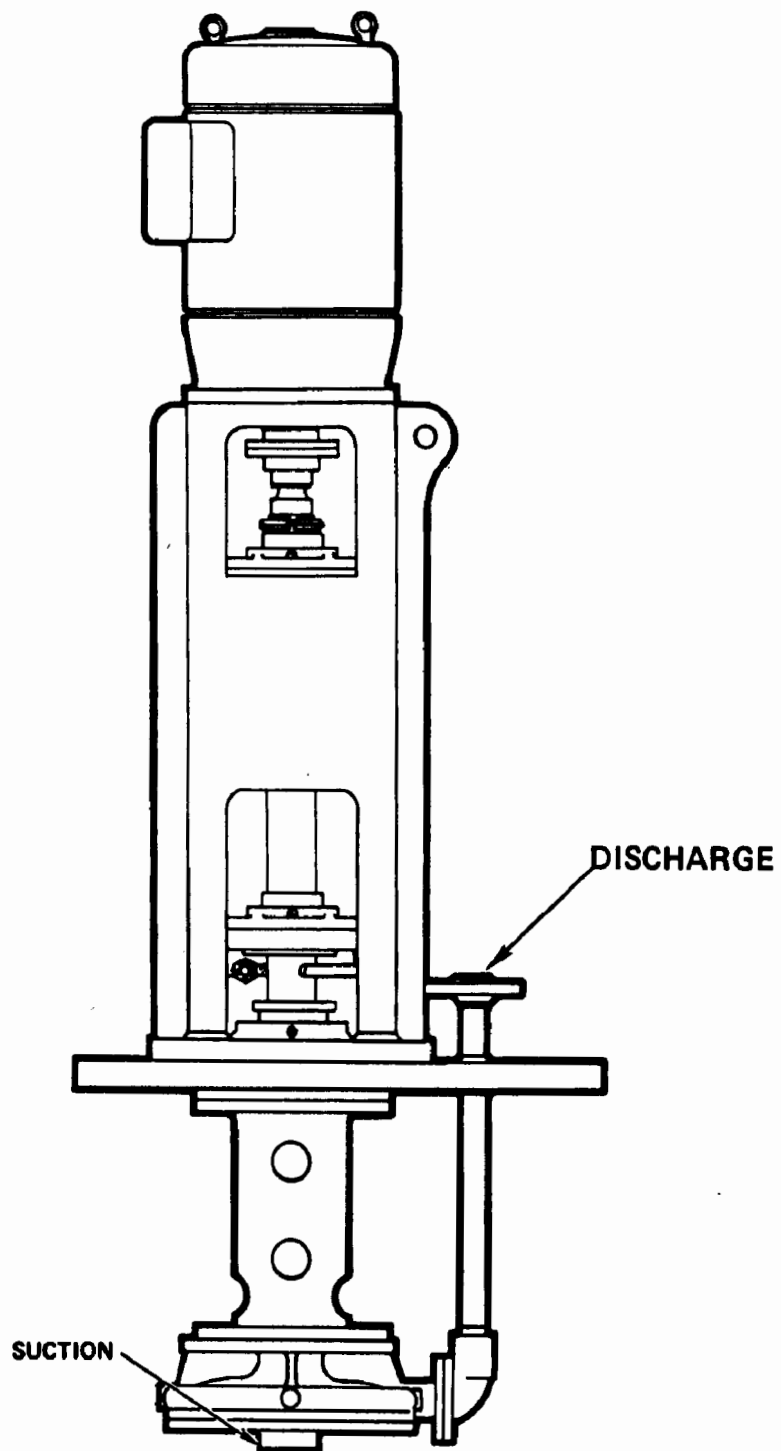


Fig. 3. Molten Salt Pump

4. Instrumentation

Process instrumentation is needed for temperature, pressure, flow and liquid level measurement and control. Temperature measurement is done with stainless steel or inconel-sheathed thermocouples, protected with alumina thermowells in the reducer. Pressure and flow measurement is done with strain gage or variable reluctance transformer sensors, designed for use at high temperatures. Liquid level measurement is done with conventional float displacement instruments designed for high temperature operation. These components are currently being tested in the test loop.

5. Trace Heating

The process equipment and piping must be heated up to about 800°F for startup, and then kept at this temperature during operation. This heating is done electrically, with resistance heaters fastened to the vessel walls and pipe walls, under the thermal insulation. SCR-type heater controllers are used to maintain the proper temperatures.

III. PILOT PLANT PROGRAM

The process described above will be tested extensively in a pilot plant being built at the Arthur Kill Power Station of the Consolidated Edison Company, on Staten Island, New York. The pilot plant program has the following goals:

- 1) Demonstrate the integrated behavior of the process in a real environment;
- 2) Provide a test facility to check out and modify equipment or internals of equipment in order to evaluate design options or improve operation;
- 3) Obtain equipment design criteria, performance, and reaction yield data for scale-up;
- 4) Establish maintenance, reliability, and availability data; and
- 5) Provide data for an economic assessment of the process.

The pilot plant will process a side stream of stack gases from a 335 Mw boiler at the Arthur Kill Station. This station will be burning 0.3% S oil during all of the test program. It is planned to vary the SO₂ concentration at the inlet to the scrubber in order to map process performance over a wide range of conditions.

A. PILOT PLANT DESIGN

The overall size of the pilot plant was fixed as small as possible, commensurate with the primary consideration that each component be large enough to yield meaningful data for scale-up to full-scale systems. The limiting component is the regenerator column, where an 18-in. ID tower was determined to be the minimum size. To operate a column of this diameter at its optimum capacity will require a throughput of 100 lb/hr of sulfur

as sulfide in the melt. This requirement then set the throughput for the reducer, and its size. The sulfur throughput required for optimum operation will be obtained from the flue gas and partially (up to 85%) from recycling sulfur dioxide from the Claus plant incinerator.

1. Flow Diagram

The flow diagram for the pilot plant is shown as Figure 4. This flow diagram differs from that of Figure 1 only in the following features:

- 1) The flue gas temperature is raised to 850°F by reheat;
- 2) Sulfur dioxide will be intentionally recycled to the scrubber from the Claus plant; and
- 3) No provision is made for on-site lithium recovery from the filter cake.

2. Flue Gas Supply

The pilot plant treats 16,700 scfm of flue gas from the oil-fired boiler, after the gases have left the boiler and passed through the electrostatic precipitator. The gases are nominally at 250°F; they are reheated to about 850°F with an inline burner firing the same No. 6 fuel oil as the boiler. The total quantity of gas from the boiler is increased by 3400 scfm from the burner, to a total flow of 20,100 scfm (equivalent to about 10 Mw). A blower upstream of the burner provides the pressure head to force the gas through the ducts, burner, and scrubber. A damper is used to adjust the flow rate to the test requirements.

The flue gases produced by the boiler will contain ~200 ppm sulfur oxides. This concentration is very low compared to the 2000 ppm typical of gases produced by boilers burning fuel containing 3% sulfur. In order to provide the flexibility needed to operate over a range of sulfur oxide concentrations, the pilot plant is designed to recycle sulfur dioxide from its Claus plant incinerator.

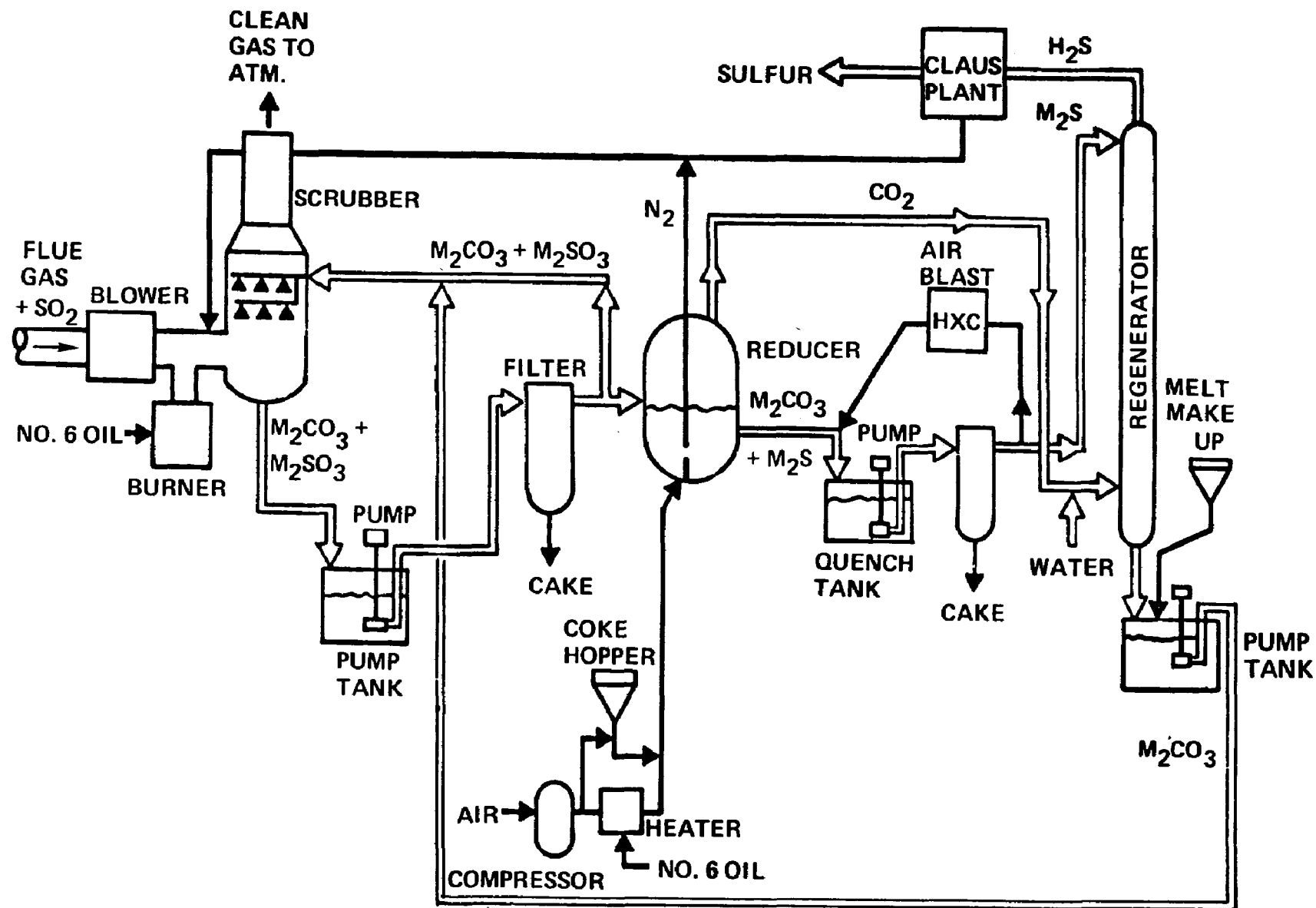


Fig. 4. Pilot Plant Flow Diagram

The flue gases produced by burning the fuel oil contain about 0.05 grains/scf of particulates after passing through the electrostatic precipitator. In high temperature electrostatic precipitators, such as would be used in a full-scale molten carbonate process installation, the particulate removal efficiency will be much higher. The quantity of ash to be handled in the pilot plant, therefore, is conservatively high. It is possible that the particulates can be burned in the reducer, thereby allowing future simplification of the process by elimination of one filtration step.

3. Component Design

a. Gas Preparation System

The side stream of flue gas is removed from the power plant ducting through a 4-ft duct, and passed through a blower fan and direct-fired reheater. A recycle line also brings SO₂-rich gas from the Claus plant to the blower inlet. The blower fan is of conventional design, with a 200 HP, 1800 RPM motor. The reheater is a refractory-lined unit which burns the same No. 6 fuel oil as the power plant. The burner discharges its 850°F gas stream directly into the scrubber.

b. Scrubber System

The pilot plant scrubber is shown in Figure 5. It is a simple spray chamber, 10 ft. in diameter and 25 ft. tall. The gas enters tangentially near the bottom, and is discharged from the top after passing through a 1 ft. thick wire mesh mist eliminator. The gas velocity is nominally 11 ft./sec.

The melt is sprayed in through 3 tiers of spray nozzles, and drains out through the bottom to the scrubber pump tank. The scrubber pump has a capacity of 33 gpm, allowing a recycle of up to 31 gpm of melt to the scrubber inlet. Flow control is provided by pump drive speed control.

The scrubber design is flexible, allowing variation in the melt and gas flow rates, the number, type and configuration of the spray nozzles, and the type and thickness of the mist eliminator.

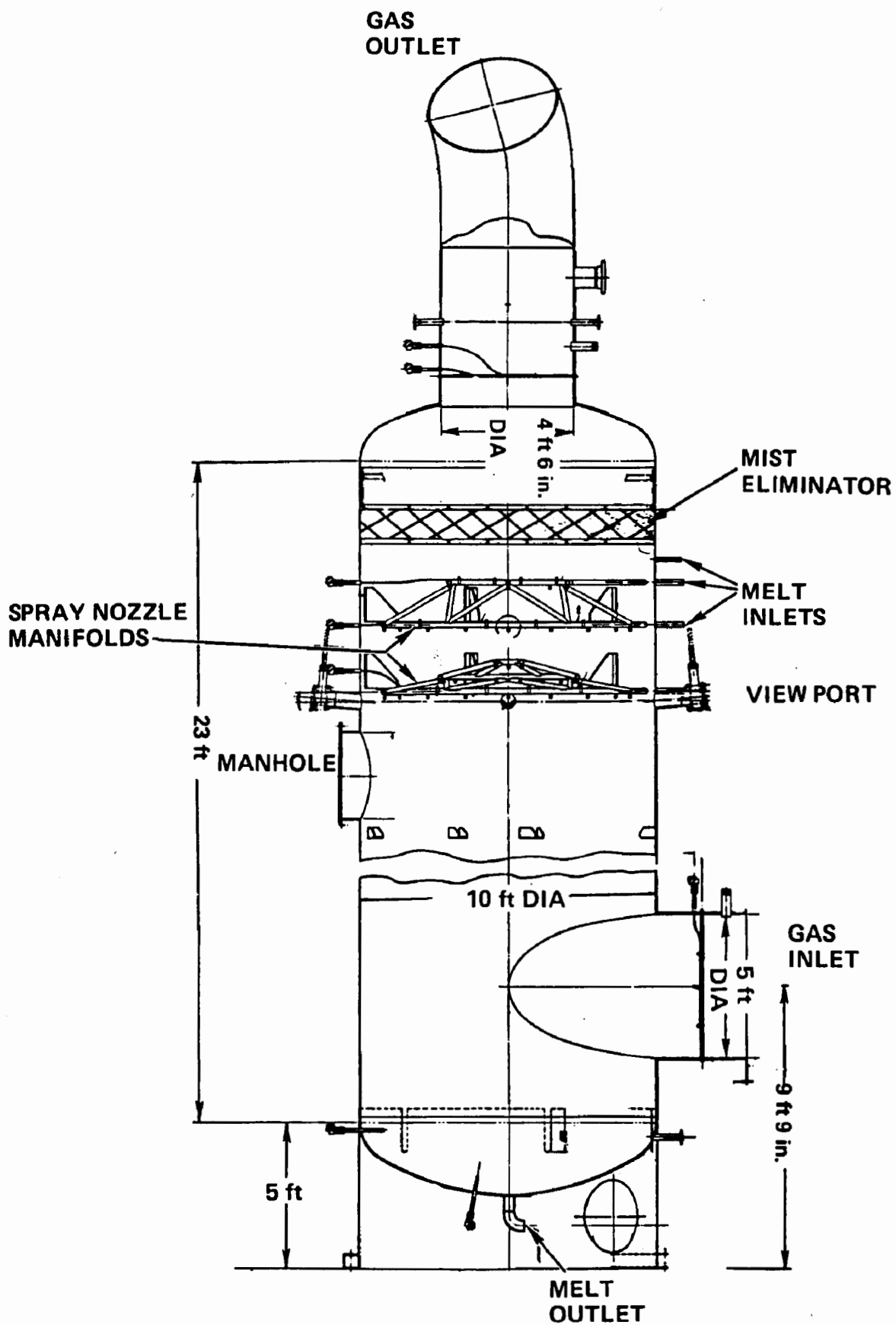


Fig. 5. Pilot Plant Scrubber

c. Ash Filters

Continuous filters with dry cake discharge are desired for the process; however, development work will be required to make them available. For the pilot plant, batch-type cartridge filters using wire-wound filter elements were selected. Two filters are provided; one is in operation while the second is being cleaned. A filter is shown in Figure 6. Each filter has an active area of 160 sq. ft., provided by 25, 2-3/4 in. diameter by 9-ft. long filter tubes in each 2 ft. diameter shell.

d. Reduction Systems

The pilot plant reducer is shown in Figure 7. It is a steel vessel 9 ft. in diameter and 16 ft. tall, lined with blocks of high density alumina. An inner concentric wall of alumina blocks divides the vessel into an inner cylindrical oxidation region and an outer annular reduction region. Holes in the inner wall allow melt circulation between the two regions. The melt is introduced into the reduction region from the top, and leaves the same region from the bottom through an underflow-overflow weir. Air and petroleum coke are introduced into the bottom of the oxidation region, and the spent gas from this region is collected at the top and carried back to the scrubber inlet, where it is scrubbed before entering the atmosphere. The carbon-dioxide-rich gas from the reduction region is collected at the top in a separate manifold, cooled to 850°F by liquid water injection, and then ducted to the regenerator.

An air compressor provides the reducer air supply. The air is preheated to 600°F in a gas-fired indirect heater, and then picks up coke particles introduced through a star feeder.

e. Quench Tank

The pilot plant quench tank is a horizontal cylindrical tank, 6 ft. 6 in. ID by 15 ft. long. It is of conventional stainless steel construction, and has sufficient excess capacity to serve as a reducer drain tank during shutdown. It is mounted in a pit directly below the reducer.

f. Coke Filters

The coke filters are identical in design and operation to the ash filters.

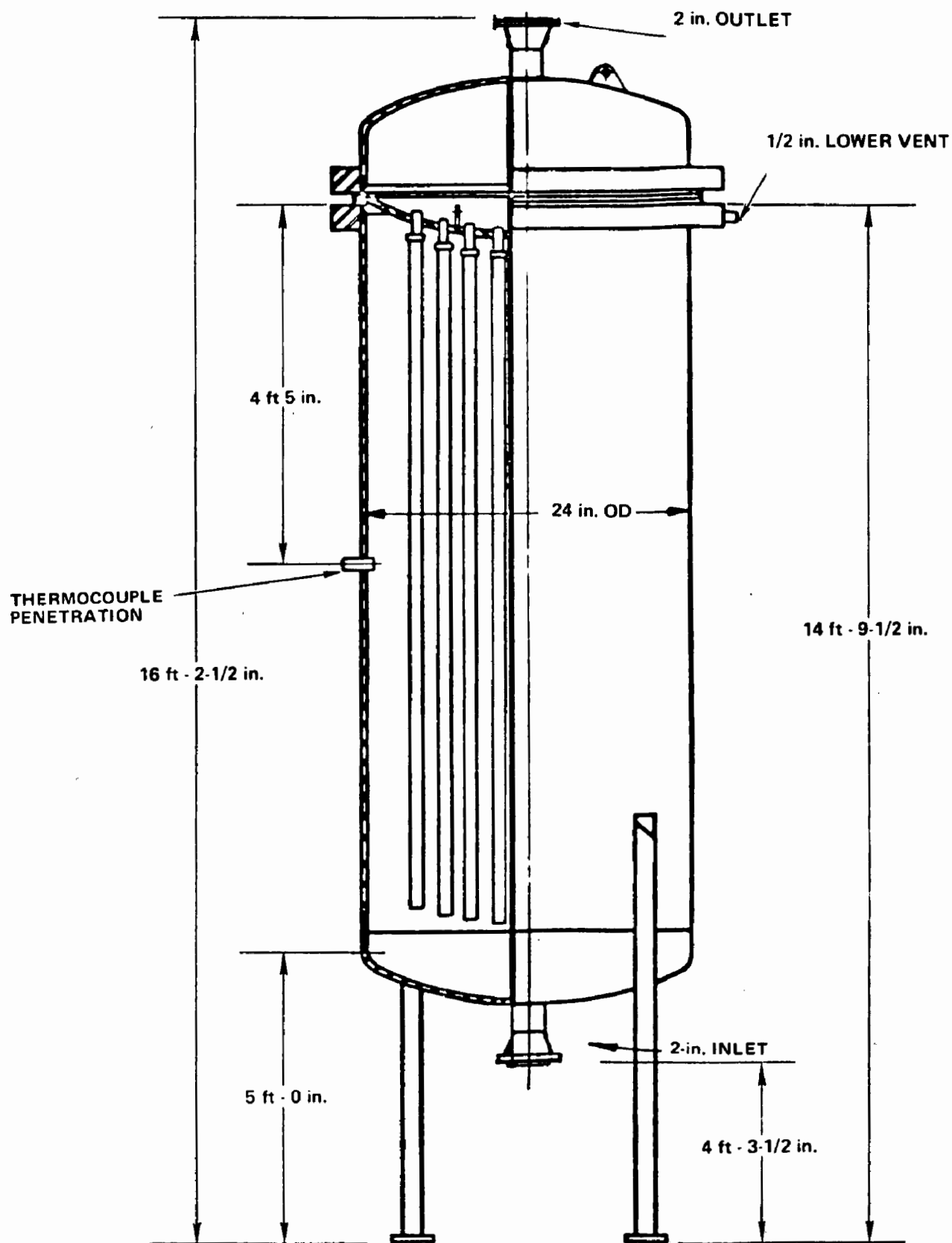


Fig. 6. Pilot Plant Filter

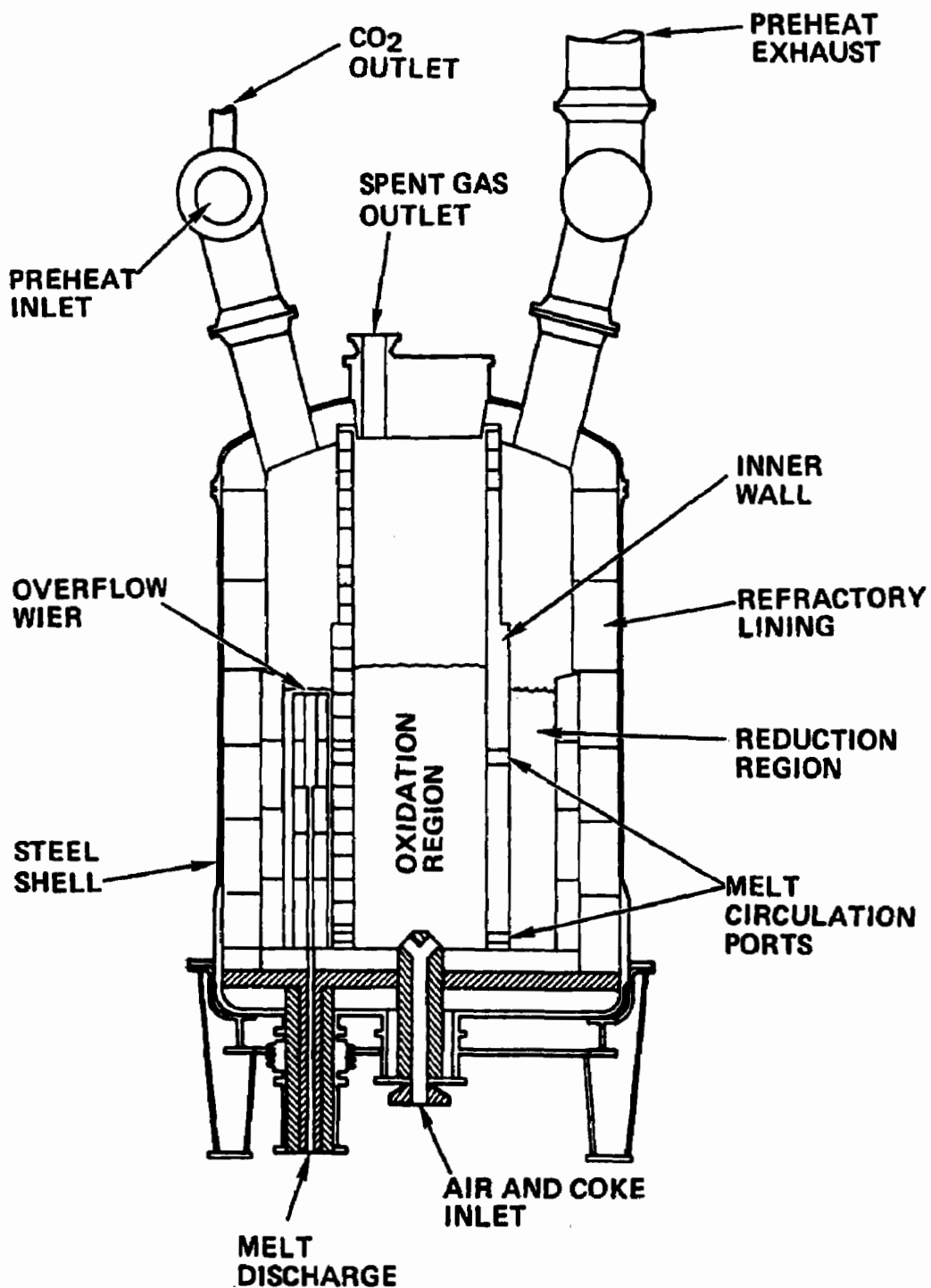


Fig. 7. Pilot Plant Reducer

g. Melt Cooler. The melt cooler is shown in Fig. 8. It is a 750,000 Btu/hr, air-blast type heat exchanger. with recirculation of the air stream to provide temperature control.

h. Regenerator. The regenerator column is shown in Fig. 9. It is a sieve-tray column, 18 in. in diameter by 36 ft. tall. It contains 15 trays spaced 2 ft. apart. Provision has been made to vary the number and spacing of the trays during the test program.

i. Claus Plant. Sulfur recovery from sour gases by the Claus process represents commercial technology and does not require testing or demonstration in the pilot plant. The Claus unit, however, had to be specially engineered as its capacity of 100 lb. of sulfur per hour is smaller than any built commercially. It provides a convenient way of recovering the sulfur removed by the pilot plant rather than burning the H_2S in the regenerator off-gas to SO_2 and returning it to the power plant stack. The Claus plant is shown in Fig. 10.

4. Component Arrangement

The pilot plant component arrangement plan is shown in Fig. 11. The pilot plant is built on a 68-ft. by 100-ft. concrete slab, and has a high-bay filter room and reducer enclosure and a control room and laboratory. The quench tank and make-up tank are mounted in a pit, and serve as drain tanks during shut-down. There is also a large, 40-ft. tall coke hopper to hold the reducer coke supply.

B. PILOT PLANT STATUS REPORT

As of November 1, 1972, the pilot plant program was well underway. The design and engineering work was completed, and all major components had been fabricated, delivered, and set in place at the site. The steelwork

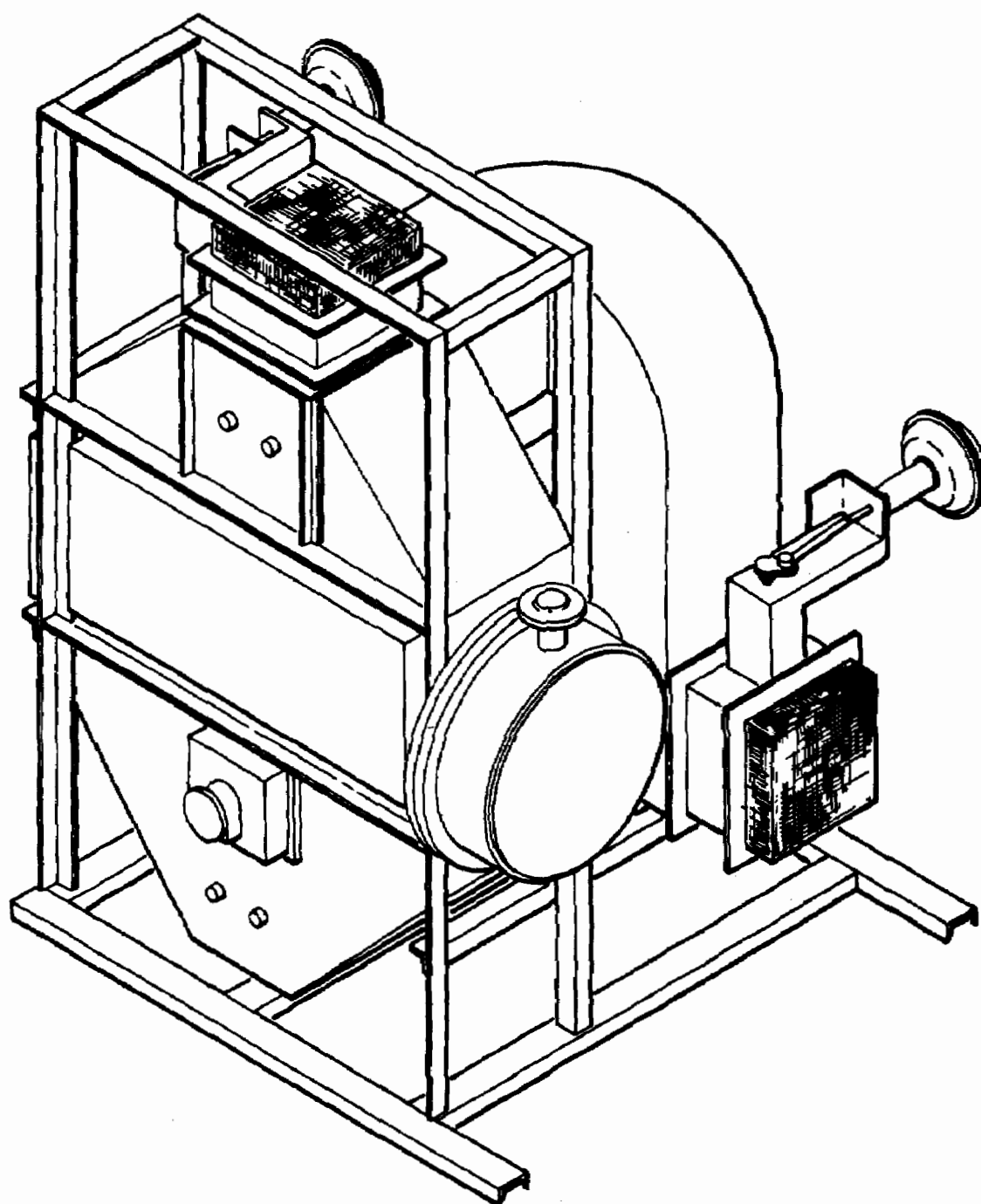


Fig. 8. Melt Cooler

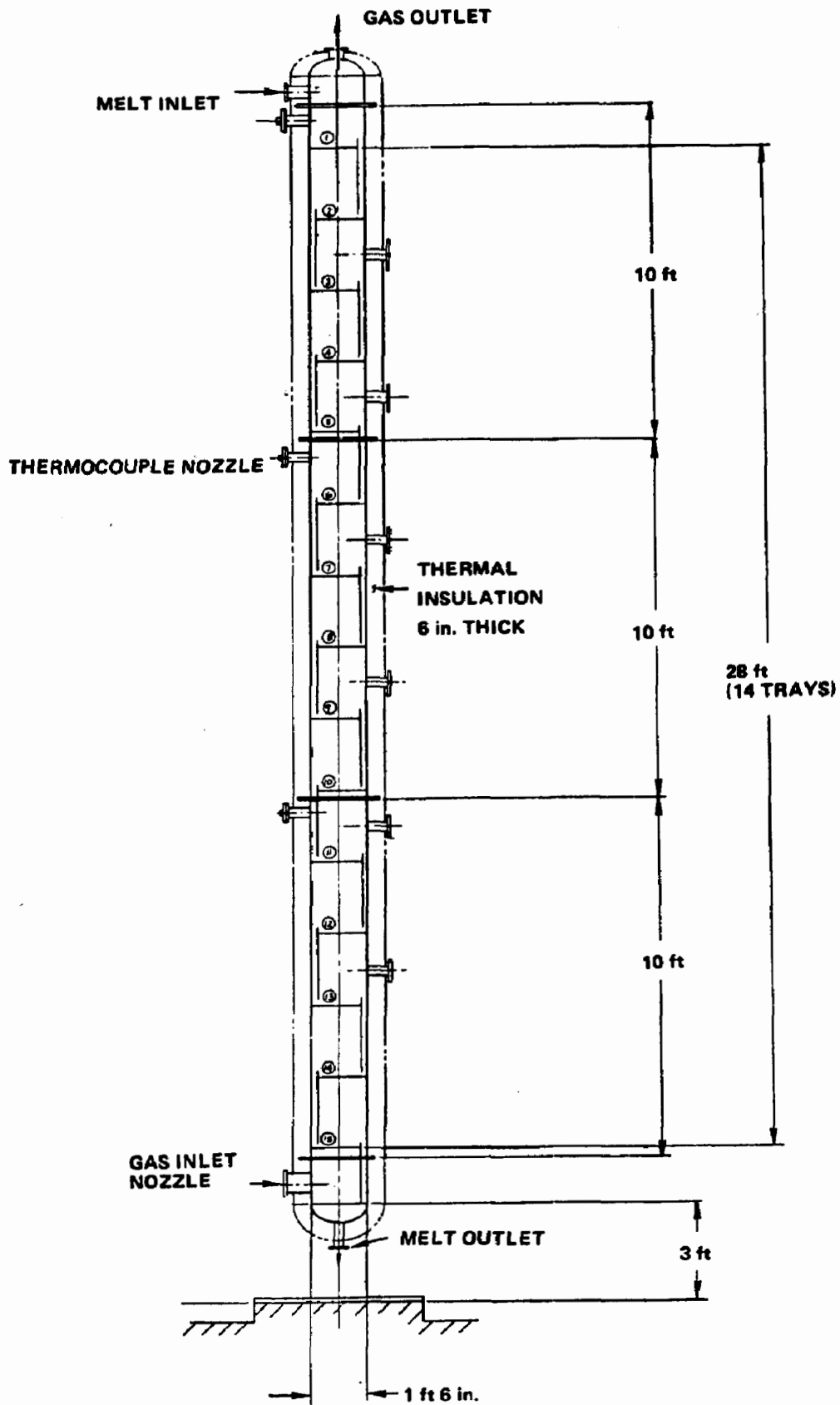


Fig. 9. Regenerator

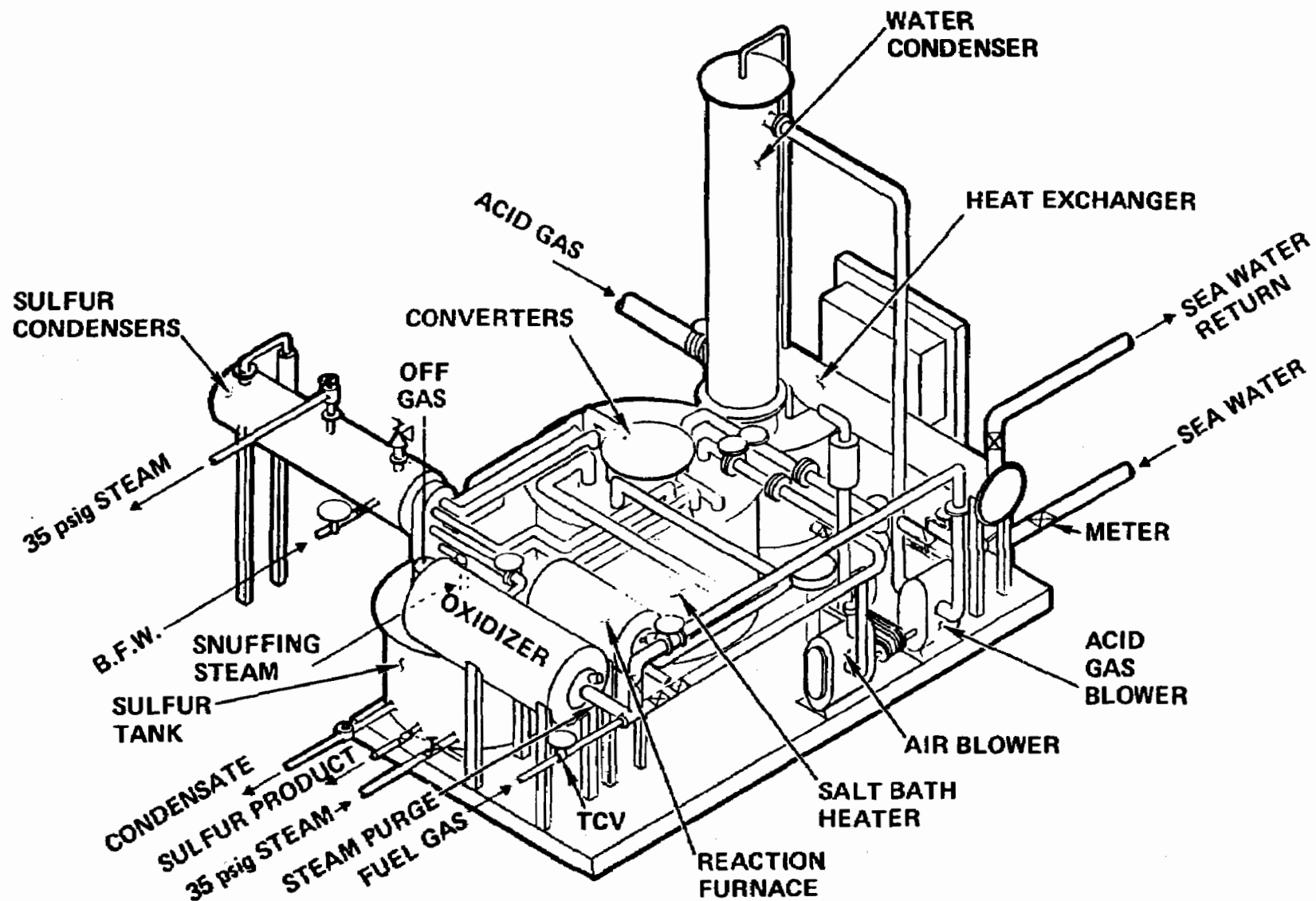


Fig. 10. Claus Plant

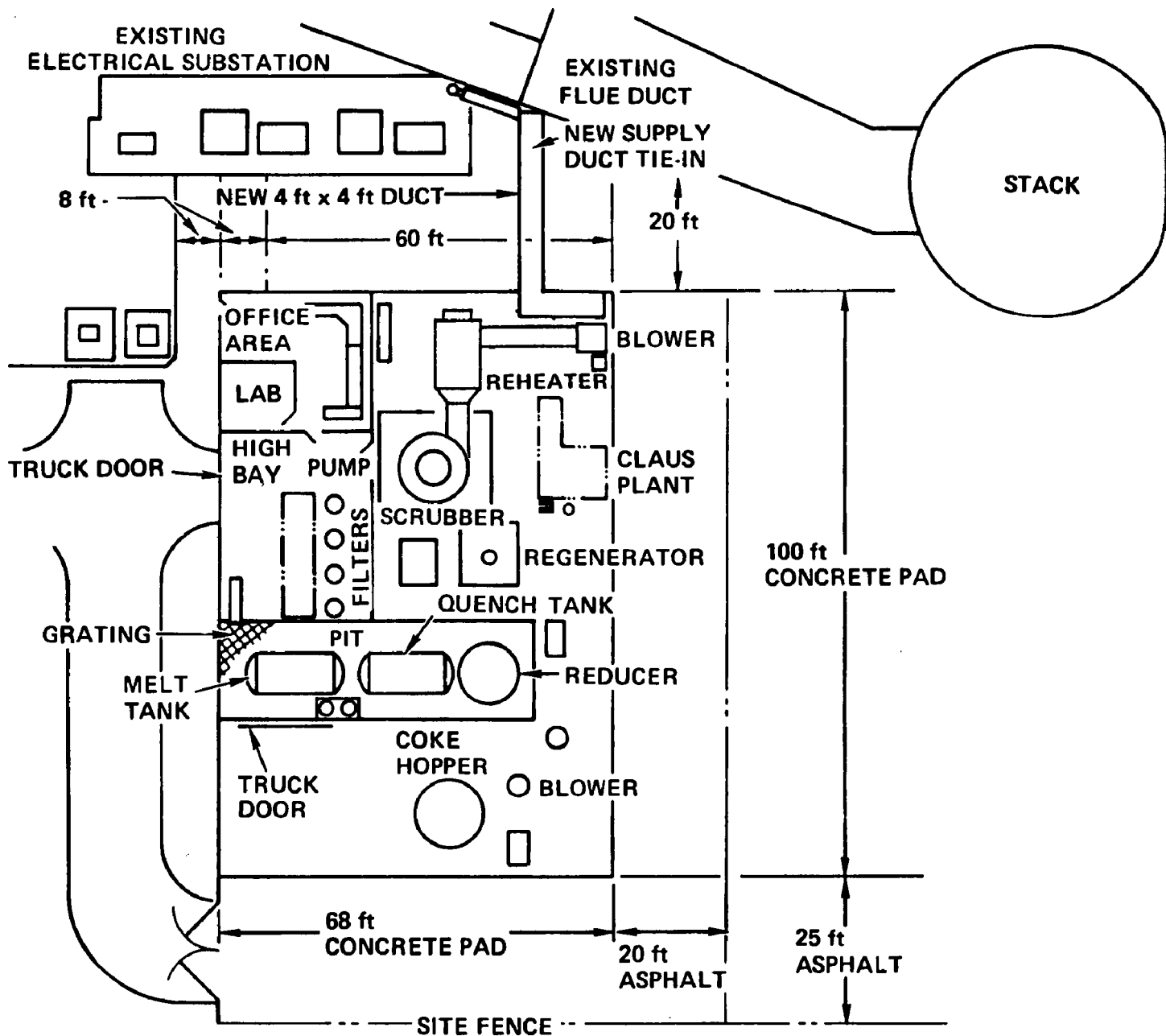


Fig. 11. Pilot Plant Equipment Arrangement Plan

for the platforms, supports, and building was being installed, and the refractory lining of the reducer vessel was about to start. Electrical heaters were also being mounted on tanks and vessels. All of the major subcontracts had been let, and construction was scheduled to be completed by February 1, 1972.

Photographs showing the construction work in progress are presented in Figures 12 to 15 inclusive.

C. TEST PLAN

The test plan covers a one-year test program. The schedule for this program is shown in Figure 16. The test period is divided up into four phases: 1) Start-up and Stabilization, 2) Design Verification, 3) System and Component Parametric Studies, and 4) Reliability and Operability Studies.

The startup and stabilization phase will require about 4.5 months to complete and will consist of a thermal test, a hydraulic simulation, fill and circulation of the molten carbonate, and activation and stabilization of the process chemical reactions.

The second phase of the test program will be the design verification, which will consist of recycling SO_2 from the Claus plant to the scrubber and operating at the design sulfur throughput of the pilot plant. About two months is scheduled for this phase, the results of which will be used to verify the design point of the pilot plant and establish system and component performance characteristics and operating cost data at the design conditions.

The third phase will involve system and component parametric studies. It is scheduled for 3.5 months. This will consist of general parameter studies of the performance of the system as a whole and of each major component. These studies will establish performance characteristics over a range of operating conditions, maximize and establish capabilities of the system and individual components, and establish design and operating criteria for a large demonstration plant.

The fourth and last phase of the currently planned test program will be reliability and operability studies. Reliability and operability of the pilot plant will, of course, be under study throughout the one-year test program. This phase will be a special two-month test at the end of the year to determine minimum operator supervision and maintenance requirements.

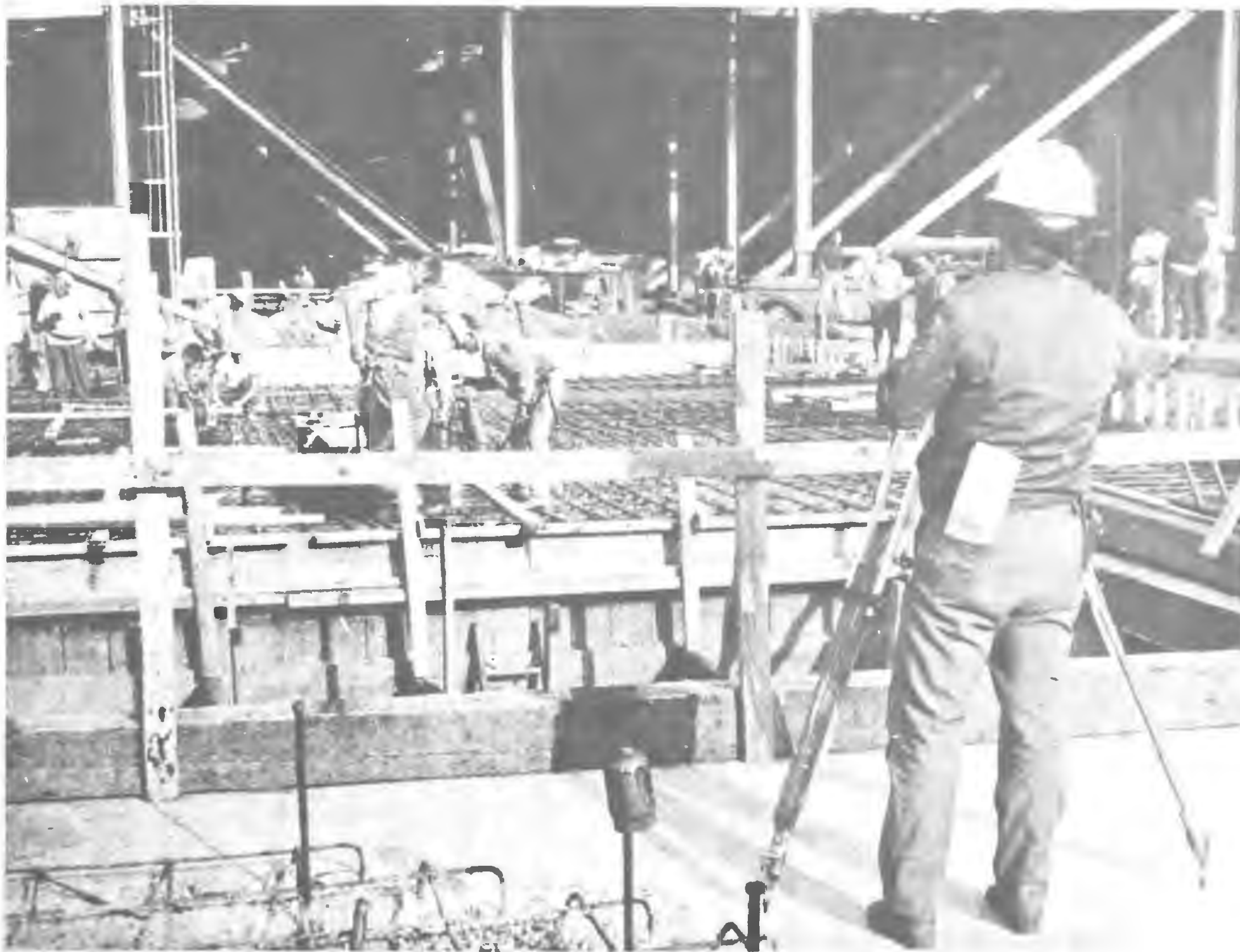


Fig. 12. Pilot Plant Foundation Under Construction

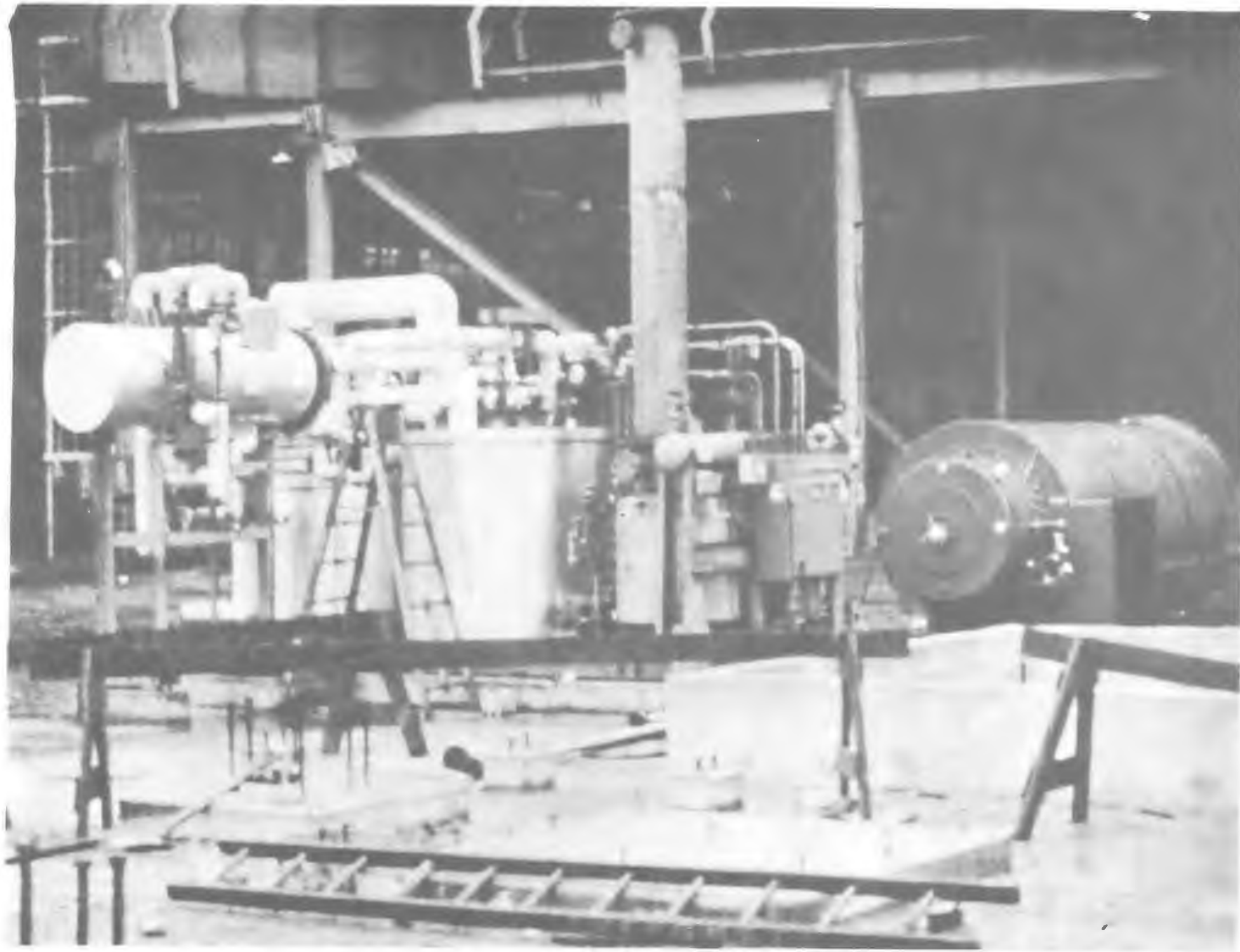


Fig. 13. Claus Plant

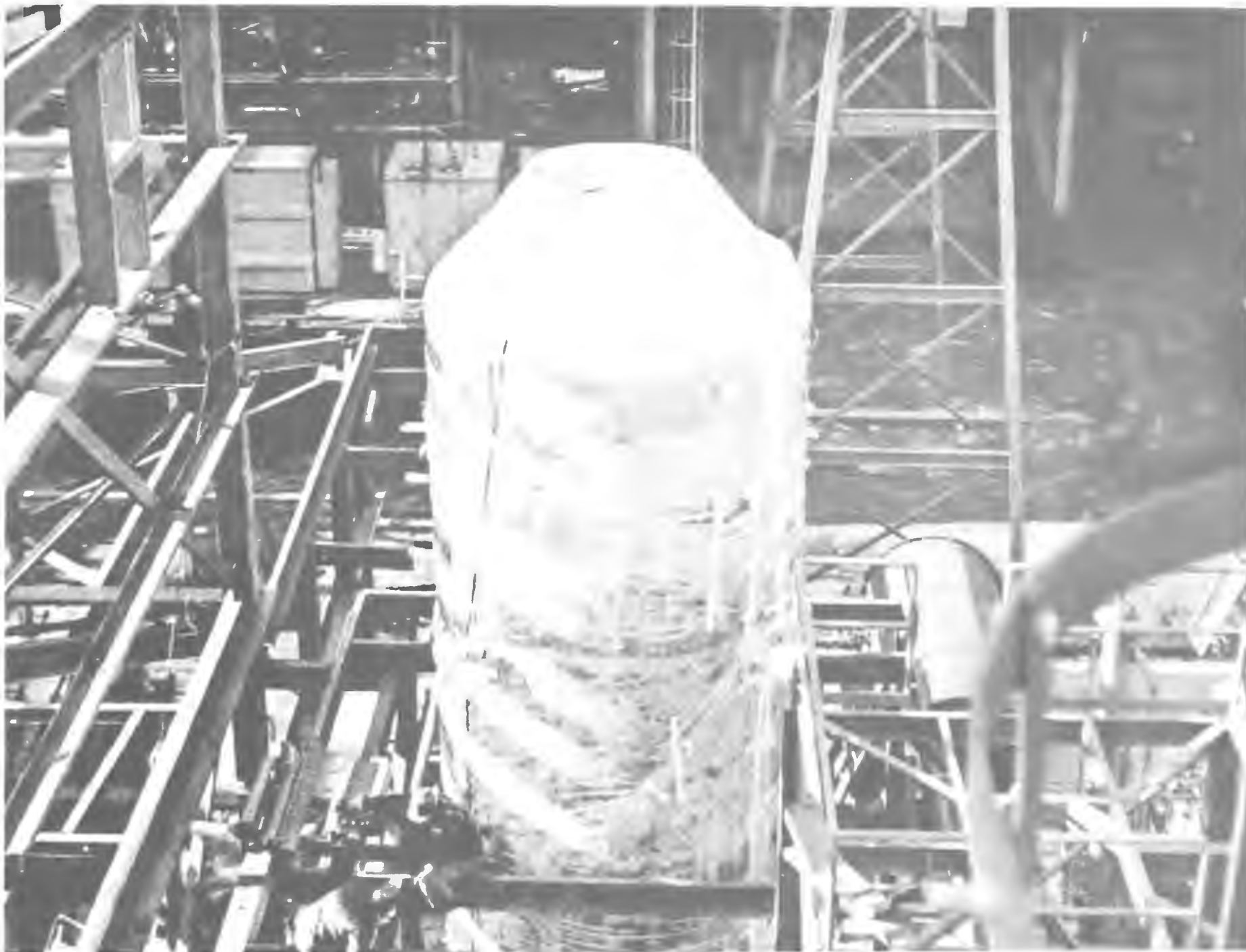


Fig. 14. Pilot Plant Scrubber Being Installed



Fig. 15. Pilot Plant Equipment Being Installed

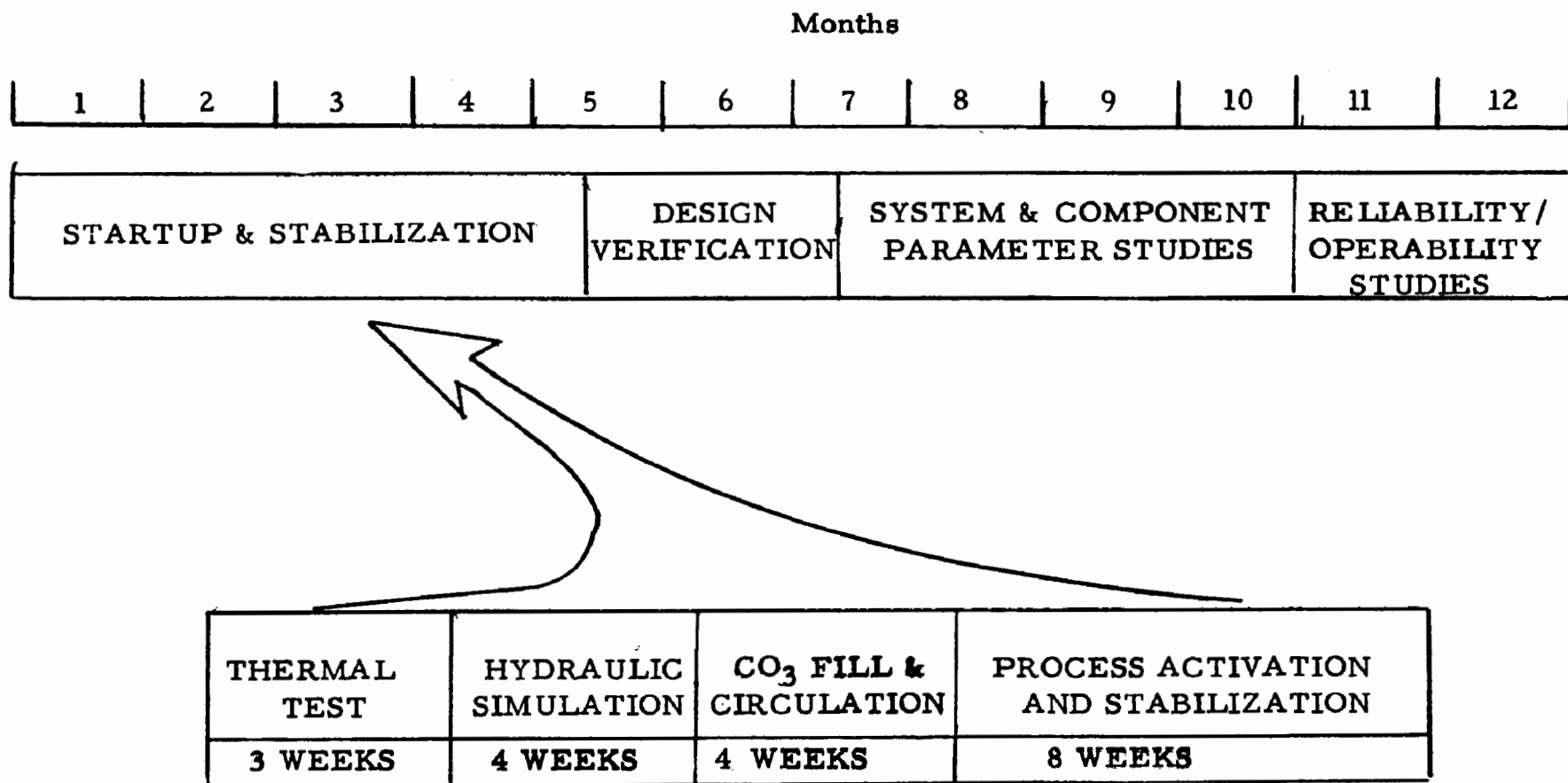


Fig. 16. MCP Pilot Plant Test Plan and Schedule

SUMMARY OF FLUE GAS
DESULFURIZATION SYMPOSIUM

SYMPOSIUM SUMMARY

E. L. Plyer (EPA) —The last part of our symposium is the summary. As you can imagine this has to be a very awesome and formidable job and I think we have a very capable person in Frank Princiotta who has agreed to do this. I would like to make a few remarks concerning this. Frank, as you might realize, has had to put this together sort of on the run here. So even in summarizing something like a symposium of this type, there's bound to be some subjectivity that comes in. And I'm sure that there will be a little bit of it here. You might not agree with everything Frank is going to say here. And what Frank has to say I don't think you can take as being EPA policy. But we do think that it would be quite helpful to you to get a summary of the highlights of the symposium. Necessarily, he will not be able to cover, even briefly, everything that has been given here. And he will have to concentrate his remarks, I think, on the large-scale demonstrations and some of the commercial units which we have tried to concentrate on in our symposium. Since Frank has already been introduced as the session chairman for the lime/limestone wet scrubbing processes, I don't think I need to repeat any biographical information on him. I will just mention that he is the Chief of the Engineering Test Section of the Control Systems Laboratory. He's had about 2 years experience there and due to his enthusiasm and drive he has become, I think, one of our real experts in flue gas cleaning. I think he will do a good job in summarizing our symposium for us.

Frank Princiotta (EPA)—Thanks, Bill, for the introduction and disclaimer. I can't get in trouble now. As Bill indicated, keeping in mind the difficulty of summarizing a symposium of the comprehensiveness that took 4 days in half an hour. I'm bound to miss some important highlights, so please bear with me. First of all, we've heard that sulfur oxides are among the most dangerous air pollutants to human health. Dr. Newill described how morbidity and mortality can be correlated to ambient SO_2 levels. He also pointed out some relatively new information that can have important repercussions. Namely, that particulate sulfates appear to be even more dangerous to human health than SO_2 alone. He stated that in cities where the primary ambient levels of SO_2 are met, high daily sulfate levels have been associated with aggravation of symptoms of heart and lung disease patients. Although further data are necessary, the sulfate particulate problem could lead to more stringent ambient SO_x levels and therefore SO_x emission control. Time will tell.

I think Dick Harrington (EPA) had some relevant points about the importance of controlling industrial boilers. He indicated that despite the fact that area sources and industrial boilers represent a relatively small percentage of total SO_x emitted, they contribute due to meteorological factors. He stressed the importance of trying to utilize stack gas technology developed for power plants on these smaller sources. It certainly seems like a

reasonable suggestion and we're hopeful that systems like double alkali, lime scrubbing, and others could fulfill this role.

Steve Gage (Council on Environmental Quality) presented a very interesting paper on the alternatives to flue gas cleaning--the technological alternatives. And really, in summary, there are none in the short term. He reviewed coal liquefaction, gasification, and advanced combustion processes. He indicated that these are in an embryonic stage with years of development necessary. Probably they will make an impact somewhere between the 1980 and 1983 time period. All of these processes, though, are expensive and, as most of you know, as you approach true hardware, they tend to get more expensive.

Therefore, flue gas desulfurization is the only alternative to flue switching now and will remain competitive for many years in the future, particularly on retrofit applications and in the important industrial boiler size applications.

We then heard from Dr. Ando (J. Ando, Chuo University) who presented the Japanese situation and I think it's of great relevance to the U.S. situation. They have a severe air pollution problem aggravated by a high population density and concentrated industrialization. The great majority of their power plants are oil-fired and, therefore, there are differences that have to be remembered. In the past, SO_x regulations in Japan were met primarily by hydrodesulfurization of

fuel oil. They import high sulfur oil and then desulfurize it. However, the recent tighter regulations, equivalent to less than 1 percent sulfur flue gas desulfurization, have led to plans for at least 100 air pollution control units on power plants, Claus plants, sulfuric acid gas treatment, industrial boilers, etc. Most of these units produce sulfur products and are either presently installed or will be installed in the near future. Sulfur products produced by these systems in Japan include sodium sulfite, sulfuric acid, sulfur, and (most importantly in recent months) gypsum. However, Dr. Ando points out that by 1976 he expects that significantly more gypsum will be produced than can be used; so they, too, may start worrying about throwaway processes. The most important Japanese systems appear to be: the Mitsui lime scrubbing unit - I will mention it briefly later; the Mitsubishi Heavy Industry-JECCO lime scrubbing process, which this unit has operated with high reliability for 9 months on a 35-Mw, oil-fired, closed-loop unit; and the Mitsubishi Chemical Machinery - Wellman Lord process, which has operated reliably for 1.5 years on a 75-Mw, oil-fired power plant. Also, there are three double-alkali systems under active development in Japan: the Kureha/Kawasaki and Showa Denko sodium double-alkali systems, and the Nippon Kokan ammonium double-alkali system. These are considered to be very important and should be followed closely.

Moving on to costs, I think Gary Rochelle (EPA) presented a very useful scheme for the rough estimation of capital and operating costs for flue gas desulfurization systems. Briefly, the following are some of the operating costs he came up with. (I will just talk about total annualized operating costs that are perhaps more important because they include capital charge considerations.) For lime/limestone and magnesium oxide processes, he found costs for a new 500-Mw, 3.5-percent sulfur coal unit to be very close for both processes at about 2.5 mills/kw-hr. Costs for the Wellman Lord system and the Stone and Webster/Ionics System under the same groundrules were about 2.7 mills/kw-hr. Operating cost for the Cat-Ox system was about 2.75 mills/kw-hr. He indicated that about 75 percent of existing plants can be retrofitted within 3 mills/kw-hr. Comparisons of this estimating technique with actual costs for six full scale installations, most of them first of a kind, indicate that he's about 9-21 percent low in his capital cost estimates. My own feeling is that this is due primarily to the fact they are first of a kind and that these estimates will come even more in line as there's more widespread application of these systems. However, there were discrepancies, You heard them and I heard them. The Will County unit and the Widow's Creek unit in particular have had recent cost escalations which make Gary's estimates look even a little bit farther off.

Most of these systems, regenerable and throwaway, look pretty similar to Gary as far as operating costs are concerned and he feels the key parameter which can turn the tide is sludge disposal costs. And he feels these operating costs are equal at \$3 or \$4 per ton of wet sludge. Additionally, interestingly, he also indicates what's obvious I guess when one thinks about it: the low load factor systems strongly favor the throwaway processes economically. And this has obvious implications for industrial boilers which ordinarily operate at low load factors.

Getting into lime/limestone scrubbing systems, I think Irv Raben (Bechtel Corporation) presented an excellent paper and I recommend that everybody review it carefully. He pointed out that 21 full-scale units, now comprising 9600 Mw of capability, will be or have been installed in this country. In particular the Ohio Edison Bruce Mansfield, the Mohave, Navajo, and Northern States units are the real biggies that contribute most to that 9600-Mw figure. His costs were in line with Gary's costs, and he estimates for a new 500-Mw unit on a similar basis for Gary, about 2.3 to 2.5 mills/kw-hr. Irv feels relatively confident, hopeful I guess is the word, that reliability will be demonstrated soon in the United States based on all the units that are going to come on to line relatively soon.

Talking about some limestone systems in particular, the Chemico Lime-Mitsui aluminum plant has to be mentioned. Of course this paper was presented by Mr. Sakanishi (Mitsui Aluminum Co.). Bob Quig (Chemico) made perhaps a controversial introductory statement when he expressed his belief that the operation to date has indicated this technology is now demonstrated by anyone's definition, including the National Academy of Sciences. As you know this system has removed 90 percent of the SO_2 on a coal-fired plant for 14 months with reliable operation; no problems of any significance were reported. Briefly mentioning, though, there were people on our panel, assembled to discuss the relevance of this system to the U.S., who felt that they have to be careful in trying to extrapolate this experience to the U.S., primarily because the system apparently operated open-loop for at least part of its time in Japan. It's a base-loaded unit with few excursions, and it's also a 2 percent sulfur coal system, which is somewhat lower than many eastern U.S. applications. Other panel members, however, felt that it is a very relevant system and has many characteristics in common with many potential eastern U. S. coal applications.

Moving on to Dr. Weir's (A. Weir, Jr., Southern California Edison) paper on the Mohave power plant results. This ties in to full-scale units. These results, like those at Shawnee and other places, indicate that the lower the SO_2 inlet in the flue gas, the easier things are as far as SO_2

removal is concerned. He was able to get down to 20 ppm and less in outlet for many of the eight scrubbers he looked at under many conditions. He was also able to get 0.001 to 0.002 gr/scf outlet for several of his scrubbers (keep in mind that this is downstream from a relatively efficient precipitator). As you know this information (and perhaps data from two big modules which will be built at Mohave) will influence the selection of the very large Mohave and Navajo plants. They add up, by the way, to over 3000 Mw of capability. So that's a real slug of capability.

Talking a little about the B&W systems, the Will County unit was described to us. It initially was a 175-Mw unit designed with a limestone tail end system for 80 percent removal. It started up about a year ago and has had many operating problems, primarily minor problems with apparently no inherent system-type problems. Perhaps the most serious of the problems has been demister pluggage. However, there appears to be relatively high probability in the near term that this system will be made to operate reliably. The next B&W unit we heard about was the Kansas City P&L La Cygne unit, which is kind of a version of the Commonwealth unit multiplied by about 7. There are seven parallel circuits in this 840-Mw system, which just recently started up. I think the boilers are now at about half load and I'm personally going to keep an eye out for that system. I suspect the unit could be very reliable since I think many of the problems they had at Will County have been corrected on that particular unit.

I think we should mention some of the Combustion Engineering units as well. But I think we should mention the Kansas City Power & Light units briefly. They have been changed to a tail end configuration; one of the two Hawthorne units (Unit No. 3) has been changed from boiler injection to a tail end limestone system. I think Irv Raben indicated that he felt this was a trend in the industry; I think this change is indicative of this trend. There has not been sufficient operating time on this tail end limestone Hawthorne unit to get much information yet. Our understanding is that they've been burning some low-sulfur coal lately. The Louisville Gas and Electric Paddy's Run Station, a 70-Mw carbide sludge tail end system, though, has started up. It has about 1 month's operation now. And, as you heard, things look pretty good. Reliability so far looks promising. SO₂ removal has been reported as very high, although I haven't heard a number yet.

Let's move on briefly now to the EPA Shawnee lime/limestone program. We heard from Dr. Epstein (M. Epstein, Bechtel Corporation) about all the SO₂ data that's been generated as a function of system parameters; this should certainly help design these systems in the future. There's information also on particulate removal; its range is from about 0.01 to 0.03 gr/scf for all three scrubbers. You might remember these are three 10-Mw scrubbers in parallel to test three different types of scrubbers.

I'll summarize reliability information and perhaps even add a bit to what Bill Elder (TVA, Muscle Shoals) said. This is hot off the press. In general, reliability tests started about 2 months ago. And we are very pleased so far with the reliability seen to date. We have had little evidence of scaling or demister problems. We feel the trick is low pH operation, high L/G's, and backing off somewhat on gas velocity. The venturi after-spray scrubber has operated for 1 month at 75 percent removal without any problems of any type. The TCA has also operated for about a month with from 85 to 90 percent removal; no demister or scaling problems occurred, although we have seen some erosion of balls and grids and some solids buildup in the inlet duct. We feel confident these problems will be resolved shortly. The hydrofilter had very few problems over about a month's tests until lately when the nozzles apparently have eroded and led to some bed and demister problems.

Moving on now to the first of the regenerable systems or saleable product systems. We heard quite a bit about the magnesia oxide process. Gerry McGlamery (TVA) described the system in detail. He compared the costs to those of wet limestone systems and found them relatively close although the magnesia oxide process was perhaps somewhat more expensive; again, sludge costs were very important for any cost comparison. He also indicated that magnesium oxide systems making sulfuric acid makes most sense in metropolitan areas where sludge is difficult to handle and sulfuric acid can be marketed.

Of course the most important Mag-Ox system is the Boston Edison system. This unit started up in April 1972 at Boston Edison's Mystic Station, a 150-Mw facility producing 50 tons per day of sulfuric acid, which is processed at a separate location in Rumford, Rhode Island. Operations to date have demonstrated each process step. Greater than 90 percent SO_2 removal has been achieved. But, as you heard, there have been several "nitty gritty" mechanical problems which have prohibited a long-term test which is really needed to check out the system. Such problems have included dryer problems, calciner seal leakage, calcined material loss of reactivity, solids handling problems, and so forth. And Chemico has indicated that top priority is going to be given to performance of some long-term testing relatively soon to really home in on the reliability of this important system.

Other Mag-Ox systems were mentioned. The Philadelphia Electric Eddystone system designed by United Engineers is a 120-Mw system that will start up in the fall of 1973. And the PEPCO Dickerson No. 3 coal-fired station, a 100-Mw station, will start up in several months.

Perhaps the most reliable of the regenerable systems, in terms of operation to date, is the Wellman Lord process of Davy Powergas. This process, at least based on what we heard today, has demonstrated the greatest reliability, I think it's safe to say, of any flue gas desulfurization system to date. There are five units presently operating reliably;

eight are under construction on power plants, sulfuric acid treatment systems, and Claus treatment systems. Perhaps the most significant is Japan Synthetic Rubber's Chiba plant, the 75-Mw, oil-fired system that has operated for over 1.5 years at a reported availability of 95 percent. Sulfur dioxide removal has been at about 90 percent. EPA is quite interested in the process and has co-funded with Northern Indiana Public Service Co. for installation of the Wellman unit at the NIPSCO station, a 115-Mw system. It's a coal-fired boiler that will produce sulfur directly using the Allied SO_2 reduction process which uses natural gas as a reductant. This sulfur-production technology was successfully demonstrated at the Falconbridge Nickel Plant near Sudbury, Canada. It should be noted, though, that for about a 1000-Mw system you need about 20 Mw worth of natural gas. Of course this is a problem in many locations; however, Allied indicated they are working very intensely for substitutes for natural gas as the reductant. Another problem attendant to that system is the requirement for a sulfate purge based on a 4,5, or 6 percent oxidation of sulfite/bisulfite to sulfate.

The Monsanto Cat-Ox process should be mentioned. This is another regenerable process somewhat unique in that it's based on the well-known contact sulfuric acid process. Flue gas is heated to 800°F and oxidized in the catalyst bed to 850°F where the sulfur dioxide is oxidized to sulfur trioxide to produce about 78 percent sulfuric acid. You heard the story about the Wood River station of Illinois Power. This is where the system has been installed; the system started up back in September of 1972. I should add that a 99.6 percent efficient ESP, which is

necessary upstream of the system, was installed in February of 1972 and has been operating well since then. Initially the system worked well when it was using natural gas as the reheating combustion medium; however, after about 17 days of successful operation, reheater problems with oil associated with soot buildup (with potential bed pluggage problems) shut down the system. As you heard, there will be modifications and it's expected the unit will be back on line in late summer of this year. One of the problems with the system is the sale of dilute sulfuric acid.

Other processes that appear to be very well along in their development and very important are the double alkali processes. I was pleased to hear the summary by Norm Kaplan and Dean Draemel (EPA) of all the variations of this process, and there are quite a few of them. And I think it's worth everyone's while, who's interested in these systems, to carefully look at a summary of these systems and see just what these differences are -- dilute versus concentrated, various ways of handling the sodium sulfate, etc. But they all seemed to have the potential for low capital and operating costs and for high reliability. Gary Rochelle indicated that the costs were approximately 15-20 percent lower than an equivalent lime/limestone system. This was based on an assumption which will be validated.

Norm Kaplan mentioned some of the corporations involved -- FMC, Envirotec, General Motors, A. D. Little, Showa Denko, and Kureha. Let me just mention some of the more significant full-scale units that are planned. The 20-Mw unit at Southern Services Scholz station of Gulf Power is of real significance; this will be an A. D. Little/Combustion Equipment Associates unit. General Motors' 40-Mw double alkali system for four stoker boilers at the Cleveland Chevrolet plant will start up late this year; this will be the first of the U.S. full-scale installations. In addition, there are full-scale units planned in Japan, one of which will start up in June, the Showa Denko 110-Mw system on an oil-fired boiler. Two additional 150-Mw units will begin operation in 1974. There is quite a bit of activity in the double alkali area and it looks like it will be a real viable alternative to lime/limestone scrubbing as far as the throwaway processes are concerned.

Let me just briefly mention other important processes which were mentioned today. I'm sure they are probably pretty fresh in your mind. The Foster Wheeler-Bergbau Forschung process, TVA-EPA ammonium bisulfate, and Stone & Webster/Ionics molten carbonate processes were described and could play an important role several years from now when these systems are able to be applied to full-scale commercial units.

Let me briefly summarize some of the things we heard about sulfur product problems. One can easily write a book on this, so I'll try to be brief. The large quantities of sulfur

inherent in flue gas must end up as a low-value sulfur product. Generally this is either a throwaway sludge, which you can call a zero value, or negative value material as opposed to a low-value sulfur or sulfuric acid type of material. Quantities are somewhat staggering. Dick Stern and Julian Jones (EPA) indicated that a 100,000-Mw capacity for 20 years of sludge storage to a depth of 10 feet would require 150 square miles of area for settled sludge. They also made some very provocative comparisons between the affected areas associated with sludge based on predictions of lime/limestone utilization and areas associated with coal strip mining. For sulfuric acid production, the same 100,000-Mw capacity will produce acid at a rate equivalent to the present total U.S. production, about 28 million tons per year. Sulfur, as far as volume and quantities are concerned, is certainly the most desirable end product.

The EPA/Aerospace program will hopefully present a complete, comprehensive evaluation of the toxicity and water pollution problems associated with throwaway sludges, and will also evaluate some sludge treatment processes. We'll look at lime/limestone and double alkali sludges, and Dick Stern has asked all relevant parties for information.

Also to be evaluated are the sludge fixation (treatment) processes. We've heard quite a few of them mentioned; IUCS and Dravo perhaps being the most important processes. These fixation processes basically

involve a recipe requiring the inclusion of flyash. The recipe calls for flyash, calcium sulfite and sulfate sludge, additional lime-based material, and perhaps an accelerator to make a cementitious type material which might have attractive landfill application. And perhaps, at least in IUCS's opinion, a potential for sale as aggregate and cementitious materials. Preliminarily, data presented by IUCS indicate that these processes lead to decreased leachability and permeability and therefore reduce water pollution potential. We hope to validate such claims during our Aerospace program.

Let me mention quickly a little bit about sulfuric acid. This has been the product of choice for the regenerable systems so far in this country. But it appears that only selective applications will be possible due to difficulty in selling large quantities of sulfuric acid. Each 1000 Mw produces approximately 1 percent of the total U.S. production. However, there seem to be obvious urban applications where such systems make quite a bit of sense.

Let me briefly discuss sulfur as the end product. As I mentioned, the storage volumes are certainly attractive; there's no question about that. Sulfur can also be stored for eventual use as opposed to sludges, which must just lie there with no potential use except as landfill. However, some problems associated with the storage of sulfur were mentioned in this symposium which were new at least to me.

They include potential flammability problems, potential H₂S evolution, and perhaps wind and water erosion and other related problems. Hopefully this will be evaluated because sulfur certainly seems (at least preliminarily) to be a very important end product. Also we heard some potential uses of sulfur. They include sulfur in asphalt materials, sulfur concretes, etc., although it should be pointed out there's quite a bit of technical and marketing work ahead before these use any great quantities of sulfur material.

As far as the symposium conclusion is concerned, I would like to be a little bit subjective now. I have tried to be objective during this presentation although somebody may disagree with that. Let me now quote from the SOCTAP report. You might be familiar with this. This is the Sulfur Oxide Control Technology Assessment Panel, a governmental interagency group which reported to Mr. Ruckelshaus (W.D. Ruckelshaus, former EPA Administrator). Its charter was basically to look into flue gas desulfurization and come up with a reasonable, objective assessment. This report is available, I might add from the Air Pollution Technical Information Center, Research Triangle Park, N.C. Let me just read briefly the most relevant conclusions. Now keep in mind, these are the conclusions of the report that I feel accurately reflect the sum total of what we have heard at this symposium:

"We (the SOCTAP group) have examined the status of stack gas cleaning technology in the United States and Japan and have concluded that sulfur dioxide removal from stack gases is technologically feasible in commercial-sized installations. We have concluded that technological feasibility should not now be considered a decisive element in utilization of these systems and that a large fraction of the nation's coal-fired steam electric plants can ultimately be fitted with commercially available stack gas cleaning systems... The reliability of currently available systems has been the subject of some question.

We concur that SO_x control systems must exhibit the high degree of reliability required by the utility industry. We believe that the required reliability will be achieved with early resolution of a number of applications engineering problems related to specific hardware components and system design parameters.... In view of the fact that a number of large scale plants scheduled for operation in the U.S. in the near future will provide additional 18 months operating experience (or by 1974) should effectively remove engineering barriers to the application of stack gas cleaning to many facilities."

The report emphasized the need for additional R & D primarily in advanced processes to cut back costs and help produce less noxious solid waste problems and for a solid waste sludge disposal evaluation program. Thank you.

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