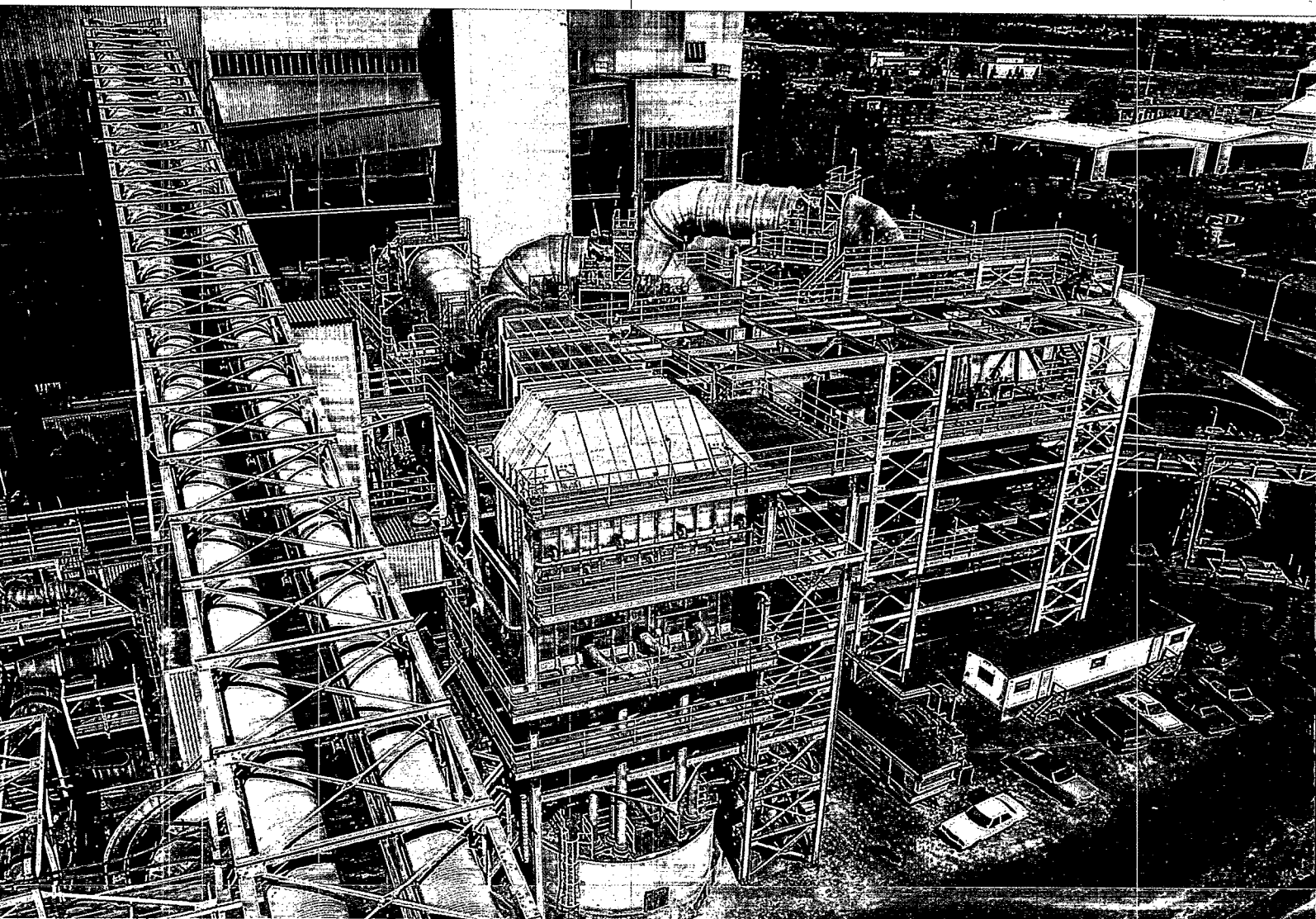


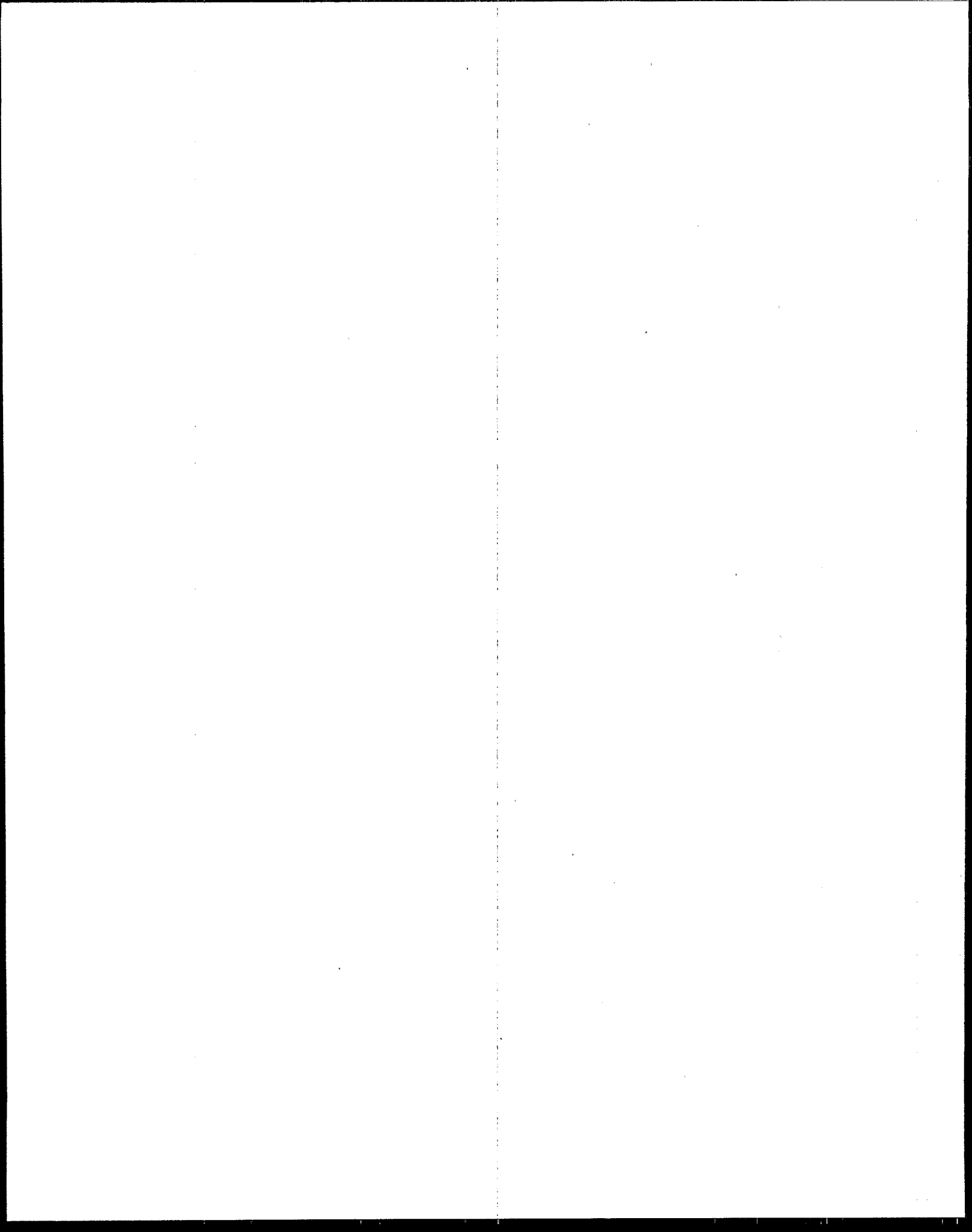


Summary Report

Sulfur Oxides Control Technology Series: Flue Gas Desulfurization

Magnesium Oxide Process





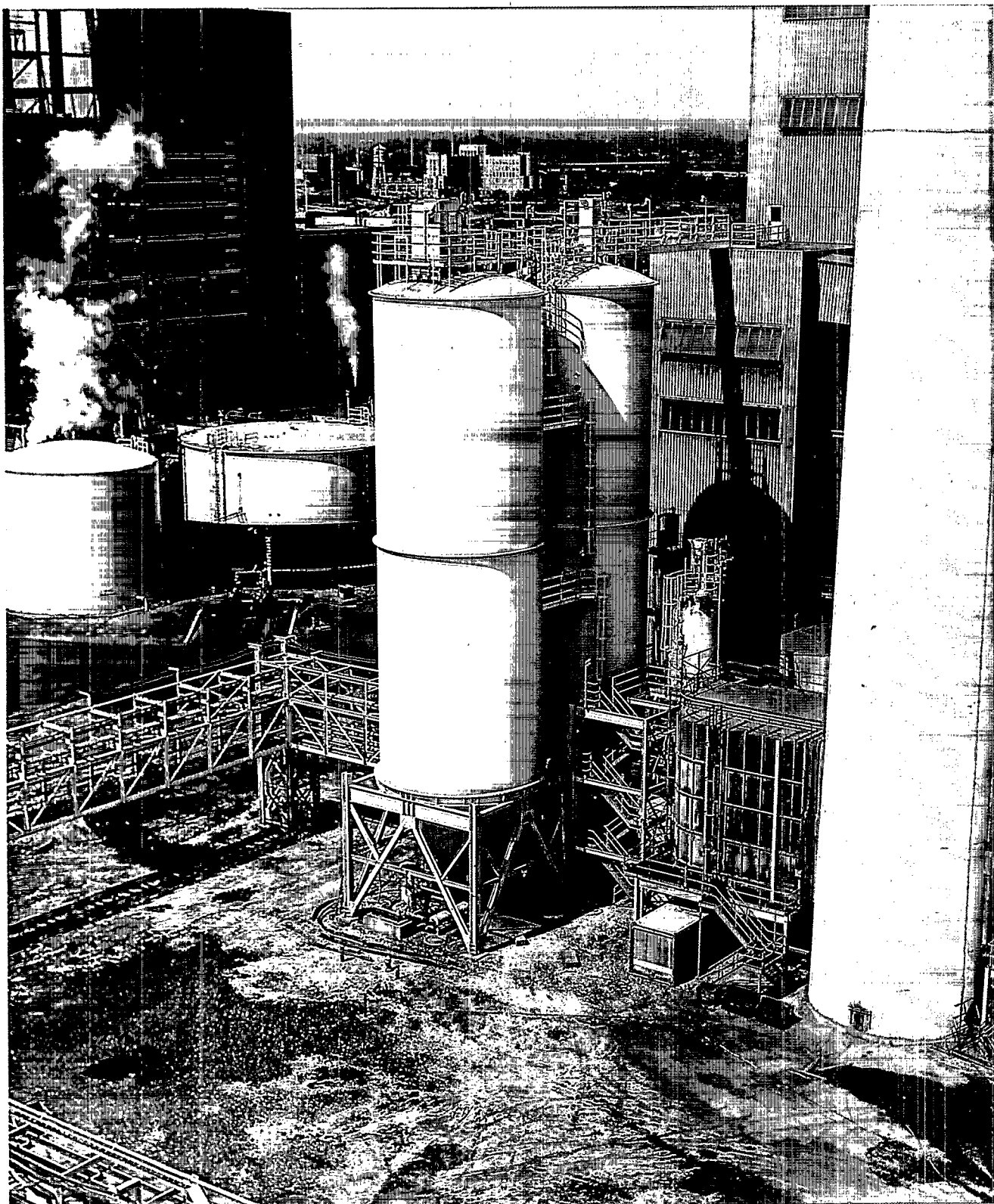
Summary Report

Sulfur Oxides Control Technology Series: Flue Gas Desulfurization

Magnesium Oxide Process

April 1981

This report was developed by the
Industrial Environmental Research Laboratory
Research Triangle Park NC 27711



Magnesium oxide storage silos

Introduction

The magnesium oxide (MgO) flue gas desulfurization (FGD) process (Figure 1) is a sulfur dioxide (SO_2) recovery system that uses a recirculating MgO slurry to remove SO_2 from stack gas. The slurry reacts with SO_2 to form magnesium sulfite (MgSO_3), which is then heated to regenerate MgO. The concentrated SO_2 released during regeneration can be converted to sulfuric acid (H_2SO_4) and other products.

Major advantages of the MgO FGD process include the ability to:

- Recover sulfite salts easily from the slurry

- Regenerate the absorbent, MgO
- Alleviate the problem of solids disposal

An analysis of these benefits, however, must consider the cost of installing and operating the MgO FGD process, or any other relatively complex SO_2 recovery system.

The U.S. Environmental Protection Agency (EPA), working with a group of chemical and utility companies, funded two MgO FGD demonstration plants. The first plant was installed on a 150-MW oil-fired boiler at Boston Edison Company's Mystic Station in Everett, Massachusetts;

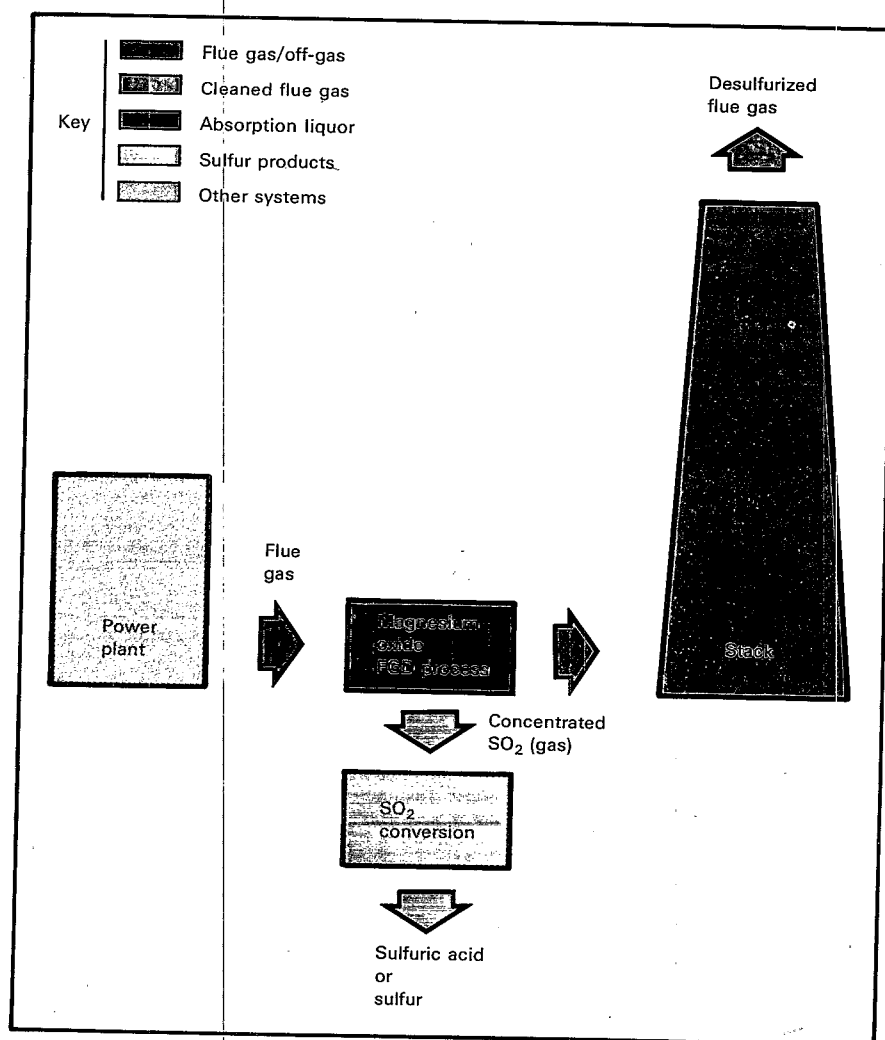
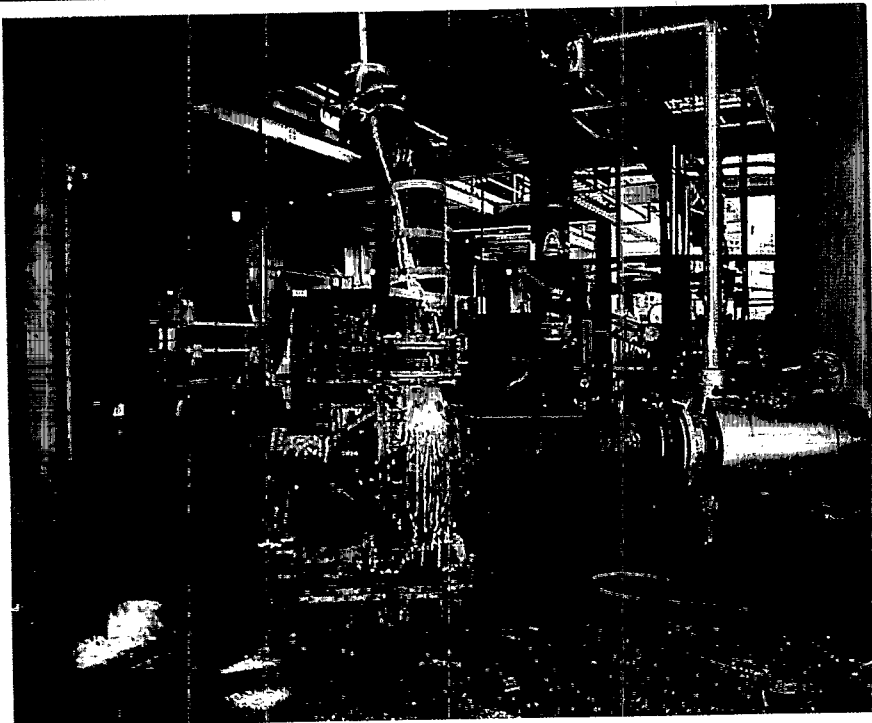


Figure 1.
Magnesium Oxide FGD Process Followed by SO_2 Conversion



Scrubber surge tank

the second was designed to desulfurize one-half the flue gas from a 190-MW coal-fired boiler at Potomac Electric Power Company's (Pepco's) Dickerson Generating Station in Frederick, Maryland. The magnesium sulfite formed in the process at these installations was regenerated, and the byproduct SO_2 stream was transported to Rumford, Rhode Island, and converted to sulfuric acid at Essex Chemical Company's plant.

The MgO FGD process can be evaluated objectively on the basis of operational experience. Boston Edison's installation operated for 27 months from 1972 through 1975, whereas Pepco's system operated for 15 months in 1974 and 1975. Results of tests conducted at both plants on such factors as design considerations, cost, and environmental impact have established the MgO FGD process as a feasible means of SO_2 emission control.

This report summarizes the MgO FGD process and provides a basic understanding of FGD technology.

Process Description

The MgO FGD process consists of four major processing steps:

1. Flue gas pretreatment
2. SO₂ absorption
3. Solids separation and drying
4. MgSO₃ regeneration

Sulfur dioxide processing may be considered a fifth step because it is often associated with the MgO FGD process.

Figure 2 illustrates the process flow for a typical MgO FGD system.

In the first step, water scrubbing cools and saturates the boiler flue gas and removes fly ash and chlorides upstream of the absorber. As a rule, flue gas from oil-fired boilers does not require pretreatment, but this step is necessary in coal-fired applications.

In the absorber (Step 2), SO₂ is removed from the flue gas by contact with a recirculating slurry of MgO, MgSO₃, and magnesium sulfate (MgSO₄). Flue gas SO₂ diffuses into this slurry and reacts with MgO to form MgSO₃, some of which reacts with oxygen present in the flue gas to form MgSO₄. Additional MgSO₄ is formed when flue gas sulfur trioxide (SO₃) reacts with MgO.

Desulfurized flue gas leaves the absorber, is reheated if necessary, and is exhausted through the stack. The sulfurized scrubbing liquor flows to a sump and is recycled to the absorber after a continuous bleed stream has been withdrawn from the recirculation loop. Fresh MgO added to the recirculation loop replaces any magnesium removed from the scrubbing liquor by the bleed stream.

In the third step, the bleed stream is routed to a centrifuge for processing into 60 percent solids by weight, and the mother liquor is recycled to the absorber recirculation loop. The stream of 60 percent solids by weight flows to a dryer where surface moisture and most of

the water of hydration are removed to produce a dry powder of MgSO₃, MgSO₄, unreacted MgO, and inerts.

Calcination of the dry powder in the regeneration processing stage (Step 4) converts MgSO₃ and MgSO₄ to MgO, which is recycled to the absorber recirculation loop. Calcination also produces an SO₂-rich byproduct stream that may be processed further to form sulfuric acid or elemental sulfur.

Thus, the MgO FGD process not only regenerates the essential absorbent, MgO, but also produces sulfur dioxide at concentrations practical for conversion to sulfuric acid or elemental sulfur.

Pretreatment

Pretreatment of flue gas in oil-fired systems is almost unnecessary because fly ash levels are minimal. Particles generated by such systems are usually carbonaceous and are consumed in the regeneration step, where they serve as a reducing agent for magnesium sulfate.

Unlike oil-fired systems, coal-fired systems require flue gas pretreatment to remove fly ash upstream of the absorber and to prevent large-scale contamination of the recirculating slurry used in the absorption step. Pretreatment is necessary for the following reasons:

- Fly ash from coal contains compounds of vanadium and iron, which catalyze the undesirable reaction of magnesium sulfite with oxygen to form magnesium sulfate.
- Fly ash is separated more easily from the water used in the pretreatment step than from the slurry mixture of the absorption process. Without pretreatment, the replacement of large quantities of magnesia removed from the slurry with the fly ash would increase the operating cost of the system significantly.

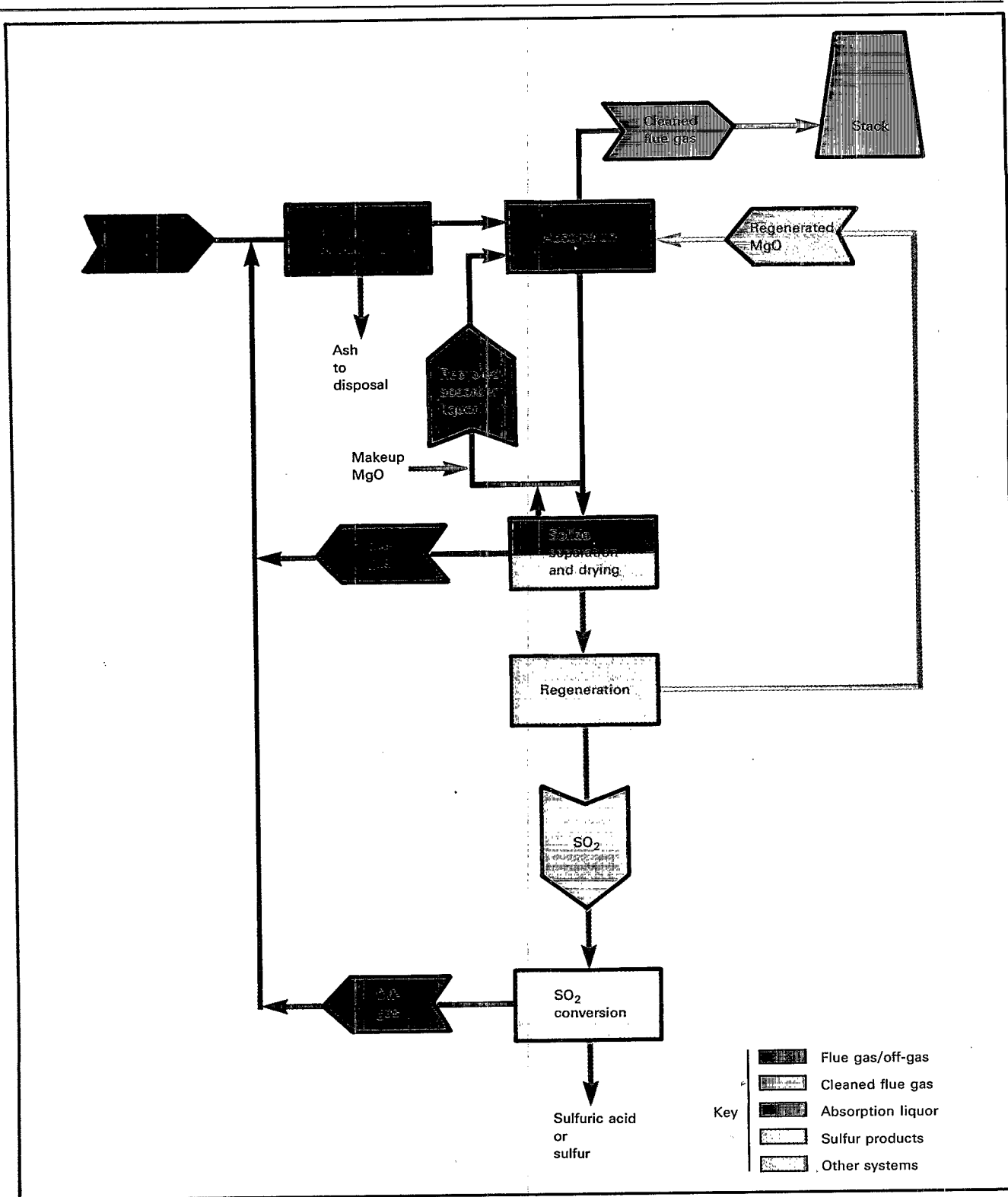


Figure 2.
Magnesium Oxide FGD Process With Regeneration and SO₂ Conversion

- Pretreatment cools and saturates the flue gas and reduces the concentrations of corrosive chloride ions entering the absorber. Typical flue gas temperatures range from 290° to 310° F (145° to 155° C) before pretreatment and from 125° to 135° F (50° to 55° C) following pretreatment.¹

Fly ash removal may occur in the first stage of a double-stage venturi scrubber (Figure 3). Flue gas entering the irrigated throat of the first stage is sprayed with water. The impact of the dispersed water droplets removes particles from the flue gas stream. Particle collection efficiencies of 99 percent or higher are achieved.

The ash-laden liquor from the first stage is recycled to the venturi converging section. A bleed stream is continuously withdrawn from the recycle line and routed to the thickener, where the particles settle. Thickener underflow is pumped to an ash disposal pond, and overflow is routed to a transfer tank where makeup water is added to the system. The liquor is pumped back to the venturi first stage.

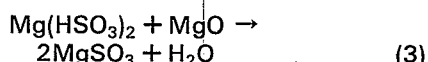
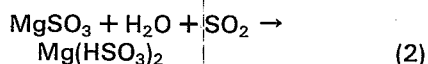
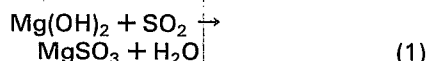
In a two-stage venturi scrubber, flue gas passes through an annular mist eliminator before entering the second stage of the venturi. The mist eliminator removes residual ash-laden droplets small enough to be carried with the gas.

Absorption

Venturi scrubbers were used at both EPA demonstration plants. Flue gas from an oil-fired boiler may be routed to a single-stage venturi for removal of sulfur dioxide. Coal-fired installations may use a double-stage venturi, which is capable of pretreatment as well as absorption. Single- and double-stage venturi scrubbers are compared in the section on Design Considerations.

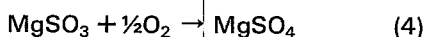
In the SO₂ absorption and venting operation (Figure 4a), flue gas entering the venturi scrubber comes into contact with the recirculating MgO slurry. The liquor is atomized by the high-velocity gas, and flue gas SO₂ is absorbed rapidly into the finely divided slurry. Desulfurized flue gas then passes through spray-washed mist eliminators and is discharged through the stack.

Removal of SO₂ from flue gas involves absorption and the following chemical reactions:



A 5-percent excess of MgO in the slurry is necessary to ensure the completion of the reaction in Equation 3 and thus to guarantee that the slurry leaving the absorber contains no magnesium bisulfite [Mg(HSO₃)₂].

Additional reactions produce magnesium sulfate:

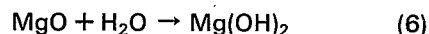


Studies indicate that most of the magnesium sulfate formed in the scrubber results from sulfite oxidation by excess oxygen in the flue gas. Air oxidation of sulfite is a light-activated, free radical reaction catalyzed by certain metallic ions, including iron and vanadium, and is inhibited by free radical scavengers.² Oxidation of sulfite occurs at every stage in the process until the salts are calcined to regenerate MgO. Surface oxidation of magnesium sulfite crystals can become excessive even when the material is stored or shipped off site for calcination. It is advantageous to limit sulfite oxidation throughout the process because a higher temperature is required for thermal decomposition of MgSO₄

than for MgSO₃. For this reason, more energy is needed to regenerate MgO from sulfate than from sulfite.²

Hydrated crystals of MgSO₃ and MgSO₄ are formed in the venturi scrubber and sump. The slurry is recirculated from the sump to the spray nozzles in the scrubber. A bleed stream is withdrawn constantly from the absorber recirculation loop to maintain the desired concentration of magnesium solids in the recirculating slurry. The bleed stream, which contains MgSO₃ and MgSO₄ crystals as well as unreacted MgO and magnesium hydroxide [Mg(OH)₂], is routed to a dewatering system.

Fresh magnesium hydroxide slurry is added to the recirculation loop to compensate for magnesium withdrawn in the bleed stream. The slurry is prepared by slaking regenerated and makeup MgO in an agitated, heated tank:



The treated flue gas is demisted to remove entrained liquid and solids and may be reheated before it is exhausted to the stack. Reheating desaturates the gas, increases buoyancy, and aids in dispersing any remaining stack constituents.

Solids Separation and Drying

Figure 4b illustrates a typical solids separation and drying system, which requires a centrifuge, dryer, and dust collector. The bleed stream from the absorber recirculation loop is routed to a centrifuge that concentrates the slurry from about 10 percent solids by weight to approximately 60 percent solids by weight. The mother liquor is recycled to the absorber recirculation loop.

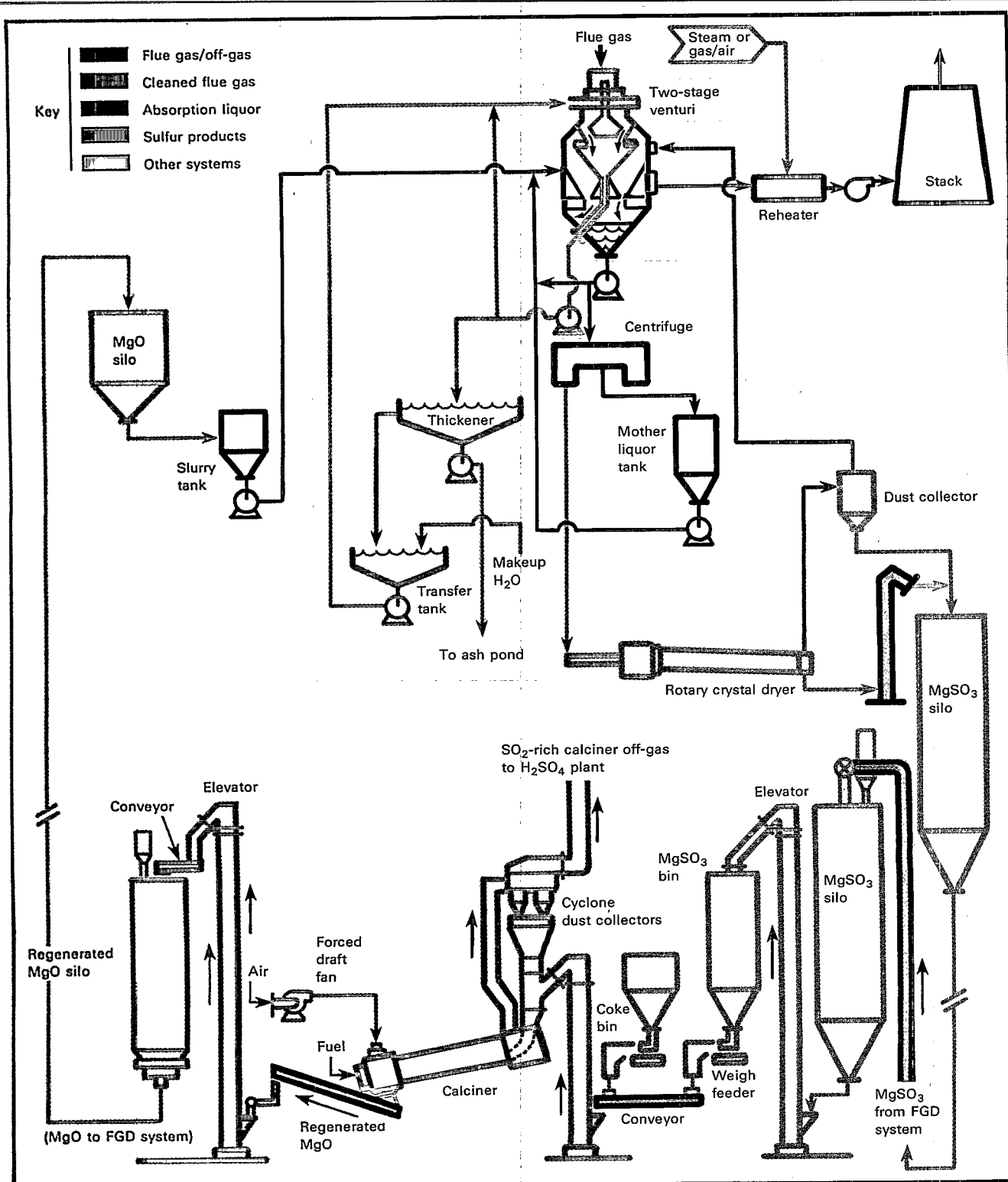


Figure 3.
Pretreatment Step in Magnesium Oxide FGD Process

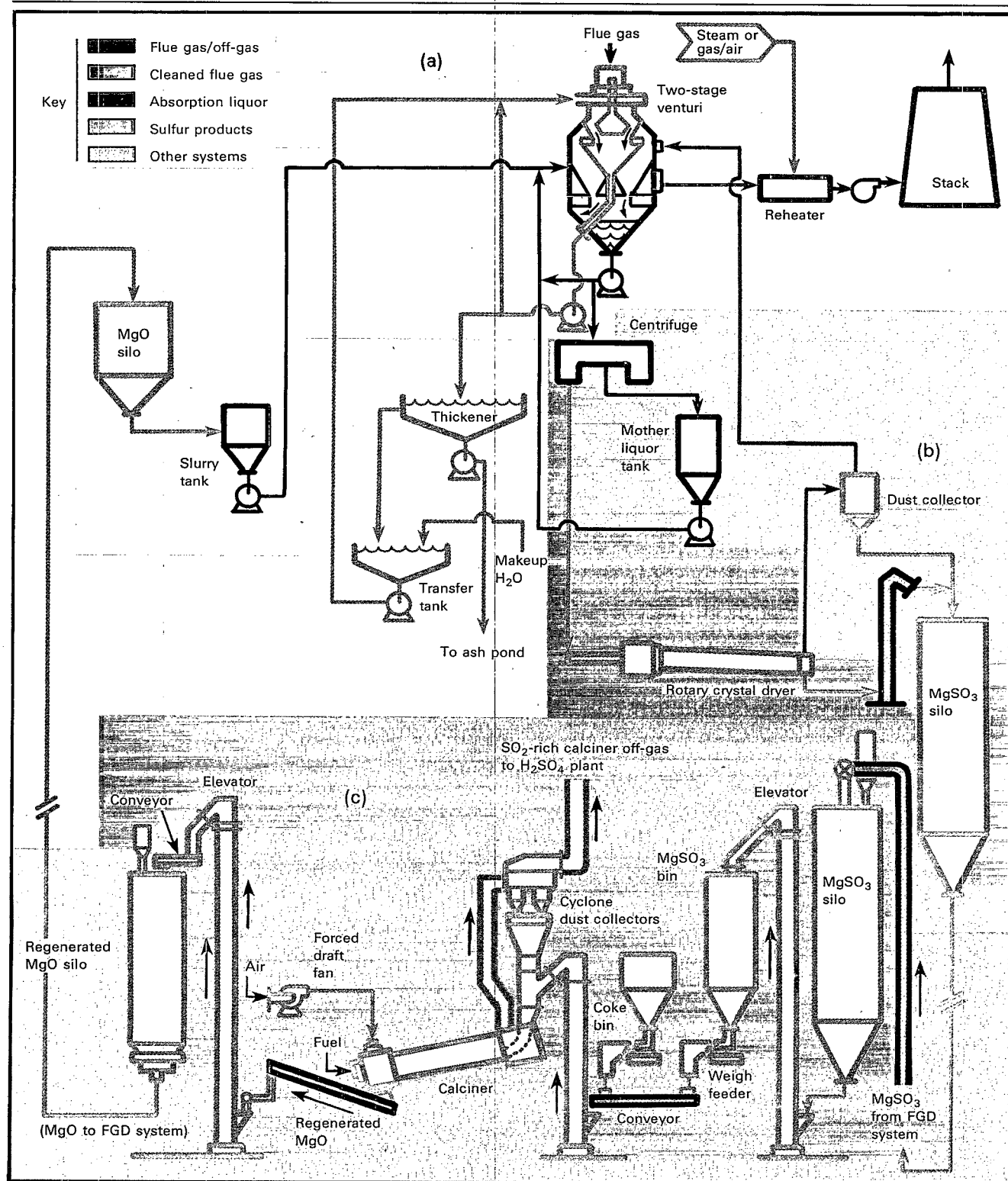


Figure 4.

Magnesium Oxide FGD Process: (a) SO₂ Absorption and Venting, (b) Solids Separation and Drying, and (c) Calcination/Regeneration

From the centrifuge the wet solids are conveyed to a dryer, typically a rotary kiln, for exposure to hot gases produced by combustion of fuel oil or natural gas. This direct firing removes surface moisture and water of hydration from the centrifuged solids to produce dehydrated MgSO_3 , MgSO_4 , MgO , and inerts (e.g., ash).

Off-gas from the dryer contains entrained solids, which are removed in a cyclone dust collector. The collected dust and the dryer product are stored in a silo for the regeneration processing step. The cleaned off-gas is routed to the venturi scrubber where it mixes with entering flue gas and is cleaned of remaining particles.

Regeneration

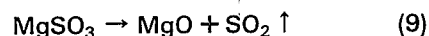
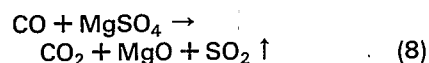
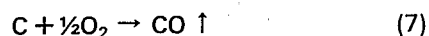
The dryer product is calcined, decomposing the magnesium salts to regenerate MgO and liberate SO_2 . Calcination temperatures are adjusted within the range of 750° to $1,850^\circ$ F (400° to $1,000^\circ$ C) for optimum reactivity and surface area of the product MgO . Calcination temperatures above $2,200^\circ$ F ($1,200^\circ$ C) will "hard burn" the MgO , whereas temperatures above $2,900^\circ$ F ($1,600^\circ$ C) will "dead burn" the material. Magnesium oxide, when it has been hard burned or dead burned, is unreactive and useless in FGD systems.

Several studies performed on thermal decomposition of magnesium sulfite revealed that some decomposition occurs even at temperatures as low as 570° F (300° C). In the range of 570° to $1,100^\circ$ F (300° to 600° C), decomposition of MgSO_3 can yield a relatively high percentage of MgSO_4 . Even at temperatures as high as $1,650^\circ$ F (900° C), MgSO_4 will form in unacceptable amounts unless gas phase compositions

are controlled carefully. At temperatures above $1,850^\circ$ F ($1,000^\circ$ C), MgO and SO_2 are the primary reaction products over a wide range of gas phase compositions.

In a typical calcination/regeneration operation (Figure 4c), dry magnesium salts from the FGD system dryer and cyclone are fed from an interim storage silo to an oil-fired fluid bed calciner. The calciner contains a single calcination bed designed to operate at $1,400^\circ$ to $1,600^\circ$ F (760° to 870° C).

Under ordinary conditions, calcination at this temperature produces high levels of magnesium sulfate. A reducing atmosphere may be achieved by adding a proportionate amount of carbon (coke) to the calciner feed. In the calciner, a reducing atmosphere prevents MgSO_4 production and ensures decomposition of any magnesium sulfate present in the calciner feed. The following reactions occur in the calciner:



Off-gas from the calciner contains about 10 percent sulfur dioxide. The gas stream is partially cleaned of particles in a cyclone and is routed to a sulfuric acid production unit. The collected particles join the incoming calciner feed stream and return to the calciner. A storage silo holds the regenerated MgO for reuse in the absorption system.

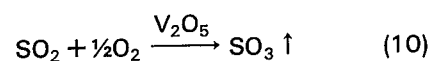
SO_2 Processing

Calciner off-gas contains approximately 10 percent SO_2 by volume, which is sufficient for the production of dry, compressed sulfur dioxide, sulfuric acid, elemental sulfur, and fertilizer materials.

Converting SO_2 to sulfuric acid requires prior treatment of the SO_2 -rich gas from the calciner. Cooling, drying, and cleaning take place in a weak acid venturi scrubber in series with a packed tower. The venturi cools and cleans the gas; the packed tower further cools the gas by contact with an acid stream. The latter step is necessary because the gas is saturated with water vapor when it leaves the venturi. The packed tower reduces the gas temperature to below 100° F (38° C), causing water to condense from the gas stream and producing a dried gas that is suitable for treatment in an acid plant.

Sulfuric acid production requires a feed stream containing 8.4 to 9.0 percent O_2 by volume. The feed gas first passes through a drying tower where it is dried by contact with 93 percent H_2SO_4 . Any SO_2 absorbed by the acid is removed in an acid-stripping tower and returned to the main gas stream. A small amount of air added to the gas with the SO_2 serves to adjust the oxygen concentration.

A blower draws the dried gas through a series of heat exchangers to raise its temperature to 815° F (435° C). This step supplies the heat necessary to sustain the subsequent reactions. As the hot gas enters a series of converter beds, it reacts with a vanadium pentoxide (V_2O_5) catalyst, and the SO_2 is oxidized to form SO_3 :



The hot, SO_3 -rich gas produced by this exothermic reaction is routed to the heat exchangers where it preheats the acid plant feed stream. The stream then enters the absorber and reacts with a weak



Surge hopper and slaking tank

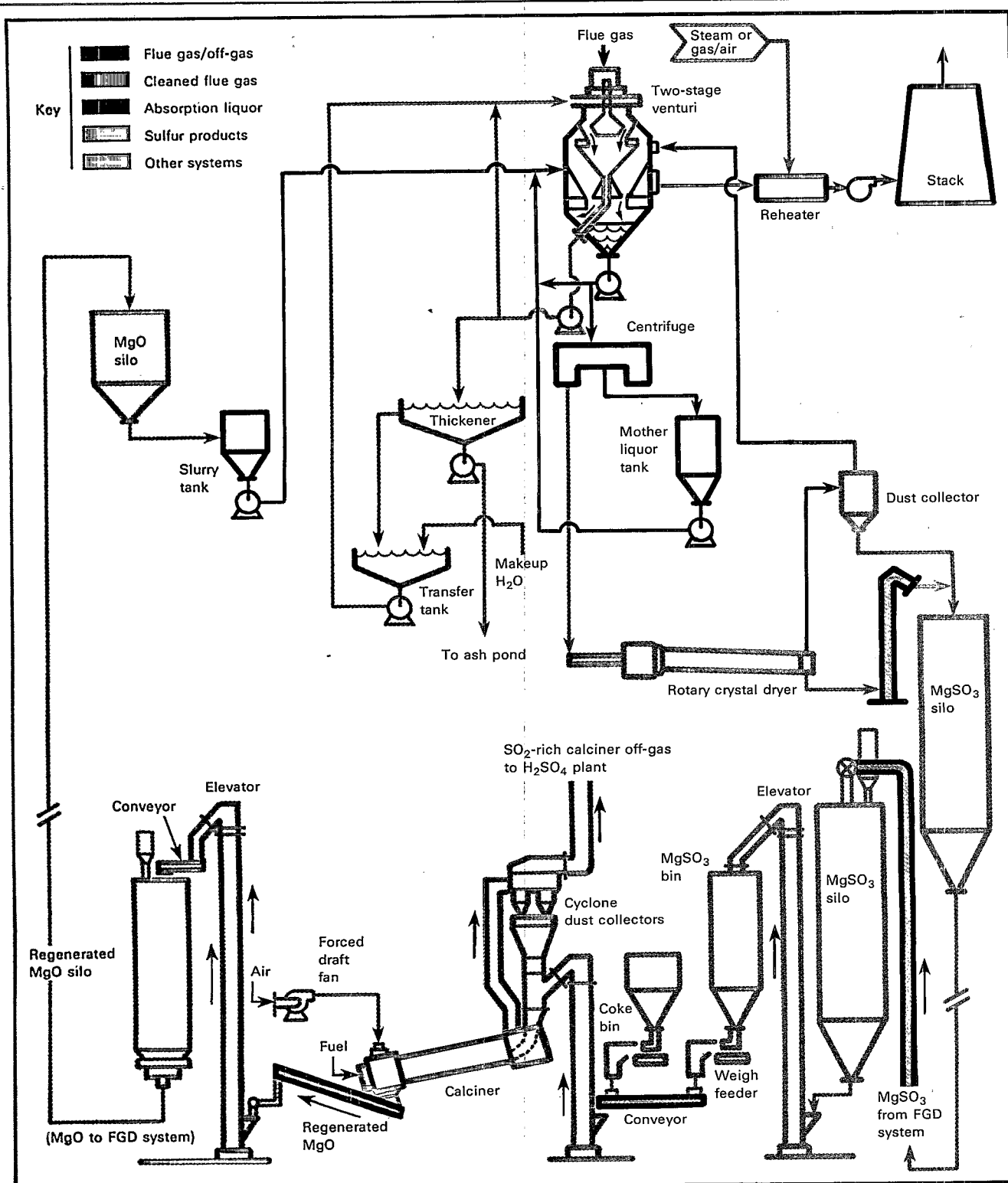
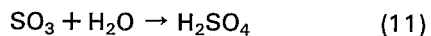


Figure 5.
General Magnesium Oxide FGD System

H₂SO₄ solution to form a more concentrated solution:



Typical SO₂-to-SO₃ conversion efficiencies for catalytic oxidation

range from 95 to 98 percent. Plants with efficiencies in the lower end of this range have high SO₂ emissions. Where regeneration and acid production are conducted on site, the acid plant tail gas can be recycled to the SO₂ absorber to achieve a higher conversion efficiency.³

Integrated System

The foregoing steps are part of the integrated system. Figure 5 shows the interrelationship of the processes of a typical MgO FGD system applied to a coal-fired boiler.

Design Considerations

Although a complete discussion of design considerations involved in the construction and operation of an MgO FGD system is beyond the scope of a summary report, the following discussion contains sufficient information to permit a general understanding of the process.

Pretreatment and Absorption

Particle and SO₂ removal efficiencies are the major concerns in the design and operation of pretreatment and absorption equipment. The venturi scrubber is preferred for fly ash removal because it attains high particle removal efficiency at minimum cost.⁴ The absorber used to remove sulfur dioxide from flue gas also may be of venturi design, though other scrubber systems, including mobile bed contactors or spray towers, are effective.² Packed towers or tray absorbers are not used often with slurry systems because they tend to become plugged.

The single-stage venturi scrubber used at Boston Edison's installation (Figure 6a) was designed by Chemical Construction Company (Chemico), which is now known as Chemico Air Pollution Control Company. A slightly different Chemico venturi was used in Pepco's coal-fired system (Figure 6b). The Pepco scrubber had two stages and was capable of flue gas pretreatment as well as absorption.

When flue gas enters a venturi scrubber, it comes into contact with a recirculating MgO slurry. At Boston Edison's installation, MgO slurry was introduced into the scrubber at three points (Figure 6a):

- Directly on the cone in the venturi throat
- On the annulus surrounding the cone
- Around the periphery of the venturi throat

The absorbing slurry entered the second stage of the Pepco venturi through tangential spray nozzles (Figure 6b). Both the Boston Edison and Pepco systems thus provided uniform slurry irrigation to the converging surfaces of the scrubbers.

Important factors to consider in the design and operation of any scrubber used in the MgO FGD process include such process variables as liquid-to-gas (L/G) ratios, pressure drop, and slurry pH. Based on pilot and operating tests with a venturi absorber, the optimum L/G ratio for SO₂ absorption is in the range of 20 to 40 gal/1,000 stdft³ (2.7 to 5.4 l/normal m³). Operating the absorber at an L/G ratio below 20 gal/1,000 stdft³ (2.7 l/normal m³) lowers the SO₂ removal efficiency. In contrast, operating with the L/G ratio above 40 gal/1,000 stdft³ (5.4 l/normal m³) results in a higher pressure drop across the absorber with marginal improvement in SO₂ removal efficiency.¹

As the flue gas accelerates through the venturi throat, a pressure drop is established. The venturi must be operated at a minimum pressure drop to keep energy consumption low. In coal-fired applications, a fixed pressure drop is essential to maintain first-stage efficiency. Maximum efficiency of particle removal results from specific droplet size distribution, which is directly related to the flue gas velocity. Second-stage efficiency, however, can be maintained over the range of pressure drops indicated in the next paragraph. Gas absorption, unlike particle removal, requires a constant specific surface area of the dispersed liquid, which, in the venturi, is self-regulating over a range of gas flows.⁵

At both the Boston Edison and Pepco installations, SO₂ removal efficiencies of over 90 percent were

attained with a pressure drop of 6 to 11 inches H_2O (1.5 to 2.7 kPa).⁶ Particle removal efficiency at Pepco's first-stage venturi was optimized at a pressure drop of 11 inches H_2O (2.7 kPa). Experiments were conducted at Pepco's installation to test the particle removal efficiency of a boiler electrostatic precipitator (ESP) operating in conjunction with the prescrubber. Particle removal efficiency was greater than 99 percent when the flue gas was taken directly from the boiler and not preconditioned by the ESP.⁷

Tests conducted at Boston Edison's Mystic Station indicate that sulfur dioxide removal efficiency is a direct function of the slurry pH.⁶ The scrubbing liquor pH is controlled by the addition of fresh MgO slurry to the absorber and the concurrent withdrawal of spent scrubbing liquor from the recirculation loop. Fresh MgO slurry raises the scrubbing liquor pH and increases the SO_2 removal efficiency of the absorber. At basic pH values, the absorbent solubility decreases, and higher L/G ratios are necessary to maintain removal efficiency.² At Boston Edison's installation, the recycle slurry pH was maintained between 6.8 and 7.5; Pepco's recycle pH was optimized at 7.0.

The MgO slaking operation presented problems at both Boston Edison's and Pepco's demonstration plants. Initial designs for the MgO FGD process specified an agitation tank for MgO slaking but did not account for differences in slaking between regenerated and fresh MgO . Because regenerated MgO was not slaked as easily as fresh MgO , problems developed in the absorber that resulted in reduced SO_2 removal efficiencies.¹ Modifying the slaking equipment to incorporate premix tanks and steam heaters alleviated the slaking problem.

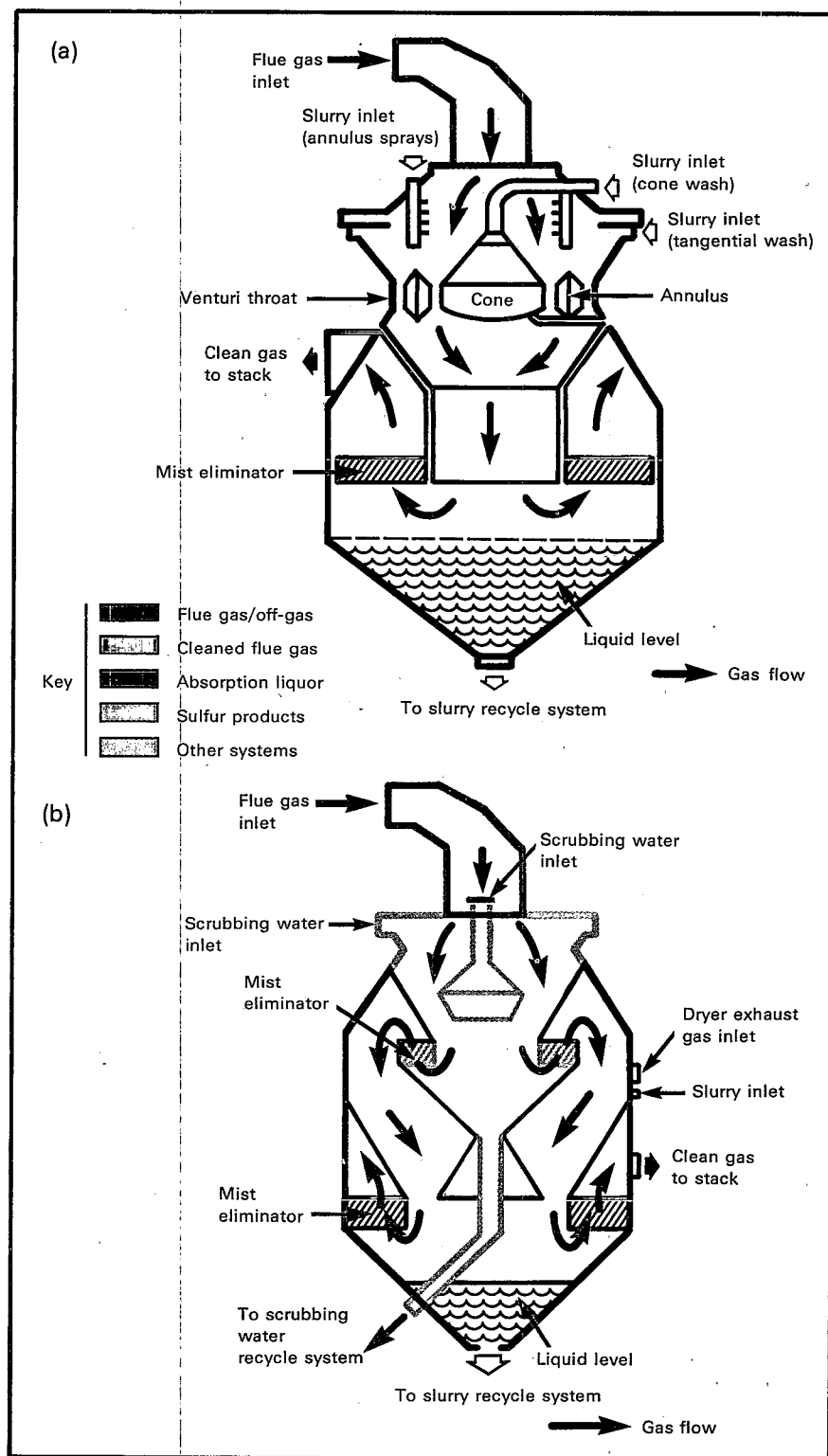


Figure 6.

(a) One-Stage Venturi Scrubber at Boston Edison's Installation and (b) Two-Stage Venturi Scrubber at Pepco's Installation

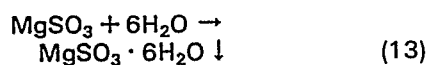
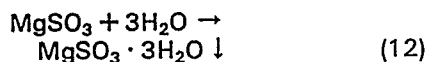
Reheating

Reheating of desulfurized flue gas may be necessary to prevent condensation of water vapor as gas is ejected from the stack to the atmosphere. Reheating may be accomplished by heat exchange with high pressure steam. A typical reheater consists of a series of shell-and-tube heat exchangers that can raise the temperature of the gas to 175° F (80° C). At the Boston Edison and Pepco installations, however, no reheating was provided for the flue gas other than that accomplished by mixing with hot, untreated gas from the boiler.

Solids Separation and Drying

Off-gas from the dryer contains entrained solids that are removed in a cyclone dust collector. At Boston Edison's installation, the collected dust and the dryer product were transferred separately to a silo for storage until regeneration processing. Because the Pepco system used a cocurrent dryer, dust recovered from the off-gas was fed directly to the dryer product, and the two were conveyed together to the storage silo. At both installations, the cleaned off-gas was routed back to the venturi absorber where it mixed with entering flue gas and was cleaned of remaining particles.

The major factor affecting the solids separation and drying equipment is the type of MgSO_3 crystals to be processed by the dryer. Both magnesium sulfite trihydrate ($\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$) and magnesium sulfite hexahydrate ($\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$) can be formed in the absorber:



Based on initial pilot tests, the Boston Edison scrubber was designed to process $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$

crystals. Shortly after operation began, however, it was discovered that $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ crystals were forming in the absorber. Because the $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ crystals are much finer than $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ crystals, excessive dusting and accumulation of solids occurred in the dryer. Drying ability decreased, and such modifications as installation of screens and lump breakers were necessary to alleviate the problem.

An EPA-sponsored study recently established parameters for predicting whether trihydrate or hexahydrate crystals will form in the absorber. Hydration formation is a function of such variables as slurry density and volume, seed crystal size and composition, solution composition, and temperature.⁸ Familiarity with these parameters will help prevent further problems in the drying operation.

Regeneration

Two important design considerations for regeneration processing equipment are the physical location of the regeneration facility and calciner design.

Both the Boston Edison and Pepco demonstration units regenerated MgO off site at Essex Chemical's sulfuric acid plant in Rumford, Rhode Island. Several factors, however, must be considered in the selection of on-site versus off-site regeneration facilities.

On-site facilities are more economical in terms of fuel and transportation costs. At an on-site facility, the dryer product enters the calciner at approximately 400° F (200° C), whereas the calciner feed stream cools to ambient temperatures en route to an off-site regeneration facility. Fuel requirements for calcination increase as a result of:

- Heat loss
- Surface oxidation of MgSO_3 crystals during storage and transportation

In addition, trucking solids to and from an off-site regeneration facility increases operating costs for the FGD system.

Construction costs for regeneration facilities also must be considered. Only minor capital expenditure was required to modify the existing Essex Chemical Company plant for the MgO FGD process. In other instances, it may be more cost effective to send the solids produced by several power plants to a single regeneration and acid production facility. Benefits from operating such a centralized plant might offset increases in fuel and transportation costs.

Two basic calciner designs must be considered for use in magnesia regeneration. Essex Chemical's Rumford plant uses a rotary calciner, although fluid bed systems also are effective. Several companies concur that fluid bed regeneration eventually will be the more attractive alternative because its estimated overall operating costs are lower.²

Essex Chemical's rotary calciner required minor modifications during the Boston Edison demonstration. A friction seal was installed to prevent air leakage into the calciner's firing hood and maintain the proper reducing conditions for the conversion of MgSO_4 to MgO. A fan and short stack also were added to the calciner to prevent hydrocarbon startup vapors from entering the sulfuric acid towers and blackening the acid.⁶

SO₂ Processing

Because SO₂ conversion is a processing step that varies depending on the end product desired, only cursory design considerations are presented here.

Cost, storage, and transportation are some of the aspects that must be considered in the production of

sulfur, sulfuric acid, and dry, compressed sulfur dioxide. The capital costs of sulfur production are high because the operation is relatively complex. In addition, raw material and utility costs are approximately twice as high for sulfur production as for sulfuric acid production.

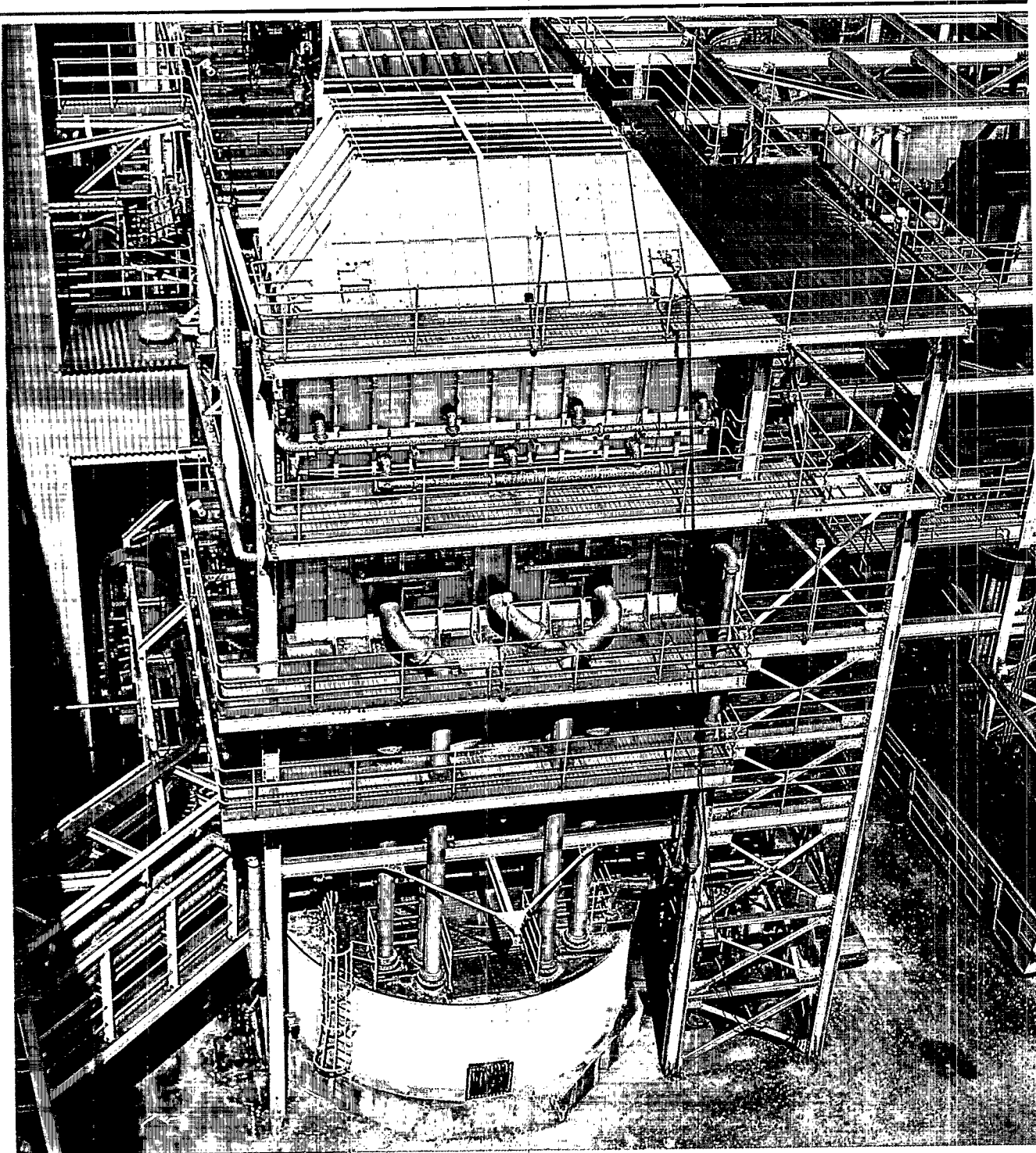
The major consideration in sulfur dioxide production is the limited market for dry, compressed SO_2 . Although liquid SO_2 is used in the food processing and paper industries, its marketing potential is low compared with those of sulfur and

sulfuric acid. For this reason, production of dry, compressed SO_2 is not a feasible alternative.

Although sulfuric acid is a highly marketable product, its generation requires considerable storage and transportation capacity. In addition, H_2SO_4 requires more care in handling because of its corrosive nature.

A trade-off exists between the reduced raw material and utility costs of acid production and the lower storage and transportation costs associated with sulfur production. Site-specific considerations, such as raw material availability, also

will affect the final SO_2 conversion process decision. A Tennessee Valley Authority (TVA) computerized marketing study of sulfur and sulfuric acid production concludes that FGD byproduct sulfur is not yet competitive with FGD byproduct sulfuric acid. Nevertheless, a relatively small reduction in total FGD byproduct sulfur costs could make byproduct sulfur production competitive.⁹ To date, all MgO FGD demonstration systems in the United States have selected H_2SO_4 production as the conversion process.



Eddystone magnesium oxide scrubber

Environmental Considerations

The MgO FGD process has demonstrated continued ability to remove sulfur dioxide from flue gas. System operation tests with both fresh and regenerated MgO at Boston Edison's Mystic Station and Pepco's Dickerson Station consistently have resulted in 90 percent or greater SO₂ removal.

As a regenerable process, MgO FGD eliminates the major waste disposal problems associated with such throwaway systems as lime/limestone and dual alkali FGD. Impurities accumulate in the closed system, however, and MgO FGD must provide for fly ash and chloride removal. Flue gas is pretreated to keep fly ash and chlorides out of the slurry. In coal-fired boiler applications, pretreatment removes over 99 percent of the particles in the flue gas stream. Boston Edison's oil-fired demonstration unit did not pretreat the flue gas and achieved particle removal efficiencies of only 50 to 70 percent. Approximately 70 percent of the chlorides can be removed in a venturi prescrubber; the remaining chlorides can be withdrawn in a spray chamber.¹⁰

Magnesium compounds are also important emissions from the MgO FGD process. Fugitive emissions of magnesium compounds include magnesium salts entrained in

flue gas vented from the absorber, scrubbing liquor spillage, and dust that escapes from the handling and transfer of dry magnesium compounds.

Measurements taken during a 13-day test at Boston Edison's Mystic Station to estimate magnesium losses from the system indicated a daily loss of 750 lb (340 kg) of magnesium from absorption and solids separation/drying. These decrements amount to approximately 3.5 percent of the MgO circulating in the FGD system. Further losses of 4.7 percent—1,000 lb/d (450 kg/d)—were measured during regeneration and acid production. These losses were caused primarily by the removal and disposal of large lumps of magnesium compounds from the calciner, however, and they can be reduced significantly by the addition of pulverizing equipment.¹

Status of Development

The MgO FGD technology was developed initially for use in the pulp and paper industry, which employs a magnesium-based liquor in the pulping operation. The pulping liquor is burned in a recovery furnace, producing MgO powder and an SO₂-rich stream. The MgO is slaked and routed to a series of venturi scrubbers where SO₂ is removed from the recovery furnace off-gas, thus regenerating the pulping liquor.

Efforts to apply the magnesium-pulping process to SO₂ scrubbing began in the 1930's. Research in Russia, Japan, Germany, and the United States to develop an FGD process using magnesia as the absorbent resulted in the following three major variations of the MgO wet scrubbing FGD process:

- A basic slurry of MgO and MgSO₃
- A slurry of MgO, MgSO₃, and a scrubbing reaction activator, manganese dioxide (MnO₂)
- An acidic solution of Mg(HSO₃)₂, MgSO₃, and MgSO₄

All three variations are feasible, but only the first two are capable of removing 90 percent SO₂ from flue gas. The high vapor pressure of sulfur dioxide over the solution of sulfites used in the third method lowers removal efficiencies to 80 to 85 percent.

Basic slurry is the process variation described in this report. The process was developed in the United States by Babcock and Wilcox Company of Barberton, Ohio, and by Chemico-Basic, a joint company formed by Chemico of New York and Basic Chemicals of Cleveland, Ohio. Russia and Japan also have concentrated on the basic slurry process, whereas Germany has investigated the scrubbing process that uses an MnO₂ activator.²

Three commercial scale MgO FGD systems have been installed on power plant boilers in the United States, and three more are being planned (Table 1). Although the EPA-sponsored demonstration programs at the Mystic and Dickerson Stations have been terminated, the testing has established the MgO FGD process as a feasible system for control of sulfur dioxide emissions.² Philadelphia Electric Company (Peco) collected valuable data at its Eddystone plant before the system was terminated. As a result of MgO FGD system performance, additional units are under construction at Peco installations.

Table 1.

Planned and Completed Magnesium Oxide FGD Systems in the United States

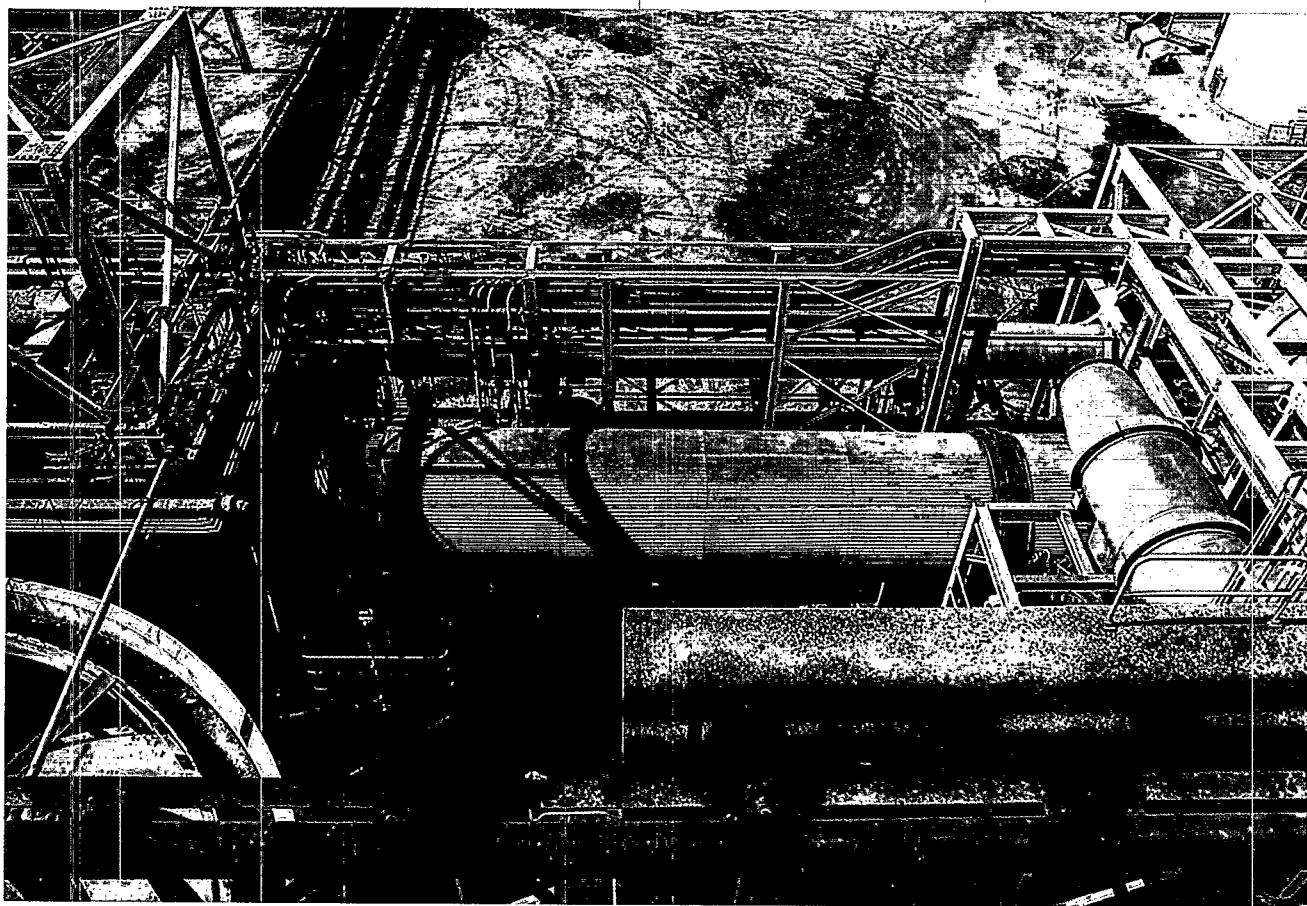
Utility company, station, and location ^a	FGD unit (MW)	Gas volume treated (1,000 stdft ³ /min)	Fuel		% SO ₂ removal (design)	Startup date	Status
			Type	% S			
Installed:							
Boston Edison, Mystic 6: Everett MA	150	307	Oil	2.5	90	1972	Terminated
Potomac Electric Power, Dickerson 3: Frederick MD . . .	95	213	Coal	3.5	NA	1973	Terminated
Philadelphia Electric, Eddystone 1A: Eddystone PA . . .	105	237	Coal	2.3	90	1975	Terminated
Planned: Philadelphia Electric:							
Cromby: Phoenixville PA	150	300 ^b	Coal	3.0	NA	1983	Under construction
Eddystone 1B: Eddystone PA	240	480 ^b	Coal	2.6	NA	1982	Under construction
Eddystone 2: Eddystone PA	334	670 ^b	Coal	2.5	NA	1982	Under construction

^aAll units shown are retrofit.

^bEstimated: stdft³/min = 2,000 × MW rating.

Note.—NA = not available.

SOURCES: Smith, M., M. Melia, and N. Gregory, *EPA Utility FGD Survey: April-June 1980*, EPA 600/7-80-029c, Research Triangle Park NC, July 1980. Smith, M., M. Melia, and N. Gregory, *EPA Utility FGD Survey: October-December 1979*, EPA 600/7-80-029a, NTIS No. Pb 80-176-811, Research Triangle Park NC, Jan. 1980. Sommerer, D. K., *Magnesia FGD Process Testing on a Coal-Fired Power Plant*, EPA 600/2-77-165, NTIS No. Pb 272-952, Research Triangle Park NC, Aug. 1977. Koehler, G., *Magnesia Scrubbing Applied to a Coal-Fired Power Plant*, EPA 600/7-77-018, NTIS No. Pb 266-228, Research Triangle Park NC, Mar. 1977. Koehler, G., and J. A. Burns, *The Magnesia Scrubbing Process as Applied to an Oil-Fired Power Plant*, EPA 600/2-75-057, NTIS No. Pb 247-201, Research Triangle Park NC, Oct. 1975. Isaacs, G. A., *Survey of Flue Gas Desulfurization Systems, Eddystone Station, Philadelphia Electric Company*, EPA 650/2-75-057f, NTIS No. Pb 247-085, Research Triangle Park NC, Sept. 1975.



Magnesium sulfite kiln heater

System Requirements

Raw Materials and Utilities

Compared with a lime/limestone process, the MgO FGD process has a relatively low raw material requirement and a relatively high FGD process energy requirement. Although the regeneration of MgO minimizes the cost of raw materials, the separation/drying and regeneration processing steps require substantial quantities of fuel oil, resulting in higher energy requirements for the process.

In terms of ground-to-ground energy requirements, MgO FGD compares more favorably with the lime/limestone process. A major factor is the energy credit for the byproduct sulfuric acid. Sulfuric acid usually is produced from elemental sulfur that is mined by the Frasch method, an energy-intensive operation. Byproduct acid production conserves the energy consumed by mining, transporting, and converting sulfur to sulfuric acid.¹⁰

Table 2 presents the estimated raw material and utility requirements for three different MgO FGD systems. The information is taken from a 1980 TVA study.

This information is based on converting the SO₂ stream from the regeneration processing area to H₂SO₄ in a conventional contact sulfuric acid plant. This conversion process requires a catalyst but generates a heat credit. Agricultural limestone is used to neutralize the chloride-rich bleed stream from the venturi prescrubber. These and other raw material and utility requirements vary for different conversion processes.

Installation Space and Land

Calculations have been made of the installation space required for an MgO FGD system applied to a new 500-MW boiler burning 3.5 percent coal. The total estimated requirement for the FGD unit and sulfuric acid plant is 2.34 acres (0.95 ha). Approximately 0.78 acre (0.32 ha), or one-third of this space, is required for the pretreatment and absorption processing equipment. An estimated 0.85 acre (0.34 ha) is required for the regeneration operation and 0.71 acre (0.29 ha) for the sulfuric acid plant. Space for the pretreatment and absorption equipment is the most critical

Table 2.

Estimated Raw Material and Utility Requirements for Magnesium Oxide FGD Process

Component	Size of new coal-fired plant (MW)		
	200	500	1,000
Raw materials:			
Magnesium oxide (tons/yr)	600	1,470	2,840
Catalyst ^a (ft ³ /yr)	26	64	120
Agricultural limestone (tons/yr)	1,330	3,240	6,260
Utilities:			
Fuel oil (10 ⁶ gal/yr)	2.6	6.3	12
Steam (10 ⁹ Btu/yr)	206	503	973
Process water (10 ⁶ gal/yr)	965	2,359	4,561
Electricity (10 ⁶ kWh/yr)	26	62	119
Heat credit (10 ⁹ Btu/yr)	55	136	262

^aCatalyst for sulfuric acid plant.

Note.—Base: 3.5% sulfur coal; plant operating time of 7,000 h/yr; meets emission regulation of 1.2 lb SO₂/10⁶ Btu.

SOURCE: Anderson, K. D., J. W. Barrier, W. E. O'Brien, and S. V. Tomlinson, *Definitive SO_x Control Process Evaluations: Limestone, Lime, and Magnesia FGD Processes*, EPA 600/7-80-001, NTIS No. Pb 80-196-314, Jan. 1980.



Figure 7 shows an example of a retrofit installation for the 150-MW Boston Edison installation. In general, retrofit installations require more and longer piping and ducting but do not require a prescrubber, because most existing boiler plants already have particle controls.

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Costs

Estimated and actual costs for an FGD installation can vary widely depending on the assumptions made, options included, degree of redundancy, and conditions of operation. Sample cost estimates prepared by TVA are presented in this report.

Table 3 delineates the capital and annual operating costs for MgO slurry FGD systems installed on different sizes and types of boilers. The costs are subject to variation, depending on site-specific factors.

Specific cases may be evaluated in terms of the bases used in Table 3.

Table 4 lists specific components of the annual operating costs for a typical MgO FGD system on a new boiler and provides examples of the contribution of each component to the annual operating cost.

MgO FGD is an equipment-intensive process with higher capital requirements than lime/limestone processes. Regeneration of the spent magnesia, including process-

Table 3.

Estimated Capital and Operating Costs for Magnesium Oxide FGD Process^a

System characteristics						Total capital investment ^b		Annual operating costs ^c	
Size (MW)	Application	Fuel		Plant life (yr)	% SO ₂ removal ^d	\$10 ⁶	\$/kW	\$10 ⁶	Mills/kWh
		Type	% S						
200	Existing	Coal	3.5	20	S	35.12	176	9.81	7.01
200	New	Coal	3.5	30	S	34.44	172	9.27	6.62
500	Existing	Coal	3.5	25	S	66.84	134	18.31	5.23
500	New	Coal	2.0	30	S	53.70	108	14.66	4.19
500	Existing	Oil	2.5	25	R	42.64	85	12.18	3.48
500	New	Coal	3.5	30	S	65.91	132	17.79	5.08
500	New	Coal	3.5	30	90	68.62	137	18.47	5.28
500	New	Coal	5.0	30	S	75.81	152	20.41	5.83
1,000	Existing	Coal	3.5	25	S	103.64	104	28.81	4.12
1,000	New	Coal	3.5	30	S	101.35	101	27.74	3.96

^aMidwest plant location. Stack gas reheat to 175° F. Investment and revenue requirement for fly ash removal and disposal excluded.

^bProject beginning mid-1977, ending mid-1980. Average cost base for scaling, mid-1979. Minimum in-process storage; only pumps are spared. Disposal pond located 1 mile from power plant. FGD process investment estimate begins with common feed plenum downstream of electrostatic precipitator. No overtime pay.

^c1980 revenue requirements. Power unit operating 7,000 h/yr.

^dS = meets emission regulation of 1.2 lb SO₂/10⁶ Btu. R = meets allowable emission of 0.8 lb SO₂/10⁶ Btu.

SOURCE: Anderson, K. D., J. W. Barrier, W. E. O'Brien, and S. V. Tomlinson, *Definitive SO_x Control Process Evaluations: Limestone, Lime, and Magnesia FGD Processes*, EPA 600/7-80-001, NTIS No. Pb 80-196-314, Jan. 1980.

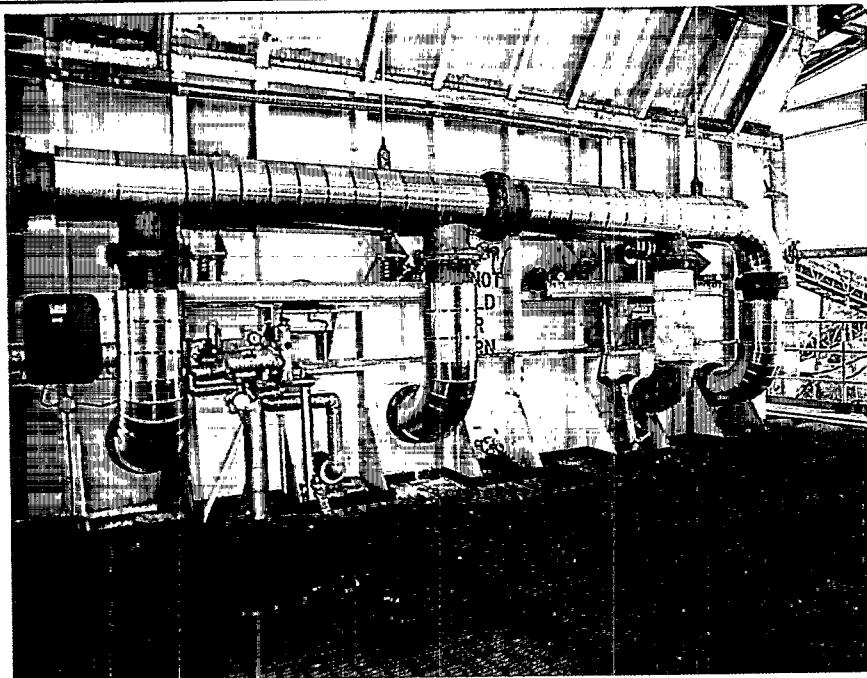
Table 4.

Annual Operating Costs for a Magnesium Oxide FGD System on a 500-MW Coal-Fired Boiler.

Component	Annual quantity	Costs		
		Unit (\$)	Annual operating (\$1,000)	Mills/kWh
Direct costs:				
Delivered raw materials:				
Magnesium oxide	1,470 tons	300.00/ton	441.00	0.126
Catalyst	64 ft ³	70.80/ft ³	4.50	0.001
Agricultural limestone	3,240 tons	15.00/ton	48.60	0.014
Total raw materials			494.10	0.141
Conversion costs:				
Operating labor and supervision	47,500 man-hours	12.50/man-hour	593.80	0.170
Utilities:				
Fuel oil	62.86 × 10 ⁵ gal	0.40/gal	2,514.30	0.718
Steam	503.4 × 10 ⁹ Btu	2.00/10 ⁶ Btu	1,006.80	0.288
Process water	2,359.2 × 10 ⁶ gal	0.12/10 ³ gal	283.10	0.081
Electricity	617.52 × 10 ⁵ kWh	0.029/kWh	1,790.80	0.512
Heat credit	135.60 × 10 ⁹ Btu	2.00/10 ⁶ Btu	(271.20)	(0.077)
Maintenance, labor and material			2,468.60	0.705
Analyses	8,500 man-hours	17.00/man-hour	144.50	0.041
Total conversion costs			8,530.70	2.438
Total direct costs			9,024.80	2.579
Indirect costs:				
Capital charges:				
Depreciation, interim replacements, and insurance at 6.0% of total depreciable investment			3,861.90	1.103
Average cost of capital and taxes at 8.6% of total capital investment			5,668.30	1.620
Overhead:				
Plant, 50% of conversion costs less utilities			1,603.50	0.458
Administrative, 10% of operating labor			59.40	0.017
Marketing, 10% of byproduct sales revenue			270.00	0.077
Total indirect costs			11,463.10	3.275
Gross average annual operating costs			20,487.90	5.854
Byproduct sales revenue, 100% sulfuric acid	108 × 10 ³ tons	25.00/ton	(2,700.00)	(0.771)
Net annual operating costs			17,787.90	5.083

Note.—Midwest plant location, 1980 revenue requirements. Remaining life of power plant, 30 yr. Power unit on-stream time, 7,000 h/yr. 1,500,100 tons/yr coal burned, 9,000 Btu/kWh. Stack gas reheat to 175° F. Meets emission regulation of 1.2 lb SO₂/10⁶ Btu. Investment and revenue requirement for removal and disposal of fly ash excluded. Total direct investment, \$35,354,000; total depreciable investment, \$64,365,000; total capital investment, \$65,911,000.

SOURCE: Anderson, K. D., J. W. Barrier, W. E. O'Brien, and S. V. Tomlinson, *Definitive SO_x Control Process Evaluations: Limestone, Lime, and Magnesia FGD Processes*, EPA 600/7-80-001, NTIS No. Pb 80-196-314, Jan. 1980.



Second-stage slurry ducting to scrubber

ing, drying, and calcination, requires a capital investment of almost \$9 million. The recovery system may also require chloride removal before the SO_2 absorber, necessitating an additional \$5 million. Sulfuric acid production, storage, and shipping increase costs another \$7 million. These capital requirements of approximately \$21 million exceed by over \$14 million the savings gained by eliminating disposal of solid waste in ponds.¹⁰

Under certain conditions, MgO FGD can be economically competitive with throwaway processes. Oil-fired installations, for instance, would not require a chloride prescrubber. At sites where disposal of slurry waste in ponds is not practical, the increased costs for fixation and landfill would also favor MgO FGD as an alternative.¹⁰

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This summary report was prepared jointly by the Radian Corporation of Austin TX and the Centec Corporation of Reston VA. Jack M. Burke and Elizabeth D. Gibson of Radian are the principal contributors. Michael A. Maxwell is the EPA Project Officer. Photographs were taken at Philadelphia Electric Company's Eddystone facility in Philadelphia PA.

Comments on or questions about this report or requests for information regarding EPA flue gas desulfurization programs should be addressed to:

Emissions/Effluent Technology Branch
Utilities and Industrial Power Division
IERL, USEPA (MD 61)
Research Triangle Park NC 27711

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COVER PHOTOGRAPH: Eddystone Unit No. 1 hardware and coal conveyor