AN EXAMINATION OF
ALKALI INJECTION - WET SCRUBBER PROCESS
DEMONSTRATION PROJECTS

NOVEMBER 1970

THE MITRE CORPORATION

MTR-1494

AN EXAMINATION OF ALKALI INJECTION - WET SCRUBBER PROCESS DEMONSTRATION PROJECTS

L. HOFFMAN

K. E. YEAGER

NOVEMBER 1970

Contract No.: F19628-68-C-0365

Contract Sponsor: National Air Pollution Control Administration

Project No.: 839C

THE MITRE CORPORATION
Washington Operations

Department and
Project Approval: Richard S Greeley

Richard S. Greeley

ABSTRACT

This paper discusses the operating experiences of two electric utility plants with prototype installations of the alkali injection-wet scrubber SO_2 removal process.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

AN EXAMINATION OF THE ALKALI INJECTION-WET SCRUBBER PROCESS DEMONSTRATION PROJECTS

INTRODUCTION

This paper describes the alkali injection-wet scrubber demonstration projects currently being performed at Union Electric Company, St. Louis, Missouri, and the Kansas Power and Light Company (KPL), Topeka, Kansas. The purpose of this paper is to examine the technical and economic factors associated with the commercial scale alkali injection-wet scrubber SO_2 emersion control systems installed in generating plants at these two utility companies. Although a number of commercial flue gas SO_2 removal systems are in various stages of development, the scrubber process installed at Union Electric and KPL is the only one for which full-scale utility operating experience is available. The use of these flue gas treatment processes in conjunction with coal pyrite removal prior to combustion may be the most practical method of achieving SO_2 emission goals without excluding the majority of utility coal fuel sources.

DESCRIPTION OF THE PROCESS

1. The tailend SO_2 removal process used by both Union Electric and KPL may be described as the Alkali Solids Injection-Wet Scrubbing Process. The utility installation of the process is diagrammed in Figure 1. In this process a solid, alkaline material (dolomite or limestone) is calcined by direct injection into the high-temperature section of the boiler. The solid calcined material reacts in the dry state with about 20% of the sulfur oxides present in the boiler gas stream, forming solid alkali-sulfur compounds. These compounds, unreacted additives, and flue gases enter a wet, turbulent-bed scrubber. The unreacted calcined additive dissolves in the solution circulating through the scrubber, supplying its alkalinity. Sulfur dioxide and any sulfur trioxide present in the flue gas dissolve in the same

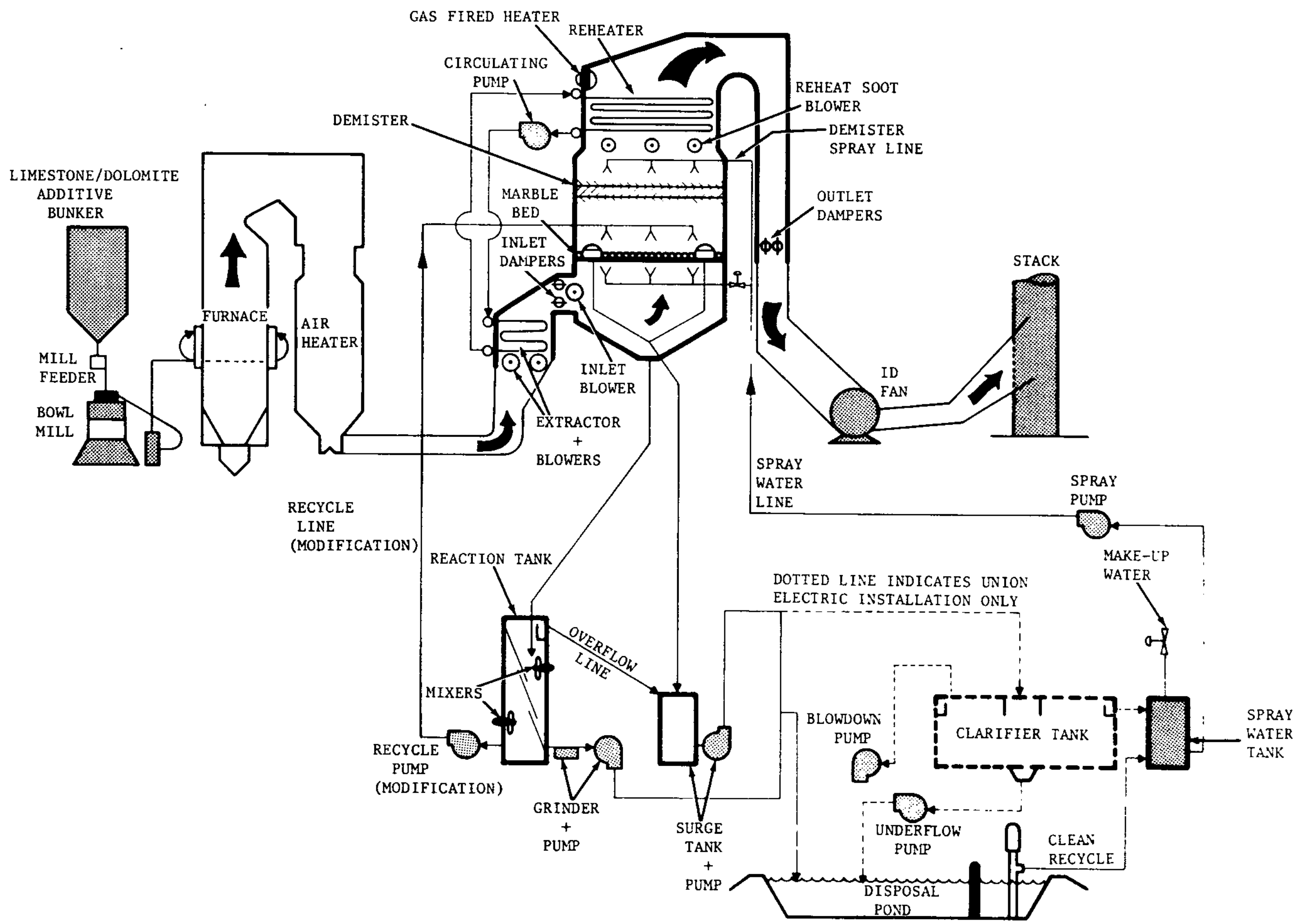

FIGURE I

ALKALINE INJECTION – WET SCRUBBING SO_2 REMOVAL PROCESS AS APPLIED TO UNION ELECTRIC MERAMEC STATION UNIT #2 AND KANSAS POWER AND LIGHT LAWRENCE STATION solution and react with the alkali to form sulfites and sulfates. In practice, this removes about 65% of the sulfur oxide in the flue gas. Because the solution circulating through the scrubber is saturated, these sulfites and sulfates precipitate and exit the scrubber as a slurry. On the order of 99% of the ash and any other particulates present in the flue gas are also removed in the scrubbing process. The settled solids from the scrubber, containing the sulfur and ash removed from the flue gas, are dewatered for disposal.

Although no efforts are made to recover marketable sulfur, the system is attractive because of its simplicity and low cost of installation relative to other tailend processes. It appears equivalent in cost to the tall stack and electrostatic precipitator combination with the advantage of both particulate and SO_2 removal.

2. Basic Operations and Probable Associated Reactions. The probable reactions occurring during each reactive phase of the alkali solid injection-wet scrubbing SO_2 removal process may be summarized as follows:

a. Injection of Alkali Solids - Calcination

$$CaCO_3 \cdot MgCO_3(s) \longrightarrow CaCO_3(s) + MgO(s) + CO_2(g) \qquad (1)$$

Reaction temperature = 850°F - 1900°F

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad (2)$$

Reaction temperature = 1400°F - 2250°F

b. Dry State Reactions in Furnace

$$CaO \cdot MgO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CaSO_4(s) \cdot MgSO_4(s) \qquad (3)$$

$$CaO \cdot MgO(s) + SO_2(g) \longrightarrow CaSO_3(s) \cdot MgSO_4(s) \qquad (4)$$

$$CaSO_3 \cdot MgSO_3(s) + \tfrac{1}{2}O_2(g) \longrightarrow CaSO_4(s) \cdot MgSO_4(s) \qquad (5)$$

Reaction temperature = 1400°F to 1550°F (lower temperature limit for calcination of $CaCO_3$ to upper temperature limit for $MgO + SO_2$ reaction)

c. Flue Gas Scrubbing

$$SO_2(g) + OH^-(l) \longrightarrow HSO_3^-(l) \quad (6)$$

$$HSO_3^-(l) + OH^-(l) \longrightarrow SO_3^=(l) + H_2O \quad (7)$$

$$CaO(s)\cdot MgO(s) + 2H_2O(l) \longrightarrow Ca^{++}\cdot Mg^{++}(l) + 4OH^-(l) \quad (8)$$

$$Ca^{++}\cdot Mg^{++}(l) + 2SO_3^=(l) \longrightarrow CaSO_3\cdot MgSO_3(s) \quad (9)$$

$$CaSO_3\cdot MgSO_3(s) + O_2(g) \longrightarrow CaSO_4\cdot MgSO_4(s) \quad (10)$$

3. The economic credit of the alkali injection-wet scrubber process is corrosion reduction at both high and low temperatures. At high temperature the sulfur contaminants in coal can form K_3-or Na_3 Fe $(SO_4)_3$, a corrosive compound which in its molten state at temperatures above 1100°F can cause corrosive damage to super-heater and reheater pipes. This has forced the utility industry to stabilize boiler steam temperature at 1000°F to avoid the costs of maintenance and power outages caused by corrosion. These costs have been estimated at 10 to 20 cents per ton of coal burned, depending on the coal composition. This corrosion "barrier" has restricted the development of higher temperature, more thermally efficient steam cycles when using coal as a fuel. Limestone and dolomite preferentially retain the alkalies as double salts of the type K_2 Ca_2 $(SO_4)_3$ thus preventing formation of the corrosive alkali-iron-trisulfate.

In the low temperature section of the boiler, the air reheater, and the flue gas ducts, sulfur trioxide reacts with water vapor in the flue gas to form sulfuric acid. If the flue gas temperature falls below the acid dewpoint, the acid condenses and corrodes the surrounding metallic surfaces. The magnesium oxide in dolomite has been shown to effectively reduce the low temperature corrosion through removal of the gaseous sulfur trioxide during the combustion process.

4. An important consideration in this wet scrubber SO_2 removal system is possible pollution of ground water by the process effluent. The calcium sulfite formed in the process is a particular danger since it will remove oxygen from ground water if settling ponds are not carefully isolated. The possible basicity of the process effluent can also seriously effect the ecological balance if drainage into surrounding streams occurs. A third factor necessitating effluent isolation is the formation of magnesium sulfate, more commonly known as Epsom salts, when dolomite is used as a reactant.

5. Both the Union Electric and KPL scrubber systems were designed and installed by Combustion Engineering, Inc. The KPL system, however, involved relatively more direct engineering support from the KPL engineering staff during design and installation.

6. Both utilities had basically fixed-price contracts with Combustion Engineering for the design, fabrication, and installation of the scrubber system. Improvement modifications after installation have been performed at Combustion Engineering's expense.

7. The wet scrubber system designed by Combustion Engineering had previously been employed on a pilot plant scale at Detroit Edison. On the basis of this experience, Combustion Engineering announced to the utility industry that they had a SO_2 removal system in which sufficient confidence was available to guarantee performance. Combustion Engineering, in addition, requested that the utility industry provide operating utility plants to demonstrate the full scale capability of the system. Union Electric and KPL responded because this appeared to be the least expensive and most reliable SO_2 removal system available to meet or exceed SO_2 emission control regulations.

8. The primary installation and operating differences between the two facilities may be summarized as follows:

a. The KPL system is designed with externally controlled baffles to quickly isolate the scrubber system for maintenance. The Union Electric system requires installation and removal of welded-in plates.

This change to take the scrubber on- or off-line requires 16 welders for 3 shifts (384 man-hours) plus boiler cool down and start up time.

b. The KPL system uses a dilute scrubber solution as produced in a 37 million gallon settling pond. The Union Electric system uses a relatively concentrated solution as produced in a 100,000 gallon clarifier.

c. The KPL system currently operates at 110% stoichiometric limestone injection, while Union Electric employs 130%. This difference may possibly be traced to excessive calcination in the Union Electric installation where injection occurs at a higher temperature furnace zone than that at KPL, plus the use of dolomite rather than pure limestone. The $MgCO_3$ in dolomite has a lower temperature zone for reactive calcination than $CaCO_3$.

UNION ELECTRIC EXPERIENCE

Discussions were held with Mr. J. F. McLaughlin, Executive Assistant, Union Electric Company, to discuss the cleaning concept and economics. The Meramec power plant was then visited where conferences were held with Messrs. Schaefer and Tapperson concerning the scrubber and its operating history. In addition, the inoperative scrubber installation was closely inspected. Observations are summarized as follows:

1. The scrubber is presently off-line with modifications being made. It is not expected that the unit will be put back into use until after the high July and August electrical load period.

2. The system was designed and installed on the Meramec No. 2 generating unit between October 1967 and June 1968. The No. 2 generating unit has a maximum generating capability of 140 MW and uses four pulverizers. When the scrubber is operating, one of the four pulverizers is used to handle the limestone.

3. The design of the system is such that the entire generating unit must be taken off-line and cooled down in order to make any modifications required.

4. Operating the scrubber system has revealed many problems that were unexpected though not surprising considering the pilot nature of the installation. Although the Union Electric scrubber installation is advertised as a "demonstrator" unit, consideration has not been given to the installation and operating implications inherent in such as innovative demonstration. The apparent expectation of immediate operating reliability has limited the operating and maintenance flexibility designed into the installation. The resultant expenses in both time and money, plus the fact that Union Electric is mainly coal oriented, with limited fuel switchover capability, has tended to create a negative reaction to the scrubber project in Union Electric management. Difficulties have arisen in the following areas:

a. The wash water system for cleaning deposits on the heat exchanger carried over to the I.D. fans and caused a heavy build-up of deposits on the fan blades. Sand blasting was required to remove the deposits.

b. In a very short time, calcium sulfate deposits restricted the overflow drain screens.

c. When operating the system longer than a few days, plugging of the marble-bed occured.

d. The marble-bed plugging caused carry over of water and solids to the demister and reheater. As a result, the reheaters of both scrubbers became plugged.

e. Deposit buildups have occured at the scrubber inlets.

f. The clarifier and slurry pumping systems have had plugging problems.

Extensive modifications have been, and are currently, in progress to overcome problems that have surfaced during system operation.

Table I shows total days during which the scrubber was operational and the type of operation during each test period:

TABLE I

SCRUBBER OPERATING LOG

From	To	No Load	Gas Firing 50-125 MW	Coal Firing 50-55 MW	Coal Firing 100-110 MW	Total Days
9-9-68	10-5-68	4	17	-	4	25
11-11-68	12-5-68	5 1/2	-	11	9	25 1/2
2-15-69	3-2-69	8	-	6 1/2	1 1/2	16
3-16-69	6-21-69	-	1/2	1 1/2	3	5
10-3-69	10-10-69	-	-	3 1/2	3 1/2	7
11-24-69	12-22-69	2	-	6	20	28
2-16-70	3-25-70*	10 1/2	-	6 1/4	20 1/4	37

*Unit was shut down temporarily from March 6 to March 17 but not converted to precipitator operation.

The actual period of coal firing at 100-110 MW output is the significant portion of the total operating period when considering system performance.

KANSAS POWER AND LIGHT EXPERIENCE

Discussions were held with Mr. C. Green, Assistant Manager of Electric Production; Mr. M. Funston, Production Engineer; and Mr. L. Brunton, Plant Engineer, Lawrence Power Station.

1. The wet scrubber system is installed on a 125 MW Unit at the Lawrence Station for evaluation purposes prior to installation on a new coal burning 425 MW Unit. The wet scrubber was chosen because studies indicated that it could be purchased and installed at the same cost as an electrostatic precipitator but with the advantage of SO_2 removal.

2. The installation on the 125 MW Unit was performed to gain operating experience and to ensure the reliability of the scrubber system prior to installation on the new coal fired 425 MW Unit, which will be in service in 1971. This attitude, which is significantly different than that of Union Electric, is reflected in the basic design of the scrubber installation which permits rapid changeover from on-line to off-line for maintenance and experimentation. The KPL Utility Company, with the exception of the new 425 MW Unit, is a gas burning system. Coal use is limited to the winter season when competing gas demands limit the amount of gas available. This reliance on gas permits continued use of the generator unit without the scrubber.

KPL installed their scrubber system as an experimental prototype to ensure ultimate success of such a system on the first primary coal fired unit in their system. It is interesting to note that the KPL purchased both the prototype scrubber and the scrubber system to be installed on the 425 MW Unit at the same time. This would motivate KPL to ensure the success of the project. Union Electric, on the other hand, did not consider their scrubber installation as a prototype and, as a probable result, did not design maintenance and experimental flexibility into their installation.

3. In the KPL system, the optimum quantity of limestone injected is about 110% of the stoichiometric amount for the $CaO + H_2SO_4$ reaction. Originally the installation used a higher percentage of limestone because of excessive calcination, thus leading to lower than expected reactivity of the alkali oxides. This was solved by moving the limestone injector higher in the furnace to reduce calcination temperature. This produces a pH of 5.5 - 6.5 in the marble bed with a resultant unreacted SO_2 emission of 300 - 350 ppm (equivalent to about 0.5% sulfur per ton of coal burned). The tradeoff involved in determining pH level is operating reliability against higher SO_2 removal. At a lower pH, for example 4.5, the reaction produces soluble bisulfite with no reliability problems but SO_2 emission increases to about 600 ppm. At higher than optimum pH, SO_2 emission as low as 200 ppm has been achieved, but sulfite production rapidly blocks the scrubber water feed and drain headers.

PROCESS COST ESTIMATES

The following discussion of alkali injection-wet scrubber economics is based on the Union Electric Company estimates. These estimates are preliminary, based on projections developed prior to actual demonstration test experience. Where noted, these estimates have been modified to account for demonstration test results to date.

TABLE II

OPERATING ECONOMICS

Costs	(cents) Per Ton Coal
Dolomite 11.2% X 2,000 lb. = 224 lb./ton coal (Dolomite $1.10/ton + frt. $1.67/ton = $2.77/ton)	31.0
Dolomite handling & grinding cost (25 cents/ton dolomite)	2.8
Calcining dolomite (extra fuel required - 120,000 BTU/ton coal; coal at 21¢/MBTU)	2.5
Power Cost	9.0
Added disposal cost at $0.50/ton	5.6
Makeup water $500/yr.	0.1
Cost Total	51.0

Credits	(cents) Per Ton Coal
Corrosion savings	5.3
Precipitator operating savings	2.0
Steam coil	1.1
Credit Total	8.4

Net Operating Costs (without fixed chgs.) 42.6 cents

TABLE III

CAPITAL COSTS FOR 140 MW UNIT WET SCRUBBER SYSTEM

Equipment furnished by Combustion Engineering	$ 830,000	($1,400,000)*
30,000 manhours @ 8.00/hr.	240,000	
Foundations and concrete	112,000	
Electrical wiring, starters, etc.	50,000	
Partition of coal bunker	15,000	
Slurry concentrate disposal	10,000	
Fly ash dust hopper discharge	20,000	
Raw water makeup piping	10,000	
Total Capital	$1,287,000	($1,857,000)
Assume 15.2% fixed charge rate	195,000	($ 282,000)

*The cost of equipment furnished by Combustion Engineering is considered to be commercially low for two factors:

(1) Operating experience has indicated that corrosion resistant materials should be used to achieve practical reliability. It is estimated that this will increase equipment costs by about 10%.

(2) Combustion Engineering sold the system at below cost in an effort to gain entry to the market. A practical market price would be on the order of 40% above that indicated.

Based on these factors, a practical 1970 planning cost estimate of the Combustion Engineering equipment would be $10 per KW of plant capacity.

TABLE IV

FIXED CHARGES, LABOR, AND MAINTENANCE

Year	Estimated Load Factor %	Coal Tons Burned 10^3	Cost/Ton Coal Burned (cents) Fixed Chgs. ($195,000)	Maint. ($39,000)	Labor ($10,000)	Total Cents
1967	65	355	55.0	11.0	2.8	68.8
1970	30	165	118.0	23.6	6.1	147.7
1971	28	152	128.0	25.6	6.6	160.2
1975	20	110	177.5	35.5	9.1	222.1
1980	15	82	238.0	47.5	12.2	297.7
1984	11	60	325.0	65.0	16.7	406.7
15 Yr. Avg. (1970-84)	19	104	188.0	37.5	9.6	235.1

TABLE V

SUMMARY OF ESTIMATED AND PROJECTED OPERATING COST

Year	Estimated Load Factor %	Net Oper. Cost (¢)	Air Pollution Control System Operating Cost/Ton Coal Burned: Fixed Chgs. (Labor & Maint.(¢)	Total Cost ($)
1967	65	42.6	68.8	1.11
1970	30	42.6	147.7	1.90
1971	28	42.6	160.2	2.03
1975	20	42.6	222.1	2.65
1980	15	42.6	297.7	3.40
1984	11	42.6	406.7	4.49
15 Yr. Avg. (1970-84)	19	42.6	235.1	$ 2.78

These figures must be taken with caution due to the developmental nature of the installation and limited operating history. Figure 2 indicates the scrubber operating cost per ton of coal burned for both (1) the Union Electric estimate and (2) a prediction for general operational application on existing stationary power plants at the conditions indicated.

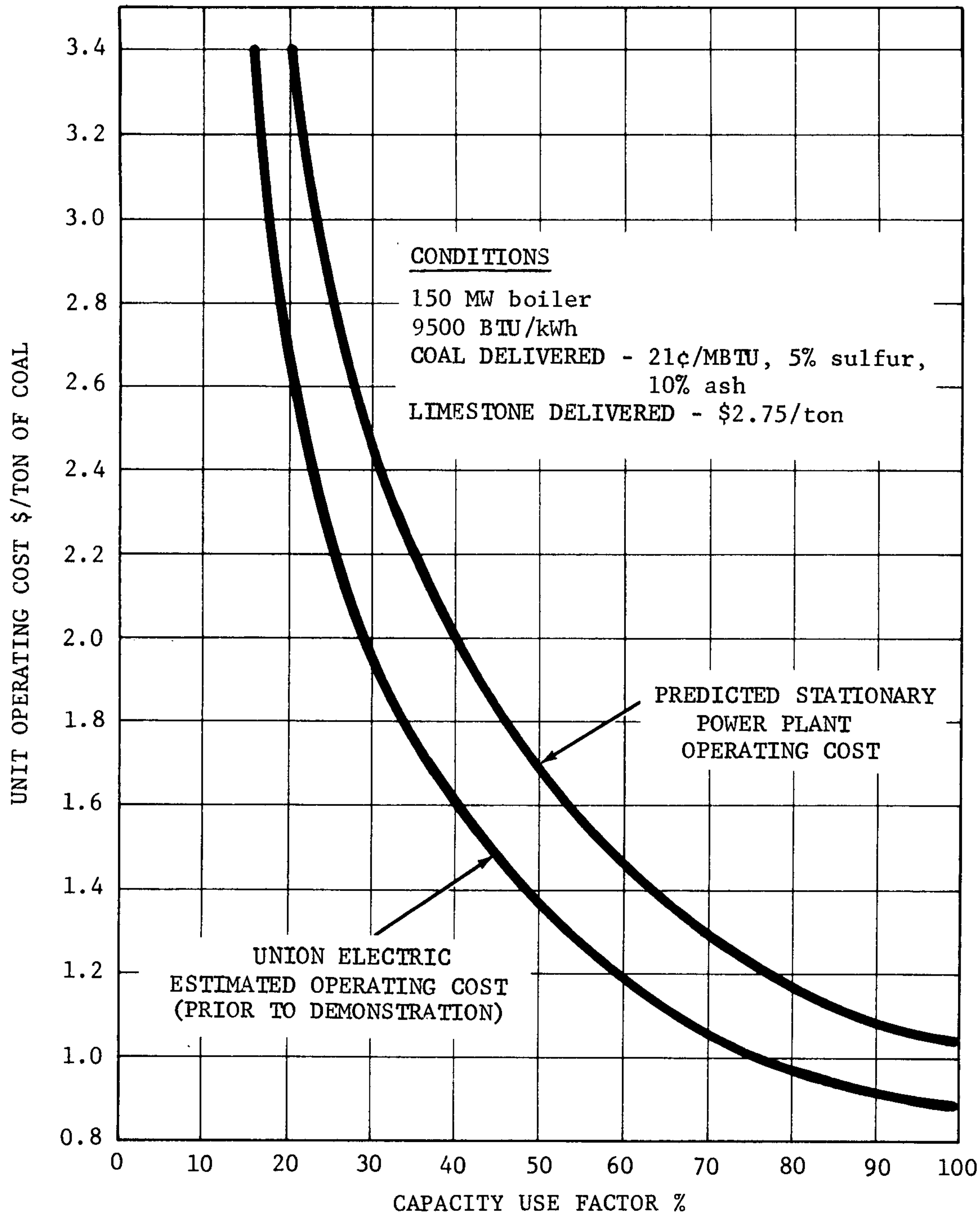

FIGURE 2
ALKALI INJECTION-WET SCRUBBER OPERATING COST

SUMMARY DISCUSSION

The comparison of the wet scrubber system installation at Union Electric and KPL are summarized in Table VI. It is evident that similar problem areas have been discovered at both. The common problems may be traced to solid deposit buildup caused by the combination of fly ash, moisture, and calcium sulfate/sulfite. This solid deposit in the dry state has structural properties similar to concrete.

The dilute scrubber solution at KPL has tended to reduce the speed of this deposit buildup and permit longer scrubber operating periods compared to Union Electric. By the same token, these longer operation periods have focused attention on corrosion problems which have not yet been experienced at Union Electric.

Analysis of Table VI indicates that the problems discovered to date in the full-scale application of the alkali injection-wet scrubber process may be traced to design deficiencies in the integration of the scrubber with the utility steam plant, not technical shortcomings of the scrubber system itself. The problems encountered thus far have not been in meeting the SO_2 and particulate removal design goals, but rather in maintaining the operating reliability of the process and the furnace components with which it interfaces. These design deficiencies may be summarized as follows:

a. Inadequate consideration given to handling and disposing of the large quantities of solid alkali/ash deposits formed during the full-scale scrubbing process.

b. Insufficient use of corrosion resistant materials in the scrubber and associated plumbing.

The factors which create these deficiencies are predictable and are routinely considered by the chemical industry in scaling laboratory or pilot plant processes to full-scale operation. Unfortunately the utility industry and their equipment suppliers do not seem to have

TABLE VI

COMPARISON OF UNION ELECTRIC COMPANY AND KANSAS POWER AND LIGHT COMPANY

	UNION ELECTRIC CO.[1]	KPL CO.[2]
1. Furnace Installation	Tangentially fired coal, gas 140 MW	Tangentially fired gas, oil, coal 125 MK
2. Reactive Additive	$CaCO_3 \cdot MgCO_3$	$CaCO_3$
3. Begin Install.	October 1967	October 1968
Begin Operation	19 September 1968	28 November 1968
4. Coal Properities	3% Sulfur, 10% Ash, 11,200 BTU	3.5% Sulfur, 11.5 - 12.5% Ash, 12,500 BTU
5. Primary System Installation Differences	(1)Concentrated scrubber solution from 100K gallon clarifier (2)Difficult on stream/off stream capability	(1) Dilute scrubber solution from 37M gallon settling pond (2) Simplified on stream/off stream capability
6. Limestone Ratio	130% stoichiometric (11% dolomite by weight)	110% stoichiometric
7. Efficiency	99% particulate removal 80% SO_2 removal	99% particulate removal 80% SO_2 removal
8. Problems [Solutions]	(1)Flue gas reheater water wash system carried moisture into ID fan causing deposit buildup on fan blades [a.installed eductor system on fan boxer. b.installed plume reheater] (2)Calcium sulfate buildup on overflow drain screen [increase drain opening size] (3)Marble bed plugging [improved gas distribution] (4)Reheater plugging [soot blowers installed] (5)Scrubber inlet deposits [soot blowers installed] (6)Excessive limestone required for SO_2 removal [recycle scrubber underflow which contains active calcium hydroxide] (7)Ash deposit buildup on underflow return lines [increase pipe dimension]	(1)Scrubber inlet deposit [modification to reduce stagnant boundary layer] (2)Reheater plugging [flow guides and soot blower installed suggest moving demister as high as possible in stack] (3)Corrosion of scrubber tank and feed lines [coat or replace with corrosion-resistant material] (4)Reheater plugging [soot blower installed] (5)Poor SO_2 removal [recycle scrubber underflow water which contains reactive calcium hydroxide] (6)Limestone overburning with resultant poor reactivity [Raise limestone injector higher in furnace] (7)Ash buildup on flow lines under scrubber falls off and blocks drain [increase drain dimensions] (8)Recycled scrubber water inpinged on drain pots causing deposit buildup [reposition drain pots]

applied chemical engineering experience with the reactants and products of the alkali injection-wet scrubbing process in their demonstration and test design. As a result, solutions to these problems are being achieved by slow, costly, trial and error methods. Since scrubber reliability directly affects the total electrical generation reliability of the utility plant with which it is integrated, such methods produce a negative reaction toward the wet scrubbing process in particular and SO_2 emission control in general. The risks which these trial and error "demonstrations" illuminate, combined with the full capacity production requirements of most utilities, may effectively stall efforts to introduce SO_2 emission control in the electric utility industry.

It is suggested that the utilization of appropriate chemical engineering expertise in the design of the wet-scrubbing installations examined could have avoided, prior to installation, many of the operational problems experienced to date.

Finally, the lack of commonality in the design of stationary power source boilers, flues, reheaters, and other components with which the scrubber system must interface does not appear to have been considered in the design and evaluation of the demonstration test projects examined. These interface variations can affect many factors involved in successfully installing a scrubber system, including the following:

- Position of alkali injection
- Alkali/coal ratio
- Concentration of scrubbing solution
- Flow characteristics of the flue system
- Corrosion sensitivity of scrubber hardware
- Dimensions of scrubber flow lines
- Position and operating characteristics of soot blowers

Disciplines normally foreign to the electric utility industry should be consulted to design both demonstration installations and systematic test programs to quantify these installation factors over the range of abatement process/stationary power source interface combinations. The ultimate success of the design, conduct, and evaluation of these qualification test programs also rests on removing them from the control of either the individual utility or the developer advocating the specific SO_2 removal system. Until the responsibility for demonstration testing is placed with an independent, inter-disciplinary organization capable of objectively viewing the entire system within which the SO_2 removal process must operate, each operational SO_2 removal installation can be expected to be an expensive and time-consuming individual "demonstration" project.

REFERENCES

1. J. F. McLaughlin and J. Jonakin, "Operating Experience with Wet-Dolomite Scrubbing", 69-139, Presented at Air Pollution Control Association Annual Meeting, New York, N. Y., June 22-26, 1969.

2. Daric M. Miller, "Experience with Wet Scrubber for SO_2 Removal at the Lawrence Station of the Kansas Power and Light Company," Special Report Number 85, Presented to Society of Mining Engineers of AIME, Salt Lake City, Utah, September 19, 1969, Kansas Engineering Experiment Station, Kansas State University.

DISTRIBUTION LIST

D-12

C. A. Zraket
R. L. Kirby

D-02

W. F. Mason

D-22

R. S. Greeley	(5)
L. Hoffman	(5)
W. D. Rowe	(5)
K. E. Yeager	(5)
Department File	(25)

A-01

C. E. Duke

NAPCA
Bureau of Engineering and
Physical Sciences (25)

Washington Library

Bedford Library