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Research and Development

PROCEEDINGS: 1991 SO₂ CONTROL SYMPOSIUM Volume 3. Sessions 5B and 6

Prepared for

Office of Air Quality Planning and Standards

Prepared by

Air and Energy Engineering Research Laboratory Research Triangle Park NC 27711

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3-6, 1991, in Washington, DC, and jointly Institute (EPRI), the U.S. Environmental I partment of Energy (DOE). The symposium ments in conventional SO2 control technolo for complying with the Clean Air Act Ameri ternational forum for the exchange of techn control technology. More than 800 represe academia, flue gas desulfurization (FGD) p turers, engineering firms, and utilities at utilities in other countries were represent presented 111 technical papers on developm wet and dry FGD, clean coal technologies, (SOx/NOx) processes.	sponsored by the Electric Protection Agency (EPA), m focused attention on re- ogies, emerging processes adments (CAAA) of 1990. Dical and regulatory information intatives of 20 countries for process suppliers, equipm tended. In all, 50 U.S. ut ed. In 11 technical session ent, operation, and comm and combined sulfur oxid	Power Research and the U.S. De- cent improve- s, and strategies It provided an in- mation on SO2 rom government, nent manufac- ilities and 10 ons, speakers nercialization of le/nitrogen oxide
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Volume 3. Sessions 5B and 6

For Sponsors:

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Brian K. Gallett Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711

ABSTRACT

These are the Proceedings of the 1991 SO₂ Control Symposium held December 3-6, 1991, in Washington, D.C. The symposium, jointly sponsored by the Electric Power Research Institute (EPRI), the U.S. Environmental Protection Agency (EPA), and the U.S. Department of Energy (DOE), focused attention on recent improvements in conventional sulfur dioxide (SO₂) control technologies, emerging processes, and strategies for complying with the Clean Air Act Amendments of 1990. This is the first SO₂ Control Symposium co-sponsored by EPRI, EPA and DOE. Its purpose was to provide a forum for the exchange of technical and regulatory information on SO₂ control technology.

Over 850 representatives of 20 countries from government, academia, flue gas desulfurization (FGD) process suppliers, equipment manufacturers, engineering firms, and utilities attended. In all, 50 U.S. utilities and 10 utilities in other countries were represented. A diverse group of speakers presented 112 technical papers on development, operation, and commercialization of wet and dry FGD, Clean Coal Technologies, and combined sulfur dioxide/nitrogen oxides (SO2/NOx) processes. Since the 1990 SO2 Control Symposium, the Clean Air Act Amendments have been passed. Clean Air Act Compliance issues were discussed in a panel discussion on emission allowance trading and a session on compliance strategies for coal-fired boilers.

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PREFACE

The 1991 SO₂ Control Symposium was held December 3-6, 1991, in Washington, D.C. The symposium, jointly sponsored by the Electric Power Research Institute (EPRI), the U.S. Environmental Protection Agency (EPA), and the U.S. Department of Energy (DOE), focused attention on recent improvements in conventional sulfur dioxide (SO₂) control technologies, emerging processes, and strategies for complying with the Clean Air Act Amendments of 1990.

The proceedings from this Symposium have been compiled in five volumes, containing 111 presented papers covering 14 technical sessions:

Session	Subject Area
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I Opening Remarks by EPRLEPA and DOE Guest Speakers

- 1 Emission Allowance Panel Discussion
- 2 Clean Air Act Compliance Strategies
- 3A Wet FGD Process Improvements
- 3B Furnace Sorbent Injection
- 4A Wet FGD Design Improvements
- 4B Dry FGD Technologies
- 5A Wet FGD Full Scale Operations
- 5B Combined SOx/NOx Technologies
- 6A Wet FGD Operating Issues
- 6B Clean Coal Demonstrations/Emerging Technologies
- 7 Poster Session papers on all aspects of SO₂ control
- 8A Commercial FGD Designs
- 8B FGD By-Product Utilization

These proceedings also contain opening remarks by the co-sponsors and comments by the three guest speakers. The guest speakers were Shelley Fidler - Assistant, Policy subcommittee on Energy and Power, U. S. Congress,

Jack S. Siegel - Deputy Assistant Secretary, Office of Coal Technology, U.S. Department of Energy, and Michael Shapiro - Deputy Assistant Adminstrator, Office of Air and Radiation, U.S. Environmental Protection Agency.

The assistance of Steve Hoffman, independent, in preparing the manuscript is gratefully acknowledged.

The following persons organized this symposium:

- Barbara Toole O'Neil Co-Chair, Electric Power Research Institute
- Charles Drummond Co-Chair, U.S. Department of Energy
- Brian K. Gullett Co-Chair, U.S. Environmental Protection Agency
- Pam Turner and Ellen Lanum Symposium Coordinators, Electric Power Research Institute

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1991 SO₂ CONTROL SYMPOSIUM

Opening Session

Session Chair: M. Maxwell - EPA

I-1 EPRI Perspective - S.M. Dalton

I-2 EPA Perspective - M. Maxwell

DOE Perspective - P. Bailey (no written manuscript)

Guest Speakers

Shelley Fidler - Assistant, Policy subcommittee on energy and Power, U. S. Congress

...

Jack S. Siegel - Deputy Assistant Secretary, Office of Coal

Technology, U.S. Department of Energy

Michael Shapiro - Deputy Assistant Adminstrator, Office of Air and Radiation, U. S. Environmental Protection Agency

Session 1 - Clean Air Act Compliance Issues/Panel

Session Moderator: S. Jenkins, Tampa Electric Co.

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Comments by: Alice LeBlanc - Environmental Defense Fund Karl Moor, Esq., Balch & Bingham John Palmisano AER*X Craig A. Glazer - Chair, Ohio Public Utilities Commission

Session 2 -Clean Air Act Compliance Strategies

Session Chair: Paul T. Radcliffe - EPRI

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	Consolidation Coal Co.
2-2	Scrub Vs. Trade: Enemies or Allies? J. Platt, EPRI
2-3	Evaluating Compliance Options, J.H. Wile, National Economic
	Research Association, Inc.
2-4	Clean Air Technology Workstation, D. Sopocy, Sargent & Lundy
2-5	Economic Evaluations of 27 FGD Processes, R.J. Keeth, United
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2-6	Strategies for Meeting Sulfur Abatement Targets in the UK Electricity
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2-7	Compliance Strategies for Future Capacity Additions: The Role of
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	Co.
2-8	IPL Petersburg 1 & 2 CAAA Retrofit FGDs, C.P. Wedig, Stone &
	Webster Engineering Corp.
2-9	Evaluation of SO ₂ Control Compliance Strategies at Virginia Power,
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Session Chair: David R. Owens - EPRI

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3A-6	Techniques for Evaluating Alternative Reagent Supplies, C.V. Weilert
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3A-7	Factors Involved in the Selection of Limestones for Use in Wet FGD
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3A-8	Magnesium-Enhanced Lime Reaction Tank Design Tests at EPRI's
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Session 3B - Furnace Sorbent Injection Session Chair: Brian Gullett - EPA

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3B-2	Studies of the Initial Stage of the High Temperature CaO-SO2 Reaction,
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3B-3	Status of the Tangentially Fired LIMB Demonstration Program at
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	Engineering Systems
3B-4	Results from LIMB Extension Testing at the Ohio Edison Edgewater
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Session Chair: Richard E. Tischer - DOE

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4A-3	Increasing Draft Capability for Retrofit Flue Gas Desulfurization
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4A-4	Development of Advanced Retrofit FGD Designs, C.E. Dene, EPRI
4A-5	Acid Rain FGD Systems Retrofits, A.J. doVale, Wheelabrator Air
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4A-7	Economic Comparison of Materials of Construction of Wet FGD
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4A-8	The Intelligence & Economics of F.R.P. in F.G.D. Systems, E.J. Boucher,
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	4B-3	Scaleup Tests and Supporting Research for the Development of Duct
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6A-3	Managing Air Toxics: Status of EPRI PISCES Project, W. Chow, EPRI
6A-4	Results of Mist Elimination System Testing in an Air-Water Pilot
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Session 5B

COMBINED SOx/NOx TECHNOLOGIES

SIMULTANEOUS SOX, NOX REMOVAL EMPLOYING ABSORBENT PREPARED FROM FLY ASH

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ABSTRACT

Hokkaido Electric Power Co. and Mitsubishi Heavy Industries Ltd. have jointly started a program for the development of a simplified, effective and economical flue gas treatment system since the beginning of last year. This system employs absorbent of a Lively Intensified Lime-Ash Compound (LILAC), which is produced by fly ash, lime and gypsum through a hot water curing process, and we therefore have named our system as the "Lilac Process".

This absorbent is highly reactive with SO2 and NOx in flue gas and is sprayed into the flue gas in the form of either slurry or powder.

The resultant solids are collected in the dust collector (Bag filter or Electrostatic precipitator) installed downstream of the absorbent spraying.

First, the Lilac Process with spraying absorbent slurry has been established mainly for SO₂ removal from flue gas through a series of bench scale tests on reactivity of absorbent, absorbent production process, SO₂ removal efficiency, quantity of the absorbent sprayed, approach temperature in the spray dryer or the bag filter, and salt addition together with a series of model tests of a rotary atomizer which MHI has recently developed,

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employing a high frequency induction motor.

In the bench scale test more than 95% SO2 removal efficiency was attained when the absorbent was sprayed at Ca/S of 1.2 with 5wt% of chloride (Cl). In order to establish the details of process and mechanical design for commercial plants, a pilot plant having 10,000m³N/h capacity is being constructed in the Tomato Atsuma Power Station of Hokkaido Electric which will be commissioned in October 1991.

Second, the Lilac Process with spraying absorbent powder has been investigated by series of bench scale test at $80m^3N/h$ capacity, and simultaneous removal of 90% SO₂ and 70% NOx has been confirmed at Ca/S of 2.7 without any additives.

The duct injection nozzle and production facility of the powder reagent are also being installed in the pilot plant mentioned above and the demonstration of this process is planned to start in 1993.

Waste disposal from flue gas treatment is one of the big concerns in view of environmental protection and the potential for effective use of disposal material from the Lilac Process has been confirmed.

INTRODUCTION

Protection of global environment has been internationally recognized to be an important issue which should be immediately Japanese government has taken a positive attitude dealt with. toward solving global environmental problems such as acid-rain and global warming by offering technologies and finance. Our companies have also formulated a policy to participate in the international technical cooperation for protection of global environment based on our technology for the flue qas desulfurization system.

Acid rain is one of the crucial environmental problems caused by SOx and NOx emitted from various types of boiler and engines. We established have already а technology for flue aas desulfurization system in which fly ash is utilized as one of the components of absorbent to adapt coal burning boiler such as for electric power generation. The commercial plant of the dry type flue gas desulfurization system has been running for more than six months at the Tomato Atsuma Power Station.

Based on the established FGD system, we have extended R & D to develop more simplified, efficient and economical flue gas treatment system for more versatile demands. In the present paper, the newly developed flue gas treatment system is presented.

LILAC PROCESS WITH SPRAYING ABSORBENT SLURRY

Bench Scale Test Facility and Procedures

The test facility consists of two units, a gas treatment unit and an absorbent preparation unit (in Figure 1). The gas treatment unit (Figure 2) consists of a gas generator which produced test gas simulated as flue gas from a coal-fired boiler at temperatures of up to 140°, a spray dryer with air atomized spray nozzle, and a bag filter which can treat up to 20 m^3N/h of gas flow.

Gas sampling was taken from the inlet/outlet of the spray dryer and outlet of the bag filter.

The absorbent preparation unit (Figure 3) consists of a mixing tank and a curing tank made of glass having a 3 liters capacity. Fly ash, slaked lime and gypsum were mixed with water weighing 5 times the total solids in the mixing tank and this mixed solution was kept agitated at 95°C for 3, 6 or 12 hours in the curing tank corresponding to each test condition. The hot water cured solutions, called absorbent slurry, was sprayed into the prepared gas stream in the spray dryer. The slaked lime slurry was also tested in this facility as a base line test for corresponding conditions of various parameters such as inlet gas conditions, Ca/S, approach temperature, etc.

The effect of salt addition into the absorbent slurry was also confirmed by this test facility. The quantity of salt added was controlled so the disposal solid material contained 5 percent in weight of chlorine.

Bench Scale Test Results

The measured desulfurization efficiency in the spray dryer and the spray dryer plus the bag filter is shown in Figure 4 for various Ca/S.

Around 30% higher desulfurization efficiency was obtained by the hot water cured absorbent (12 hours) as compared to the slaked lime, which proves higher reactivity of amorphous compound of SiO₂, Al₂O₃, Ca(OH)₂ and CaSO₄ formed by a hot water curing.

The effect of the duration on hot water curing in absorbent preparation is shown in Figure 5. Comparing desulfurization efficiencies of various absorbent prepared by different curing time, the test results advise us that curing time should be around 6 hours. The microstructure of various absorbents are shown in Figure 6. The existence of amorphous compound showed higher reactivity of absorbent.

The effects of salt addition into the absorbent slurry is shown in Figure 7. Comparing desulfurization efficiencies of absorbent with/without seawater addition, the test results indicate about

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20% improvement in the desulfurization efficiency by the addition of seawater. This improvement would be understood as longer existence of water in the absorbent resulting from the effect of boiling point raise of salted water.

Pilot Plant

In order to demonstrate performance of the Lilac Process and to establish design parameters necessary for constructing a commercial scale plant, a pilo² plant having the following specifications is being constructed in the adjacent area of the No.2 boiler unit of Hokkaido Electric's Tomato Atsuma Power Station.

Capacity	: 10,000 m ³ N/h
Inlet SO2	: 370 - 2,000 ppm
NO	: 150 - 500 ppm
Fly ash	: 10 - 15 g/m ³ N ⁻
Temperature	: 130 - 150 C
Spray Dryer	: 2.8 mø × 12.9 mH
Rotary Atomizer	: 7.5 KW, 17,500 rpm
Dry Electrostatic Precipitator	: 94 m ²
Bag Filter	: 87 m ²
Curing Tank	: 1.11 $m^3 \times 4$ sets

The pilot plant has been so designed as to confirm process performances of ;

- 1. Hot water cured absorbent slurry production.
- 2. Hot water cured absorbent powder production.
- Desulfurization/denitration by combination of a spray dryer and a dry electrostatic precipitator or a bag filter.
- 4. Various combinations of SO2 and NO in the inlet gas by supplemental addition of these gases into the flue gas from the commercial 600MW coal-fired boiler.

The flow diagram of the pilot plant is shown in Figure 8 and a photograph of the side view of the plant in Figure 9. The rotary atomizer is the key piece of equipment for the plant and is specially designed to meet requirements for spraying the absorbent slurry.

The construction of the rotary atomizer using a high frequency induction motor is illustrated in Figure 10. Before installing it in the pilot plant, the rotary atomizer has been tested in the shop with absorbent slurry and .ts estimated performance was confirmed both in sprayed droplet size and power consumption, as shown in Figure 11.

LILAC PROCESS WITH SPRAYING ABSORBENT POWDER

Bench Scale Test Results

<u>Bench Scale Test Facility and Procedures</u>. The test facility for gas treatment unit was constructed at the Tomato Atsuma Power Station. The absorbent powder was prepared at a different place, and brought to the test facility. A part of flue gas from the coal-fired boiler of the commercial plant was diverted to the test facility as an inlet gas. The inlet gas volume was $80m^3N/h$.

Effect of SO2/NOX ratio on the removal of SO2 and NOX. The effect of SO2/NOX ratio on the simultaneous removal of SO2 and NOX was examined. The SO2/NOX ratio was varied by injecting of SO2 and/or NOX to the flue gas from the commercial boiler. Figure 13 shows the effects of the SO2/NOX ratio on the removal of SO2 and NOX. As the SO2/NOX ratio increased, the NOX removal rate drastically increased, but the SO2 removal rate gradually decreased.

Effect of reaction temperature on the removal of SO2 and NOX. As shown in Figure 14, SO2 removal rate is constant in the temperature range 70 - 130 C. NOx removal rate, however, is drastically increased between 70 - 90 C, and become constant above 90 C.

Effect of moisture on the removal of SO2 and NOX. As shown in Figure 15, as moisture of flue gas increased, both SO2 and NOx removal rate increased.

Reaction Mechanism of SO2, NOx removal

The tracer study in which $N^{18}O$ and ${}^{18}O_2$ were used demonstrates that the main species to oxidize SO₂ is the NO_2^- adsorbed on the surface of the absorbent. We propose the desulfurization

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reaction mechanisms as shown below:

Overall $2CaO + 2SO_2 + O_2 = 2CaSO_4$ Elementary process $2NO + O_2 = 2NO_2$ $SO_2 + NO_2 = SO_3 + NO$ $CaO + SO_3 = CaSO_4$

In contrast to the desulfurization mechanisms, the denitration mechanisms are not definite yet. However, it is known that NOx is fixed in the form of CaNO3 and that SO2 is associated with the oxidation of NO, because NOx removal rate increased with an increase in the SO2/NOx ratio, as shown in Figure 16 In addition, the NOx removal rate increases linearly with the SiO2 content in the absorbent, suggesting that SiO2 plays an important role in the denitration. mechanism (Figure 17)

POTENTIAL UTILIZATION OF SPENT ABSORBENT

Waste disposal material from the LILAC Process named Spent Absorbent (SA) is a neutral and a stable material. The leaching value examination for its harmful components was within the acceptable limit of the Japanese quality standard for landfill materials.

SA can be used as one of the raw materials for preparation of the absorbent in place of gypsum, because SA contains a high percentage of gypsum. For the same reason, SA is expected to be used as a construction material.

Other utilizations of SA are now examined for use in the following.

Treatment for sludge

Since SA is a porous material and has ability to coagulate and deodorize, it can be used for sludge treatment and cleaning of muddy water.

Deodorizing agent

The ability of SA to absorb NH3 and H2S makes it a possible deodorizing agent.

CAPITAL COST AND LEVELIZED COST

In order to evaluate economic aspect of the Lilac process FGD plant, investment costs and operation costs of the following three FGD plants were estimated under the same process design criteria and economic criteria.

- 1. Lilac Process (with Bag Filter)
- 2. Spray Dry Process with lime absorbent (with Bag Filter)
- Wet Limestone Gypsum Process (with Dry Electrostatic Precipitator)

For the scope of complete FGD plant (including desulfurization towers and dust collectors, absorbent storage and preparation facility, by-product/waste material storage and loading facility) for a 250MW pulverized coal-fired generating plant, the investment cost of the Lilac Process is found to be 80 while that of the Spray Dry Process is 80 and that of the Wet Limestone Gypsum Process is 100.

The operation costs (total cost of raw materials, utilities, operation and maintenance, finance and management) levelized as expense per ton of SO2 on the other hand is 95 for the Lilac Process, 110 for the Spray Dry Process and 100 for the Wet Limestone Gypsum Process .

CONCLUSION

The Lilac Process is featured for its higher SO2 removal with absorbent slurry spraying and for its simultaneous SO2 and NOx removal with absorbent powder spraying, which the existing flue gas treatment systems are unable to achieve costwise as well it is competitive with the presently available systems. In addition its spent absorbents are valuable utilizable resources for deodorization agent and construction material production. From all considerations, Lilac Process is a promising comprehensive flue gas treatment system of high performance.

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Note: (5): Gas Sampling



Figure 2 Bench Scale Test Facility for Gas Treatment Unit



Figure 3 Bench Scale Test Facility for Absorbent Preparation Unit











Figure 5 Activity of Absorbent by Curing Time



Curing Time = 3 hours Curing Time = 12 hours Figure 6 Microstructure of Absorbent (×50,000)



Figure 7 Effect of Salt Addition into Absorbent



Figure 8 Process Flow Diagram of Pilot Plant

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I.

Figure 9 Pilot Plant



Figure 10 Construction of Rotary Atomizer









Figure 12 Flow Diagram of Bench Scale Test Facility (Absorbent Powder)



Figure 13 Effect of SO2/NOx Ratio on SO2. NOx Removal Rate



Figure 14 Effect of Reaction temperature on SO2, NOx Removal Rate







Figure 16 Effect of SO2/NOx Ratio (Laboratory Test)



Figure 17 Effect of SiO₂ Content on the activity (Laboratory Test) (Activity: Defined to be a period to keep removal % above 80%)

Furnace Slurry Injection for Simultaneous SO₂/NOx Removal

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ABSTRACT

This paper discusses the results of a cooperative research venture between the U.S. Environmental Protection Agency and Nalco Fuel Tech investigating furnace urea/sorbent slurry injection for joint SO_2/NO_1 removal. This emission reduction technology has been developed as a low capital cost option for electric utilities and industrial sources in response to the 1990 Clean Air Act Amendments. The slurry was composed of a urea-based solution and various Ca-based sorbents, totalling 30% solids by weight. Testing on a natural gas pilot scale reactor achieved 80% reduction of SO_2 and NO_4 at reactant/pollutant stoichiometric ratios of 2/1 and 1/1, respectively. SO_2 emission reductions from slurry injection were enhanced compared with dry Ca(OH)₂ sorbent injection methods possibly due to sorbent fracturing to smaller, more reactive particles. Further, the addition of the urea-based solution for NO₄ reduction had a synergistic effect upon SO₂ reduction. The effect of injection temperature and stoichiometric ratio upon SO₂, NO_x , NE₃, and N₂O was determined for the combined sorbent and urea-based solution. Emissions of NE₃ and N₂O when using a modified urea-based formulation were found to be significantly lower than previously reported data. The results of this pilot scale study have shown high reduction of both SO₂ and NO₄, suggesting the need for full scale studies to further assess this combined sorbent/urea-based solury injection technology.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

Passage of the 1990 Clean Air Act Amendments has initiated extensive evaluation and planning for strategies to meet these stricter emission requirements. In a two phase approach, the Clean Air Act requires reduction of SO₂ emissions at 265 units by about 40% to 1075 ng SO₂/J (2.5 lb SO₂/million Btu) (based on 1985 to 1987 emissions) by January 1, 1995. By 2000 all SO₂ sources are affected and must reduce emissions to 516 ng SO₂/J (1.2 lb SO₂/million Btu). In addition, the second phase brings a cap on emissions at 8.08 million Mg SO₂ (8.9 million tons), or about 9.08 million Mg (10 million tons) less than SO₂ emissions in 1980. Thus, new sources must be offset by further reduction in emissions from existing sources. The regulations call for reduction in NO₂ emissions consistent with capabilities of low-NO₂ burner technology, which is, as of yet, undefined. Additionally, the possibility of trading NO₂ for SO₂ emissions is under consideration [1].

Installation of wet scrubbers or fuel switching/modification is projected to account for up to 65% of the first phase compliance strategies [2]. However, utilities have an option for earning emission credits by adopting early compliance strategies or further reducing emission levels below those required. Among the early compliance options available to utilities is furnace sorbent injection technology. This retrofittable, lower capital cost technology may also be a likely candidate for long term compliance on older or smaller boilers, plants that are limited by physical space, or utilities that opt for low capital technologies.

Furnace sorbent injection is a technology that has been field tested on a number of units, achieving, for example, 63% removal at a Ca/S = 2/1 with a calcium hydroxide [Ca(OH)₂] sorbent and 72% with a surfactant-modified Ca(OH)₂ sorbent on a 105 MW(e) wall-fired unit [3]. A field demonstration on a 180 MW(e) tangentially fired unit should produce preliminary results around mid-1992 [4].

The anticipated NO_x regulations are likely to be met by a number of varied technologies including low NO_x burners, gas reburning, and selective or non-selective catalytic reduction. These technologies represent a range of removal efficiencies and costs. One of the more low cost, retrofittable options is selective non-catalytic reduction (SNCR) which has been shown to achieve 63% NO_x reduction on a 150 MW(e) coal boiler at a reductant/NO_x stoichiometric ratio (NSR) of $\approx 2/1$ [5] and has been the subject of numerous laboratory or pilot scale studies [6,7]. SNCR involves high temperature (about 800 to 1100°C) furnace injection of a N-based reducing agent such as urea (NH₂CONH₂) or ammonia (NH₃) which converts NO_x to N₂.

Most concerns with use of SNCR center around NH₃ slip resulting from incomplete reaction and production of nitrous oxide (N₂O) due to incomplete reduction. NH₃ slip can result in formation of ammonium bisulfate (NH₄HSO₄) and ammonium sulfate [(NH₄)₂SO₄] which readily deposit upon air preheater surfaces causing reduced heat transfer, increased pressure drop, and formation of NH₄Cl which causes a visible white plume in the stack emissions. N₂O has been implicated as a contributor to stratospheric ozone depletion [8] and global warming, the latter due to its ability to absorb infrared radiation [9]. Research has demonstrated that levels of N₂O and NH₃ emissions from various SNCR compounds are extremely sensitive to injection temperature [10,11]. Efforts to widen the applicable temperature injection window and control NH₃ slip and N₂O production through use of additives [12] have brought about some success, yet these remain concerns that need to be addressed on any SNCR-type process.

The U.S. EPA has conducted research at its Air and Energy Engineering Research Laboratory (AEERL) with Nalco Fuel Tech to investigate a combination of the furnace sorbent injection and SNCR technologies for simultaneous SO_2/NO_x control. The mechanism for this industry/Government research was the Federal Technology Transfer Act's (FTTA) Cooperative Research and Development Agreement (CRDA), an agreement whereby EPA can conduct research with private industry at EPA's research facilities. Research on a similar SO_2/NO_x control process has shown considerable merit [13], yet significant questions still remain in the industry concerning NH₃ emissions and N₂O by-product formation.

The objective of this research was to develop the technology of simultaneous SO_2 and NO_1 removal by injection of a Ca- and urea-based slurry while minimizing emissions of N_2O and NH_3 . Variables of operation included injection temperature, stoichiometric ratio, sorbent type, and urea-based solution composition. Emissions monitoring results for SO_2 , NO_2 , N_2O_3 , CO, and NH_3 are reported.

EXPERIMENTAL

Furnace

Dry sorbent and slurry injection tests were run on a pilot scale 14.7 kW (50,000 Btu/hr), refractory lined, down-fired cylindrical furnace capable of firing natural gas or coal. The furnace, termed the "Innovative Furnace Reactor" (IFR), has an inner diameter of 15.2 cm and an overall length of about 4 m (see Fig. 1). View and injection/probe ports traverse the length of the furnace for testing flexibility. The furnace is used to simulate the gaseous combustion environment and quench rate conditions anticipated in utility and industrial boilers. During natural gas firing, this is accomplished by doping the fuel with NH, (which is oxidized to form NO_x) and SO₂. Typical operating concentrations were 600 ppm NO_x and 2500 ppm SO₂. The furnace was operated with tangential and axial air totalling 0.39 m³/min (13.72 ft³/min) STP, including an excess air of 50%.

Emissions Sampling

Gas emissions are sampled in the horizontal arm section of the IFR (see Fig. 1) and pass through heated sample lines to continuous emission monitors (CEMs). Analysis of SO₂ concentration by an ultraviolet analyzer follows particle traps and a heated sample line (=350°C). SO₂ removal percentages reported in this work are typically determined by running at least six tests between Ca/S = 1/1 and Ca/S = 3/1. These values are then curve fit by a regression technique and interpolated to the reported removal at Ca/S = 2/1. NO_x is analyzed by a chemiluminescent method. This method reports NO_x concentrations that do not include NO₂; earlier tests showed that the NO₂ concentrations were below 5% of the total NO_x concentration. All gas emission results are corrected to 0% O_x levels.

Gases analyzed for CO_2 , O_2 , and CO were first passed through a gas dryer and a desiccant canister of anhydrous $CaSO_4$. All of the above on-line CEMs are zeroed and spanned with gases of known concentration both before and after each daily trial.

 N_2O concentrations were monitored by both on line gas chromatography (GC) and tunable diode laser infrared (TDIR) spectroscopy methods. The GC was used for analysis of grab samples taken before and during testing using procedures in Reference [14]. The TDIR was used to monitor real time stack N_2O emissions. The TDIR compares the infrared absorption of the gas sample to a known concentration of N_2O span gas at the wavelength of N_2O . This method and apparatus, which are detailed further in Reference [15], were calibrated for this work over the 20 to 80 ppm range, with an accuracy of +/- 0.75 ppm. The two methods' results were comparable. Tests conducted at six varying conditions showed a linear correlation coefficient exceeding 0.99 between the two methods (for further comparison of N_2O analytical methods see Reference [16]).

The analysis of stack gas NH₃ concentration was completed by wet methods using a Fisher Accument ion selective electrode. The stack gas was drawn through an impinger system containing 0.02N H₂SO₄. Prior to measurement, the pH was adjusted with 10M NaOH solution. The ion selective electrode, coupled with a pH meter, determines the NH₃ concentration. The meter and electrode were calibrated prior to analyses with known standards and checked throughout the testing to ensure that the values fell within the manufacturer's limits.

Sorbent/Urea Solution Injection

Testing during this work included dry sorbent injection, slurry sorbent injection, injection of two Nalco Fuel Tech-supplied urea-based solutions termed NO_xOUT A and NO_xOUT A+, and simultaneous injection of a NOxOUT A/sorbent slurry. The sorbents tested consisted of CaO, Ca(OH)₂, and CaCO₃, all supplied by the Tenn Lutrell Company. Dry sorbent was fed by a K-Tron loss-in-weight, twin screw feeder which was calibrated prior to and after each run. Slurried sorbent at 30% solids by weight was continually mixed in a tank and metered into a Turbotak nozzle by a calibrated peristalic pump. Baseline emission values prior to testing slurry injection were monitored while injecting an equivalent amount of deionized water (H₂O). NOXOUT (A or A+) was metered into the water or slurry injection by means of a calibrated dual syringe pump. A typical test scenario involved baseline emission monitoring during H₂O injection without NOXOUT (A or A+) flow, then addition of NOXOUT (A or A+) to the slurry flow, and a final return to H₂O-only injection to ensure return to baseline emission concentrations.

Both dry sorbent and slurry were injected through water-cooled probes that inject coaxially to the process gas. The dry sorbent probe injects 15.7% of the total IFR air flow to effect sorbent conveyance and dispersion. The Turbotak slurry probe uses air (18% of the total IFR air flow) to effect droplet atomization.

The slurry droplet size distribution exiting the Turbotak nozzle was determined through use of a Munhall particle size analyzer which determines droplet size by measuring diffraction of laser light. These droplet sizes were measured outside of the IFR using H₂O flow rates and pressures identical to in-furnace operation. The nozzle had a droplet size distribution with a D₂₀ of 13 μ m and a D₂₀ of 88 μ m. Prior to IFR testing, analysis of the slurry droplet size distribution with a spray trajectory model [17] ensured that the large droplets would not impinge on the furnace walls or remain unvaporized. Sorbent particle sizes were determined in a bench top measurement using a Micromeritics Sedigraph Model 5100.

Solid Sampling

IFR solid samples were collected isokinetically with a water-cooled sample probe. Gases passed through a particle filter and ice bath impingers then into a dry gas meter with flow rate control to ensure isokinetic sampling. These solid samples were analyzed by x-ray diffraction to identify compounds of reaction. Diffraction analyses were run on a Siemens diffractometer with a copper K α target source running at 50 kV and 40 mA.

Temperature Profiles

The temperature profiles through the IFR firing natural gas were determined by using a suction pyrometer and a type R thermocouple. Temperatures were determined during injection of air or air/H₋O to mimic the conditions expected during dry sorbent and slurry/NOXOUT (A or A+) injection, respectively. The temperature at the point of the injection nozzle was calculated by extrapolation of the temperature values from downstream ports. The quench rate for natural gas firing with slurry and dry sorbent injection was nominally 240 and 293°C/s, respectively, over the range of injection ports.

RESULTS

Sulfur Dioxide Tests

Initial tests compared the SO, removal of slurry versus dry injection modes for both Ca(OH)₂ and CaCO₃. Figure 2 shows the effect of varying injection temperature upon the SO₂ removal by CaCO₃ at a Ca/S ratio of 2/1. The SO₂ removal during both dry and slurry CaCO₃ injection was fairly independent of injection temperature, given the relative error in the plotted values. Both dry and slurry injection appear to have relative maxima in SO₂ removal, about 50%, around the 1000°C injection temperature. The addition of NOXOUT A solution to the slurry water (replacing an equal volume of water) may have caused a slight increase in SO₂ capture, but insufficient runs were completed for statistical certainty.

The same tests for dry injection of $Ca(OH)_2$ (Fig. 3) indicate that SO, removal, with a maximum around 1200°C, was relatively independent of injection temperature. The slurry injection curve is similar to the dry sorbent injection

curve except for a significant maximum in SO₂ removal around 1000°C, where SO₂ capture increases to about 73%. Tests with NOXOUT A addition to the slurry water mimic the temperature response of the sorbent-alone slurry, but indicate significantly higher SO₂ removal (about 10%, absolute) up to a maximum around 85% capture.

Limited tests were also done with commercially available Tenn Luttrell CaO (lime). In these tests, as-received $Ca(OH)_2$ was tested against a CaO slaked with the slurry injection water prior to injection. The results (also shown on Fig. 3) indicate that injection of a CaO slaked under non-optimized hydration conditions yields equal SO₂ capture to the as-received Ca(OH)₂. Similarly, injection of the slaked CaO slurry with NOXOUT A resulted in similar capture to the as-received Ca(OH), with NOXOUT A, about 85% at Ca/S = 2/1.

Tests varying the particle size of the $CaCO_3$ sorbent were conducted for dry, slurry, and slurry with NOXOUT A injection conditions. Results at the optimum injection temperature for SO₂ removal and at a Ca/S ratio of 2/1 are compared against the Ca(OH)₂ results (Fig. 4). Smaller particles react more quickly, whether they are Ca(OH)₂ or CaCO₃. The likely enhancement of dry sorbent SO₂ capture from either slurry injection or NOXOUT A addition is maintained independent of particle size. Results for the smallest particle sizes tested show that, while grinding CaCO₃ to sizes comparable to Ca(OH)₂ results in equal reactivity through dry sorbent injection, the same is not true for slurry injection and (especially) slurry injection with NOXOUT A.

Nitrogen Oxide Tests

Tests were conducted over a range of temperatures to measure the temperature sensitivity of two urea-based NO_x reductants, NOXOUT A and NOXOUT A+. NOXOUT A is a concentrated solution of urea in water with an antiscalant and dispersant formulation. Tests varied from about 821 to 1170°C with an NSR of 1/1. The results of testing with NOXOUT A, including NO_x, NH₃, N₂O, and CO, are shown in Fig. 5. For reference, SO₂ removal results from slurry injection are superimposed on this figure, although these results were not obtained simultaneously (other results showed that the effect of concurrent sorbent injection upon NO_x removal is unnoticeable; tests with and without sorbent in the slurry did not prove to affect NO_x removals). For NOXOUT A, a peak NO_x reduction of 82% is achieved at the optimum temperature of about 1100°C, while NO_x reductions greater than 70% were obtained between injection temperatures of about 980 and 1140°C.

In comparison to these results, Fig. 6 shows the results of NOxOUT A+, which includes a proprietary chemical modification formulated to reduce NH₃, N₂O, and CO emissions while expanding the temperature range to lower temperatures. The maximum NO₂ reduction was 81% at the optimum injection temperature of around 1100°C and an NSR of 1/1. However, NO₂ removals of greater than 70% were achieved at injection temperatures ranging from 930 to 1110°C, about 50°C lower than with NOXOUT A.

<u>NSR Variation</u>. Results of varying the NSR near the optimum NO_x removal injection temperature for both NOXOUT A and A+ are shown in Fig. 7. Increases in the NSR (to 2/1) result in greater NO_x removal to about 87%, although above an NSR of 1.5/1 (NO_x removal of =80%), little additional NO_x reduction is noted. For NSR values below 1.5/1, NO_x reduction with NOXOUT A is about 10% (absolute) higher than that for NOXOUT A+, while above an NSR of 1.5/1, little distinction in NO_x reduction is seen. NO_x removal results at NSR = 1/1 are slightly lower than in Figs. 5 and 6, likely due to injection at non-optimal temperatures and/or normal variation in system performance.

<u>N.O.</u> N₂O emission levels (Fig. 5) for NOXOUT A generally appear to follow NO_x removal levels; peak N₂O emission (90 ppm) occurs at the same temperature as peak NO_x removal, about 1100°C. Peak N₂O emissions using NOXOUT A+ (Fig. 6) appear to occur about 50°C higher than the optimum injection temperature for NO_x removal. For NOXOUT A and A+, N₂O emissions follow a similar temperature response, although levels for the latter (peak value of 34 ppm) are consistently about one-third of the former.

For tests conducted near the optimum injection temperature for NO₁ removal (1087°C), increasing NSR values results in greater N₂O emissions for both NOXOUT A and A+ (Figs. 8 and 9, respectively). N₂O concentration ranges from 29 to 91 ppm for an NSR of 0.5/1 to 2/1, respectively, for NOXOUT A. NOXOUT A+, appears to be

less sensitive to NSR increases, ranging from 10 to 50 ppm for NSR values of 0.5/1 to 2/1. For both NOXOUT chemicals, N₂O emissions are only slightly affected by changing NSR values between 1/1 and 1.5/1.

<u>NH</u>. NH, concentrations for NOxOUT A injection (Fig. 5) reach a maximum of 88 ppm at 821°C. Increases in injection temperature show declining concentrations with increases in injection temperature. Peak NH, levels of 83 ppm for NOXOUT A+ (Fig. 6) at 821°C are reduced below 5 ppm at injection temperatures of 887°C and higher.

Changes in NSR values affect NH₃ emissions, as seen in Figs. 8 and 9. Increases in NSR for both NOXOUT A and A+ result in higher levels of NH₃. As with N₂O, NH₃ levels with NOXOUT A are only a weak function of NSR changes from 1/1 to 1.5/1.

DISCUSSION

Sulfur Dioxide Tests

<u>Comparison</u>. The SO₂ removals (=40 to 50%) reported in Fig. 2 for dry CaCO₃ particles (all reported SO₂ values are at Ca/S = 2/1) somewhat exceed previous results (=40%) for testing in this furnace [18] and others [19]. The SO₂ removal results for dry Ca(OH)₂ sorbent injection, =62%, are consistent with earlier testing in this reactor [1,20] and numerous tests by others [21]. While it is difficult to compare results between dissimilar furnaces, fuels, initial SO₂ concentrations (SO₂), and sorbents, the results for CaCO₃ slurry injection (=50 to 60% at Ca/S = 2/1) are consistent with results from Reference [22] of about 40 to 55% at Ca/S = 2/1 and four different coal/sorbent combinations. Later work [13] indicates SO₂ removals with a Ca(OH)₂ slurry (Ca/S = 2/1) of 78%, comparable to our peak value of =74%.

<u>Temperature</u>. The results for both dry and slurry Ca(OH)₂ injection (Fig. 3) are similar to those found for dry and slurry CaCO₃ injection in that they are, with one significant exception, relatively insensitive to temperature. While greater sensitivity to injection temperature for dry sorbent injection may be observed in other facilities (see, for example, References [19] and [21]), this phenomenon is a strong function of reactor quench rate; the temperature response profile of SO₂ capture becomes flatter for lower quench rates. The IFR has a fairly moderate quench rate of about 250°C/s. Results from a pilot facility [22] operating at a guench rate of 500°C/s did show greater temperature sensitivity of SO₂ capture with slurry injection. As expected with this higher quench rate, the optimum slurry injection temperature (\approx 1200°C) was determined to be about 150°C higher than in our work (\approx 1050°C).

Dry Versus Slurry Injection. The equal or greater capture by CaCO₃ slurry versus dry injection has been attributed to particle fragmentation or delayed sintering [23]. However, the range of data on these tests is insufficient to be conclusive - certainly there is not a significant effect of slurry injection with CaCO₃.

The levels of SO₂ removal from the upper 50% to about 70% (excluding the NOXOUT addition results) are typicol for dry Ca(OH)₂ sorbents. Significantly greater SO₂ removals (about 10%, absolute) with slurry versus dry injection result at one temperature (1000°). Unfortunately, further definition of this temperature peak was impossible due to injection port limitations. The mechanism for this enhanced removal during slurry (versus dry) injection remains speculative.

Effect of NOXOUT A. Tests with NOXOUT A added to the sorbent slurry show significant improvement over the slurry alone or dry tests. Improvements in SO₂ capture exceeding 10% absolute occur throughout the 880 to 1170°C injection range. This phenomenon was also observed [6] when testing a hydrated lime-urea mixture and comparing it with the hydrated lime alone. It was speculated that the enhancement was due to either increased sorbent surface area and porosity from urea decomposition in the sorbent crystal structure or reactions between SO₂ and urea decomposition products in the sampling system. Our results suggest, however, that the mechanism of enhancement of the sorbent's ability to capture SO₂ is likely the reaction of the sorbent and urea-based compound with SO₂. X-ray diffraction results from IFR solid sampling during NOXOUT A injection indicate, along with the expected CaSO₄, the significant presence of $(NH_4)_2Ca(SO_4)_2$ H₂O (koktaite). It is clear at these high temperatures, that CaO, SO₂, and the urea breakdown product (NH_3) react together to increase SO₂ removals beyond that expected simply from the presence of CaO [from Ca(OH)₂ or CaCO₃] alone.

<u>Particle Size Effects</u>. The effect of particle size for the CaO/SO, reaction has been well documented [24,25]. Thus, the trends observed in Fig. 4 of increasing reactivity with decreasing particle size were anticipated. The effect of sorbent diameter is inversely related to particle size to the 0.14 power.

For CaCO₃ injection, the results for three particle size classes show that SO₂ capture increases from dry to slurry to slurry with NOXOUT A injection. While the magnitude of the increase during NOXOUT A injection is within the error range of the furnace results, the consistency of this rank across the particle sizes implies that more exhaustive testing might verify this enhancement for CaCO₃, however slight. Comparison with the Ca(OH)₂ results indicates that equal capture of SO₂ can be expected for dry injection of CaCO₃ particles ground to similar sizes. An explanation for the enhancement of SO₂ capture with Ca(OH)₂ is beyond the scope of this effort; however, the higher initial porosity of Ca(OH)₂ than CaCO₃ may allow for greater infiltration of the slurry water into the particle fracturing due to water vaporization.

<u>Ca(OH). Versus CaO Slurry</u>. The inability to distinguish between the SO₂ reactivity of the slurries from commercially available Ca(OH)₂ versus laboratory-slaked CaO suggests the simplicity of the hydration process towards production of reactive sorbents. Purchase costs of hydration and transportion of the added weight of H₂O in Ca(OH)₂ to the site can be avoided if CaO is mixed at the boiler site. While it is likely that improved methods of CaO slaking will increase the sorbent reactivity, our rudimentary methods of sorbent slaking were sufficient to match the results of manufacturer-supplied Ca(OH)₂.

Nitrogen Oxides Tests

<u>Comparison</u>. IFR test results show NO_x removals (~75%) with NOXOUT A at 1000°C and an NSR of 1/1 that are virtually identical to those demonstrated in Reference [13] under similar conditions with injection of a urea-based solution. Other similar results have been reported by References [11] and [12] with urea injection, given consideration for different NSR and NO_x values.

<u>NOXOUT A Versus NOXOUT A+</u>. Use of NOXOUT A+ in this work improved the NO_x removal values at lower temperatures. Changing NSR values also yields NO_x removal responses similar to those reported by Reference [11]. Thus, NO_x removals effected by changes in both injection temperature and NSR are consistent with pilot and field results, indicating the technical success of SNCR.

The ability of NOXOUT A+ to perform well at lower injection temperatures than NOXOUT A raises the possibility of staged injection of NOXOUT A and A+ at high and low temperatures, respectively. This has the additional benefit of reducing the local "load" of the nitrogen reductant injected into the flue gases, thereby minimizing potential NH₃ slip problems.

<u>N.O.</u> Values of N₂O production as a function of NO_x reduction (plotted as $\Delta NO/\Delta NO_x$ in Fig. 10) for both the NOXOUT A and A+ urea-based solutions were almost exclusively less than those of References [11] and [26] with pure urea. Work reported in Reference [11] was done on a pilot scale, natural-gas-fired combustor (described more fully in Reference [12]) doped with NH₃ to produce NO_x, and Reference [12] used a pilot scale 2 MW(t) coal-fired circulating fluidized bed. This suggests that technical improvements to the pure urea solution, represented here by the NOXOUT A and A+ formulations, can have an impact upon N₂O emissions in SNCR processes.

<u>NH</u>, Levels of NH, emissions, usually termed NH, "slip" in reference to the unreacted N-based reductant, for both NOxOUT A and A+ show trends of reduction with increases in temperature consistent with results of others [12]. For purposes of comparison, Fig. 11 replots the NH, slip emissions during both NOxOUT A and A+ injection with those from Reference [12]. Despite an initial NO_x level over twice

that of Reference [12], NH₃ slip values in our work are significantly less throughout the full temperature range. This may likely be due to differences in the experimental combustors combined with the increased reactivity of the NOXOUT A+ formulation at lower temperatures.

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CONCLUSIONS

This work has demonstrated on the pilot scale the successful coupling of Cabased sorbent injection and SNCR technologies in a slurry injection process. SO_2 and NO_2 removals of about 70 to 80% at Ca/S = 2/1 and an NSR = 1/1, respectively, have been observed.

Different formulations of the tested modified urea solutions result in varying sensitivity and effectiveness with temperature, acting to broaden the applicable injection region of the combined process.

SO₂ emission control is enhanced by the combined technologies; identification of $NH_3/Ca/SO_4$ compounds suggest that the urea-based solutions react with Ca and SO₂ to effect additional SO₂ removal. Some evidence exists for the enhancement of SO₂ capture during slurry versus dry injection of sorbents, albeit over a narrow temperature range.

Levels of NH₃ and N₂O are significantly reduced below levels previously reported for urea injection through use of modified urea-based solutions. Near the peak NO_x removal levels for NOXOUT A+ of 80% (NO_x = 600 ppm, NSR = 1/1), emission levels of NH₃ and N₂O were below 5 and 20 ppm, respectively.

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Figure 1. Schematic of the Innovative Furnace Reactor.





Figure 3. Effect of varying injection temperature on SO ₂ removal for Ca(OH)₂.



Figure 4. Effect of sorbent particle size on SO_2 removal.



using NOxOUT A+.



Figure 7. Effect of NSR on NO $_{x}$ removal for NOxOUT A and NOxOUT A+.



Figure 9. Effect of NSR on emissions using NOxOUT A+.



Figure 10. N_2O production from NO_x at varying injection temperatures.



Figure 11. Effect of injection temperature on ammonia emissions.

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Combined SO₂/NOx Abatement by Sodium Bicarbonate Dry Injection

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ABSTRACT

Following laboratory tests at the CER, SOLVAY's Centre d'Etudes et de Recherches in Dombasle (France), which confirmed suitability of Sodium Bicarbonate for the simultaneous elimination of SO₂ and NOx present in flue gas, SOLVAY has started demonstration trials in actual power plants.

Laboratory tests have shown that SO_2 abatement with Sodium Bicarbonate also entails a significant decrease of NOx in certain cases, depending on the ratio of SO_2 to NOx in the flue gas, the temperature, the granulometry of Bicarbonate, the residence time, etc...

The first confirmation trial was performed in Rosignano, Italy, on flue gas generated by a 20 MW steam generator fed with a 3 $1750 \text{ Nm}^3/\text{hr}$ of flue gas containing 4500 mg SO₂ and 300 mg NOx/Nm³ were treated at 116-124°C with dry injection of ground Bicarbonate (mean particle size 25)m) prior to passing through a bag house filter. At stoichiometric Bicarbonate addition the resulting abatement was 60 SO₂ and 90 NOx.

The second confirmation trial was performed at Geilenkirchen, Germany, on the flue gas of a 9.7 MW steam generator fed with 1 % sulfur coal. 11.000 Nm³/h flue gas containing 1000 mg SO₂ and 200 mg NOx/Nm³ were treated at 110-120°C with dry injection of coarse or ground Bicarbonate (120, resp. 7.5)m mean particle size) before passing through a bag house filter with an excess of 20 % Bicarbonate. In the case of the ground reagent the abatement was 98 % SO₂ and 64 % NOx, and in the case of the coarse material 42 % SO₂ and 19 % NOx.

Consequently of these good results, it was decided to study the mechanism of the reactions during the simultaneous abatement of SO₂ and NOx. SOLVAY asked IFP, "Institut Français du Pétrole", to do this study in its specially equiped laboratory.

The IFP laboratory study gives confirmation of the ability of Sodium Bicarbonate to abate simultaneously SO_2 and NOx in flue gas. Moreover the principal reaction mechanism of the abatement seems to be as follows :

- Sodium bicarbonate sulfitation :

 $NaHCO_3 + SO_2 \longrightarrow NaHSO_3 + CO_2$

- Sodium bisulfite dehydratation :

2 NaHSO₃ \longrightarrow Na₂S₂O₅ + H₂O

- Sodium pyrosulfite nitration : $Na_2S_2O_5 + 2 NO + O_2 \longrightarrow NaNO_2 + NaNO_3 + 2SO_2$

- Sodium bisulfite nitration :

2 NaHSO₃ + 2 NO + $O_2 \rightarrow NaNO_2$ + NaNO₃ + 2 SO₂ + H₂O

All these reactions begin to become important in the temperature range 370 to 450 K.

INTRODUCTION

Early Informations

In recent years, international pressures to decrease NOx emissions are becoming as strong as those regarding SO_2 . Till now the technology of choice to achieve this requirement is SCR, selective catalytic reduction.

Due to the high investment and operation costs of the SCR process, the interest in the development of lower-cost NOx/SO_2 abatement processes has been renewed (1,2).

Now, it is well established that Sodium Bicarbonate is a very effective reagent for SO_2 removal in flue gas by a low investment cost dry injection process (3,4,5). More than 15 years ago, during trials at the Mercer station of New Jersey's Public Service Electric and Gas Co., it was observed that NOx removal of up to 40 % occured during the SO_2 abatement by Sodium Bicarbonate dry injection (7).

Solvay was interested to confirm the ability of Sodium Bicarbonate for the simultaneous SO_2 and NOx abatement by dry injection in the flue gas and to determine the best conditions of operation range.

Laboratory Trials at CER-Dombasle

The Solvay "Centre d'Etudes et de Recherches" (CER) in Dombasle (France) made some preliminary laboratory trials to verify the simultaneous SO_2/NOx abatement in a synthetic flue gas. The purification of this gas composed of air, SO_2 and NO was obtained by passing it through a little Sodium Bicarbonate fluidized bed.

The conclusions of these trials were :

- in all cases, high SO₂ abatement (about 100 %) ;
- NO abatement increased from 35 to 50 % with the ratio SO₂/NO in the inlet gas (0 to 3 ppm SO₂/ppm NO) ;
- NO abatement increased from 45 to 85 % with the residence time of the gas in the fluidized bed (0,5 to 2,5 s) ;
- very low influence of the temperature on the NO abatement in the range 90 to 200°C.

The NO abatement was about 30 to 40 % in this temperature range for 0,5 s residence time and 2 ppm SO₂/ppm NO in the inlet gas.

After this good results, it was decided to carry on the study doing confirmation trials in actual power plants.

CONFIRMATION TRIALS IN ACTUAL PLANTS

CER Pilot mobile Equipment

To confirm the ability of Sodium Bicarbonate for SO_2 abatement, the Solvay CER of Dombasle has constructed a pilot mobile equipment.

This device includes (see figures 1 and 2) :

- . a Bicarbonate hopper filled with 50 kg bags,
- . a screw conveyor feeder,
- . a Bicarbonate screw flowmeter,
- . a pin mill Alpine 315 UPZ (9000 revs/min, 22 KW) (figure 3).

The CER pilot equipment injects crushed Bicarbonate (mean
particle size smaller than 10 jm) at the rate of 50 to 250 kg/h
in flue gas stream. It has been used for demonstration trials :
- on a municipal waste combustor in Antwerp (Belgium) for HCl
and SO₂ abatement (test period : May 30 to June 3, 1988) (3);
- on a power plant in Heilbronn (Germany),
 (test period : September 6 to October 27, 1988) (4);
- on a thermal power station in Gardanne (France),
 (test period : February 27 to March 3, 1989) (5);

- on a municipal waste combustor in Padua (Italy) for HCl abatement,

(test period : May 21 to 24, 1990) (6).

It was decided to utilize the CER pilot equipment to confirm the ability of Sodium Bicarbonate for simultaneous SO₂/NOx abatement in flue gas of an actual thermal power plant.

Demonstration Trial at Geilenkirchen

A demonstration trial of SO_2/NOx simultaneous abatement has been done with the CER pilot mobile equipment on the steam generating station flue gas of the NATO air base in Geilenkirchen. This trial was jointly undertaken with Wulff GmbH which has manufactured the flue gas treatment equipment designed with hydrated lime injection. During these tests, the lime injection was replaced by Sodium Bicarbonate injection. The amount of SO_2 and NOx contained in the flue gas was measured both before and after purification by the CER and, at the same time, monitored by Wulff.

The Sodium Bicarbonate used is of hydrophobic Venale "Fein" quality (a treatment which makes Sodium Bicarbonate free flowing), provided by Rheinberg Solvay plant (Germany).

The effect of following parameters on the SO₂ and NOx abatement effectiveness has been studied :

- size of the Bicarbonate (injected without or after crushing),
- quantity of Bicarbonate injected,
- influence of recycling abatement residues which still contain reagent.

Venale Fein Bicarbonate has a mean diameter of 120 الملر ; after crushing, this diameter is reduced to 7.6 الله.

The steam-generating station at Geilenkirchen is equiped with two boilers. The tests were carried out downstream one of the boilers, the characteristics of which were as follows :

- thermal power : 9.7 MW,
- vapour production at 10 bars : 14 metric tonnes/hour,
- fuel : Ruhr coal with 1 % S ; PCI = 7500 kcal/kg,
- flue gas flow rate : 11,000 Nm³ dry/h (+/- 15 %).

Details of the purification equipment installed by Wulff are given below (figure 4). The flue gas leaving the boiler may be sent directly to the chimney using a bypass. After cooling down to about 130°C in a heat exchanger, it passes through a cylindrical reactor, into the base of which the Sodium Bicarbonate has been injected. The Bicarbonate comes out of the silo and flows into the CER mobile crushing device.

The flue gas passed through a bag house filter, at the bottom of which a certain quantity of solid residues remains in a fluid

state (a quantity which amounts to around 5 to 6 tonnes) with a view to possible recycling so as to consume the reagent. The residence time between the point of injection of the Bicarbonate in the reactor and the inlet of the bag house filter is approximately 3 to 4 seconds.

The SO_2 and NOx content was measured by bubbling a part of the flue gas through H_2O_2 and potassium dichromate solutions. The analyses were carried out using a chromatograph with DIONEX QIC anions. The flow rate of the flue gas and their O_2 content were also measured.

At the injection point of the Bicarbonate, the average content of SO_2 and NOX respectively reaches 1650 and 325 mg/Nm³ dry with 7 % O_2 . The average temperature of the flue gas during purification was between 112 and 122°C in the case of uncrushed Bicarbonate and 110°C in the case of crushed Bicarbonate. The quantity of reagent injected in relation to the stoichiometry of the simultaneous purification reactions of SO_2 and NOX varied between 1.54 and 2.28 for the uncrushed Bicarbonate and between 0.93 and 1.68 for crushed Bicarbonate.

Figure 6 shows the results obtained during purification tests. The rate at which impurities were removed are given in relation to the quantities of Bicarbonate injected, indicated on figure 7 for SO_2 and on figure 8 for NOx respectively.

The results obtained through the injection of crushed Bicarbonate were highly satisfactory : 95 % of the SO₂ was removed using a stoichiometric quantity of Bicarbonate whilst 60 % of the NOx was eliminated through the injection of a quantity of Bicarbonate in excess of 45 % of the stoichiometry.

The injection of uncrushed Bicarbonate did not achieve such good results.

However, during the course of two tests carried out by injecting uncrushed Bicarbonate and recycling the residues separated in the bag house filter, similar results to those obtained when using crushed Bicarbonate were achieved.

Confirmation Trial at Rosignano

Another SO_2/NOx simultaneous abatement confirmation trial was made during the period October 2 to November 9, 1989 on the flue gas of a steam generator at the Solvay Rosignano plant (Italy). This trial was jointly undertaken with Termomeccanica, an Italian equipment company.

The crushed Sodium Bicarbonate dry injection was made with a pilot equipment manufactured by Termomeccanica with a subsidy of ENEA (Ente Nazionale Energie Alternative). The pilot equipment is composed of :

- . a tubular reactor (length : 28,5 m, 14" diameter),
- . a flue gas fan, flowrate : $3000 \text{ Nm}^3/h$,
- . a bag house filter, 72 m^2 ,
- . a pin mill Danioni in order to crush the Sodium Bicarbonate.

The trial was made on a by-pass of the flue gas of a 20 MW steam generator fed with a 3 sulfur fuel. A flowrate of 1750 Nm³/hr of flue gas containing 4500 mg SO₂ and 300 mg NOx/Nm³ were treated at 116-124°C.

The measurement of SO_2 and NOx content in the flue gas was made by bubbling a gas sample respectively in a H_2O_2 solution and in a sulfochromic solution

Figure 6 gives the results obtained during the purification tests. The rate at which impurities were removed in relation to

the amount of Bicarbonate injected are given on figure 7 for SO2 and on figure 8 for NOx.

These results show that :

- . the percentage of SO₂ removal is comprised between the results obtained at Geilenkirchen. In fact, it depends of the size of the Bicarbonate injected ;
- . the NOx removal is very high. This very good result is probably due to the high SO_2/NOx inlet ratio.

STUDY OF SO2/NOX ABATEMENT REACTION MECHANISM

IFP Laboratory Equipment

The "Institut Français du Pétrole", IFP, in Rueil Malmaison, near Paris (France) has a specially equiped laboratory able to study the SO_2/NOx abatement reaction mechanism with Sodium Bicarbonate dry injection. It was agreed between Solvay and IFP to do this study during the beginning of this year 1991.

IFP Laboratory is equiped with a little fluidized bed reactor (figure 9), inside diameter 22 mm, fed with gas at the rate of 40 cm³/s. The bed is filled with 6 g of solid matter. It is heated in an electric furnace with temperature programme. The gas injected is a mixture of argon with SO₂, O₂, NO₂, NO and N₂O as the case may be.

The gas composition at the outlet of the bed is determined by continuous measurements and the data are stored in a PC 386.
Results of IFP study

IFP made two kinds of trials :

- trials with increased temperature : usually increasing 2 to 6 K/min ;
- trials with constant temperature, eventually putting the solid matter in the fluidized bed reactor after reaching the temperature chosen for the trial.

It appears that Sodium Bicarbonate gives rise to NO abatement in the temperature range of 400 to 500 K (figure 11). On the contrary Sodium Carbonate has no effect on NO abatement (figure 10).

After this, IFP made trials with different compounds apt to occur during the SO_2 abatement with Sodium Bicarbonate dry injection.

Whereas Na_2SO_3 , produced by sulfitation of Na_2CO_3 , has no action on NO abatement (figure 12), NaHSO₃, produced by the sulfitation of NaHCO₃ and subsequently transformed into $Na_2S_2O_5$, induces a considerable NO abatement in the temperature range 400 to 550 K (figure 13).

A comprehensive view of the whole set of trials has led IFP to propose the SO_2/NOx abatement mechanism described on figure 15.

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The principal reactions leading to the SO_2/NOx simultaneous abatement seem to be :
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    Sodium bicarbonate sulfitation :
NaHCO<sub>3</sub> + SO<sub>2</sub> -----> NaHSO<sub>3</sub> + CO<sub>2</sub>
    Sodium bisulfite dehydratation :
2 NaHSO<sub>3</sub> -----> Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O
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- Sodium pyrosulfite nitration : Na₂S₂O₅ + 2 NO + O₂ \longrightarrow NaNO₂ + NaNO₃ + 2 SO₂ - Sodium bisulfite nitration :

2 NaHSO₃ + 2 NO + $O_2 \longrightarrow$ NaNO₂ + NaNO₃ + 2 SO₂ + H₂O

Finally, the maximum value of NOx abatement measured during the IFP study is given on figure 14 as a function of the ratio of NOx/SO_2 content in the inlet gas. The NOx abatement achieved at Rosignano and at Geilenkirchen during the industrial trials are also given on figure 14.

SUMMARY

Solvay trials in actual power plants at Geilenkirchen (Germany) and at Rosignano (Italy) have once more demonstrated the ability of Sodium Bicarbonate dry injection for SO_2/NOx simultaneous abatement in flue gas. These trials have shown the necessary conditions to reach a high yield of NOx abatement :

- . high ratio of SO2/NOx content in the flue gas
- . suitable temperature range
- . utilization of a bag house filter ensuring the SO₂/NOx abatement continuation during the flue gas flow through the solid deposit on the sleeves.

For SO_2 abatement only, it is known that the investment cost of the Sodium Bicarbonate dry injection is about the half of the investment cost of a spray dryer system (bag house filter included). But the price of the reagent handicapes the economy of the process (8).

At the contrary, for SO_2 and NOx abatement the economy of the Sodium Bicarbonate dry injection seems to be very competitive comparatively with wet FGD for SO_2 abatement + SCR for NOx abatement, particulary for medium capacity power plants (9). The IFP Laboratory Study has shown the principal reaction mechanism occuring during SO_2/NOx abatement by Sodium Bicarbonate dry injection.

Particulary, it appears from this study that an high NOx abatement occures by contact of the flue gas with Sodium Pyrosulfite and Sodium Bisulfite formed by the SO₂ abatement. Sodium Pyrosulfite and Sodium Bisulfite can also be produced industrially for this application.

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Fig. 1 - SOLVAY Pilot Mobile Equipment General View



Fig. 2 - SOLVAY Pilot Mobile Equipment Details



Fig. 3 - Pin Mill ALPINE 315 UPZ



Fig. 4 - Flue Gas Purification Equipment at Geilenkirchen

Trial	39	40	41	42-1	42-2	43-1	43-2	44
Flue gas flowrate, Nm3/h dry	1600	1600	1600	1750	1750	1750	1750	1750
SO2 inlet, mg/Nm3 at 7 % O2	4730	4610	4760	4730	4750	4660	4810	4810
NOx inlet, mg/Nm3 at 7 % O2	196	200	230	163	300	300	352	394
Temperature inlet, ⁰C	178	178	178	131	132	135	138	192
02 inlet, vol. X	3, 2	3, 2	3, 2	3, 9	4, 0	4, 1	4, 2	4, 0
SO2 outlet, mg/Nm3 at 7 % O2	2365	1980	1620	2030	2000	1540	1600	1870
NOx outlet, mg/Nm3 at 7 % O2	45	18	0	18	75	75	95	71
Temperature outlet. [©] C	122	122	123	96	98	101	102	129
O2 outlet, vol. X	5, 2	5, 2	5, 2	5, 9	5, 9	6, 0	6, 1	5, 9
Sodium bicerbonate :								
- flowrate, kg/h - mean diameter, µ m - 90 % smaller than, µ m	17, 3 24 83	24, 0 24 83	29, 6 24 83	17, 7 21 67	17, 6 21 67	23, 9 21 67	23, 9 21 67	23, 6 16 44
NSR (SO2 + NOx)	0, 84	1, 20	1, 44	0, 81	0, 80	1, 12	1, 09	1, 04
SO2 removed, X	50	57	66	57	58	67	66	61
NOx removed, X	77	91	100	89	75	75	73	85

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Fig. 5 - SO₂/NOx Removal - Results of the Trials at Rosignano

Trial	4	5	6	7	12	13	15	17
Flue gas flowrate, Nm3/h dry	10100	9650	10100	10100	10800	12000	10200	11000
SO2 inlet, mg/Nm3 st 7 % O2	1650	1570	1569	1552	1624	1573	1926	1393
NOx inlet, mg/Nm3 st 7 % O2	306	300	254	310	353	269	339	356
Temperature inlet, °C	125	125	115	115	120	120	121	120
02 inlet, vol. X	11, 2	12, 0	11, 9	11, 8	11, 0	10, 3	11, 8	10, 5
502 outlet, mg/Nm3 at 7 % 02	835	826	979	840	37	43	14	37
NOx outlet, mg/Nm3 at 7 % O2	190	250	211	257	140	105	115	219
Temperature outlet, ^o C	119	119	110	115	105	105	104	105
02 autlet, vol. X	12, 2	12, 0	11, 8	12, 5	13, 0	13, 1	11, 5	11, 6
Sodium bicarbonate :								
– flowrate, kg/h – mean diamater, д m – 90 % emaller than, д m	74, 2 121 195	48, 9 121 195	40, 9 121 195	74, 2 121 195	60, 0 7, 6 13, 8	62, 0 7, 6 13, 8	50, 0 7, 6 13, 8	36, 0 7, 6 13, 8
NSR (SO2 + NOx)	2, 01	1, 59	1, 54	2, 28	1, 60	1, 41	1, 24	0, 93
SO2 removed, X	49, 7	47, 4	37, 6	45, 9	97, 7	97, 3	99, 3	97, 5
NOx removed, %	37, 8	16, 5	16, 9	17, 1	60, 4	61, 0	66, 1	38, 4

Fig. 6 - SO2/NOx Removal - Results of the Trials at Geilenkirchen

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Fig. 7 - SO₂ Removal as a Function of the Amount of Bicarbonate Injected

Fig. 8 - NOx Removal as a Function of the Amount of Bicarbonate Injected



Fig. 9 - Fluidized Bed Reactor for Laboratory Trials

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Fig. 10 - 420 ppm NO + 675 ppm SO₂ + 2.3 % O₂ In Ar ON Na₂CO₃ (Trial 316)

Fig. 11 - 412 ppm NO + 675 SO₂ + 2.3 % O₂ In AR ON NaHCO₃ (Trial 293)

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Fig. 12 - 393 ppm NO + 0.29 % O2 In Ar ON Na2SO3 (Trial 469)

Fig. 13 - 410 ppm NO + 2.3 % O2 In Ar ON Na2S2O5 (Trial 346)



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Fig. 15 - Mechanism of SO2/NOx Removal by Sodium Bicarbonate Injection

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SO₂ AND NO_x CONTROL BY COMBINED DRY INJECTION OF HYDRATED LIME AND SODIUM BICARBONATE

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ABSTRACT

The dry sorbent injection process for SO_2 and NO_x removal from coalfired boiler flue gas consists of the use of low NO_x burner technology for primary NO_x reduction, injection of hydrated lime at economizer temperatures for primary capture of SO_2 , and injection of sodium bicarbonate at the air heater exit for additional SO_2 and NO_x removal. This concept has been separately tested at the .25 and 50 million Btu/hour scales, utilizing test systems that duplicate the flue gas time-temperature profile found in commercial boiler systems. The testing procedures and results, including the effects of the sorbent injection on particle control devices, are described in this paper.

INTRODUCTION

The team of Research-Cottrell Environmental Services and Technologies and Riley Stoker is conducting a proof of concept demonstration of an Integrated Dry Injection process for coal-fired boiler SO_2 and NO_x control, under a U.S. Department of Energy (DOE) contract with cofunding by the Electric Power Research Institute (EPRI). The process consists of combustion modification using low NO_x burners to reduce NO_x emissions, dry injection of hydrated lime at the economizer for primary capture of SO_2 , dry injection of a commercial grade sodium bicarbonate at the air heater exit for additional SO_2 and NO_x removal, and flue gas humidification for precipitator conditioning. This concept is illustrated in Figure 1. The Integrated Dry Injection Process offers the potential for simultaneously achieving 90+% SO_2 removal and 75+% NO_x removal from flue gas. The process is well suited for new or retrofit applications since it can be incorporated within existing economizer and downstream ductwork. In addition, capital costs are kept to a minimum since no large system components such as catalytic beds, spray dryers, or scrubbers are required.

The SO₂ and NO_x removal technologies, which are combined in this demonstration test, have been independently evaluated but have not yet been tested as an integrated system. The integrated tests are important to determine and characterize any interactions between the technologies, either positive or negative. Some conditions that favor SO₂ removal inhibit NO_x removal. For example, high levels of SO₂ removal by economizer injection of calcium hydroxide will adversely affect NO_x removal by sodium bicarbonate, which depends on high SO₂ concentration.

SORBENT EVALUATION

To identify the best calcium and sodium sorbents to use for the proofof-concept demonstration, subscale tests were performed that involved the injection of calcium hydroxide and sodium sorbents at various points of the flue gas system downstream of a 0.25X10⁶ Btu/hr coal fired combustor. The subscale system is shown in Figure 2. The flue gas flow from the furnace was approximately 56 scfm, and the gas residence times, cooling rates, and temperatures were comparable to those found for full-scale utility boilers. Sorbents were injected by means of a compressed air-driven eductor. Water injection could be performed upstream or downstream of the heat exchanger. The water injection position upstream of the heat exchanger was used for lowering the temperature of the flue gas stream while the position downstream of the heat exchanger was used to inject a urea solution for NO2 suppression.

Calcium Hydroxide Sorbents

The ability of hydrated limes to react rapidly with SO_2 at temperatures below 1200°F was first noted in the EPRI-sponsored Dry Sorbent Emission Control program. Tests conducted under this program showed that SO_2 capture levels with pressure-hydrated dolomite decreased as the injection temperature was gradually reduced from 1800°F to approximately 1200°F and then again increased with further reductions in injection temperature. This prompted a short study at the Southern Research Institute where pressure-hydrated dolomite was injected at temperatures ranging from 2400°F to 200°F, and a second sulfation window was verified between 1200°F and 800°F.¹

Unlike the higher temperature sulfation window level of 2000° F, where $CaSO_4$ is the only thermodynamically stable compound, the temperature range 1200° F - 800° F also contains the stable species $CaCO_3$. Thus the amount of SO_2 capture in the lower temperature range will initially depend on the rate of three competing reactions,² which are shown below.

$Ca(OH)_2 + SO_2 \longrightarrow$	$CaSO_3 + H_2O$	(1)
$Ca(OH)_2^2 + CO_2^2 \longrightarrow$	$CaCO_3 + H_2O$	(2)
$Ca(OH)_2$ — — — — — — — — — — — — — — — — — — —	$CaO + H_2O$	(3)

Maximizing SO_2 removal by hydrates injected at the 1000°F level requires optimization of both sorbent and process parameters and requires that reaction (1) is favored over reaction (2). Two parameters control the hydrate's ability to remove SO_2 . The initial sorbent porosity (or surface area) is a good indicator of the hydrate's ability to react with either SO_2 or CO_2 . The second important hydrate characteristic for enhancing SO_2 removal is particle size. Because the chemical reaction rate is so fast, bulk diffusion of SO_2 (but not CO_2 , which has a concentration 50 times greater than SO_2) to the particle can be a controlling factor. The diffusion of SO_2 to a particle is inversely proportional to particle diameter, and unless the particles have a mass mean diameter of less than 5 microns,² most of the hydrate will react with CO_2 via reaction (2).

The lime hydrates that were evaluated in the subscale tests are given in Table 1. The first six hydrates are commercially available and were produced by conventional dry hydration of lime. The alcohol hydrate was produced by hydrating lime with a water/methanol mixture, and the lignosite hydrate is produced by hydration with a calcium lignosulfanate solution.

The hydrates were injected into the convective section of the pilotscale combustor as indicated in Figure 2. The injection points correspond to gas temperatures of 1100, 1000, and 900°F, with constant quench rates of 1000°F/sec. The SO₂ inlet concentration for all hydrate injection tests was 2600 ppm, and the Ca/S mole ratio was 2 for all tests. The results are shown in Figure 3, which gives SO_2 removal in the convective section as a function of injection temperature. The peak effectiveness of all hydrates is achieved at about 1000°F, and the clear superiority of the alcohol hydrate is evident. The single most important hydrate characteristic for good SO_2 removal is surface area, and it was found that utilization is almost directly proportional to surface area.

Sodium_Sorbents

When sodium bicarbonate is injected into a flue gas between 200°F and 400°F, the following reactions can occur.

2NaHCO ₃	$Na_{2}CO_{3} + CO_{2} + H_{2}O$	(4)
$Na_2CO_3 + SO_3 \longrightarrow$	$Na_2SO_3 + CO_2$	(5)
$Na_{2}CO_{3} + SO_{2} + 1/2 O_{2} \longrightarrow$	$Na_2SO_4 + CO_2$	(6)
$2N\bar{a}_2C\bar{O}_3 + S\bar{O}_2 + 2NO + 2O_2 \longrightarrow$	$Na_{2}SO_{4} + 2NaNO_{3} + 2CO_{2}$	(7)
$4NaHCO_3 + SO_2 + 2O_2 + 2NO \longrightarrow$	$Na_2SO_4 + 2NaNO_3 + 4CO_2 + 2H_2O$	(8)
$2NaNO_3 + SO_2 \longrightarrow$	$Na_2SO_4 + 2NO_2$	(9)

At higher temperatures, the bicarbonate decomposes to sodium carbonate before reacting with SO_2 (reactions 4-6). This decomposition results in a sodium carbonate product with a large surface area, thus enhancing reaction with SO_2 . Nitrogen oxide can react with sodium carbonate or, at lower temperatures, with sodium bicarbonate, but only in the presence of SO_2 . The sodium nitrate product can react with SO_2 to yield NO_2 , which can cause a brown stack plume under certain circumstances⁴ when its concentration in ppm exceeds a value equal to 200 divided by the stack diameter in feet. To suppress the NO_2 production, urea can be added to the sodium bicarbonate⁵, or the flue gas can be humidified.

The sodium compounds evaluated in the subscale tests were sodium bicarbonate, NaHCO₃, and sodium sesquicarbonate, Na₂CO₃·NaHCO₃·2H₂O. The mass mean diameter particle sizes were 12.9 microns for the bicarbonate and 12.2 microns for the sesquicarbonate. For all tests, the inlet SO₂ concentration was 2600 ppm and the inlet NO concentration was 350 ppm. The alcohol hydrate was injected at 1000°F for all tests and the sodium compounds at temperatures between 250°F and 500°F. For some tests, 5% urea (relative to the sodium sorbent on a weight basis) was injected as a solution downstream of the final heat exchanger. The baghouse temperature was lower than the injection temperature, due to heat loss through the walls. The injected sodium compounds were entrained in flue gas at the injection temperature for about one second, after which they entered the baghouse, where they remained until removed from the bags. The reactions between the sodium compounds and SO₂ and NO_x therefore took place initially at the injection temperature (minutes).

Figure 4 shows the SO_2/NO_x removal as a function of sodium injection temperature. Alcohol hydrate was used at an injection temperature of 1000°F for the data of this figure, and accounted for 60-70% SO_2 removal. Overall SO_2 removal remained at about 90% for the full

injection temperature range. NO_x removal improved with increasing temperature when the urea additive was used, but NO_x removal remained relatively constant at injection temperatures or as injection temperatures fell below 350°F. A fifty percent NO_x reduction was the assumed contribution of a low NO_x burner for the purpose of this Figure. It can be seen that the sodium bicarbonate gave slightly better removal of SO_2 and NO_x than did sodium sesquicarbonate.

PROOF-OF-CONCEPT TESTING

The proof-of-concept demonstration is being conducted on the large combustor at the Riley Stoker Research Facility in Worcester, MA. As a result of the subscale tests described above, an alcohol water hydrate is used as the principal calcium sorbent in the proof-ofconcept tests. Sodium bicarbonate will be the principal sodium sorbent, because of its availability relative to sesquicarbonate.

Figure 5 shows a plan view of the equipment arrangement. The demonstration plant begins with a combustor equipped with a low NO_{χ} burner firing at a rate of 50 million Btu/hr. A slip stream of 7,000 scfm of flue gas from the combustor is routed to a heat exchanger to reduce the temperature of the gas entering the simulated economizer to 900-1100°F. A 6-ft long section of open duct separates this heat exchanger from the economizer tube banks to accommodate hydrate sorbent injectors. The economizer is simulated with two air-cooled heat exchangers.

The gas exits the economizer section at 650-750°F and is then cooled in a simulated air heater to 300°F. The duct is straight except for one 180-degree turn to bring the flue gas back to the particulate control devices. Dry sodium bicarbonate is injected into the flue gas exiting the air preheater. Subsequent humidification of the flue gas with a water spray is expected to enhance precipitator performance. The 30inch duct continues into a pulse-jet baghouse, and a 15-inch duct takes a portion of the flow into an electrostatic precipitator. Separate venturis and dampers are used to control flow through the baghouse and ESP. The gas streams are combined and returned to the scrubber using a booster fan.

The parametric test program consists of a series of tests for the purpose of demonstrating SO_2 and NO_x reductions. The program is designed to allow a determination of the influence of each parameter on SO_2 and NO_x removal. The parameters that will be investigated are given in Table 2, along with the range of each.

The selected program lime hydrate is an alcohol hydrate, with a surface area of $35 \text{ m}^2/\text{gm}$, and a mass median particle size of 2.3 microns, and the selected sodium bicarbonate has a mmd of 15 microns.

It is expected that flue gas humidification will allow the precipitator to control outlet particulate loading and opacity to baseline levels when subjected to increased inlet loads due to hydrate injection. Evaporative cooling to about 200 deg. F upstream of the precipitator results in decreased gas volumetric flow and conditions the collected fly ash layer yielding lower resistivity.

The testing described here is expected to define the operating limits of the technology. Curves of removal efficiency versus sorbent to SO_2 and NO, mole ratios will be generated. The effects of the parameters of Table 2 on these removal efficiency curves will be quantified. Finally, the effects of these injected sorbents on the downstream precipitator will be determined and mitigation techniques, such as humidification, will be evaluated.

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Figure 1 Integrated Dry Injection Concept



Figure 2 Subscale System



Figure 3 SO₂ Removal For the Hydrates of Table 1





Figure 4 Combined SO₂ and NO_x Removal



Figure 5 Proof of Concept System

Table 1

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Test Hydrates

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	Hydrate	Surface Area m²/g	ММД (ДДД)	
1.	Mississippi	23.5	2.2	
2.	Marblehead Lime	16.0	3.4	•
з.	Bellefonte Lime	20.5	2.8	
4.	Tenn-Luttrell	19.0	2.7	
5.	Chemical Lime	19.1	3.4	
6.	Colton Lime	19.0	2.6	
7.	Alcohol Hydrate	38.0	1.7	
8.	Lignosite Additive	15.1	2.6	

Table 2

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Test Parameters

Parameter	Range		
Economizer Inlet Temperature	900 - 1100°F		
Air Heater Exit Temperature	250 - 350°F		
Precipitator Inlet Temperature	160 - 350°F		
Ca(OH),/SO, Mole Ratio	1.5 - 2.5		
$2NaHCO_{2}/(SO_{2} + 2NO)$ Mole Ratio	0.5 - 2.5		
Inlet SO	600 - 3100ppm		
Inlet NO _x	240 - 600 ppm		

Engineering Evaluation of Combined NOx/SO₂ Controls for Utility Application

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ABSTRACT

This project evaluated the potential for developing combined NO_x/SO₂ technologies to provide attractive alternatives to conventional flue gas desulfurization (FGD) and selective catalytic reduction (SCR). The technical feasibility of candidate processes was determined through a specially-developed <u>process evaluation methodology</u>, that rated candidate processes according to over 20 criteria. This analysis identified several processes that appear favorable to conventional FGD/SCR, as well as potential improvements for additional processes that elevate their rating to be equivalent or preferable to FGD/SCR. For new plants, the NOXSO, Copper Oxide, and Zinc Oxide *absorption/regeneration* processes, and the WSA-SNO *catalytic reduction/oxidation* process were rated equivalent or preferable to FGD/SCR. For retrofits, the electron beam process rates equivalent or preferable to FGD/SCR. Other processes - such as activated carbon, wet chemical additives, and SNRB - appear favorable pending certain process improvements, and under selected conditions.

Cost estimates for NOXSO, WSA-SNOx, and electron beam show all require higher capital cost than conventional FGD/SCR (\$200/kW), a consequence of the more complex and numerous components to regenerate SO2 and NO_x into reusable byproducts, recover heat for use in plant, etc. All processes potentially can implement improvements to reduce capital cost; however only NOXSO has potential to be equivalent to FGD/SCR. For levelized costs, candidate SO2/NO_x processes required higher levelized cost than equivalent to FGD/SCR (8.8 mills/kWh). Similar to capital cost, all candidates have potential improvements which if successfully implemented could reduce levelized costs to be competitive with FGD/SCR.

The results of this project are not intended to endorse any specific processes. Accordingly, additional processes will be analyzed to evaluate process improvements to elevate the technical feasibility rating. Where appropriate, capital and levelized costs will be determined.

INTRODUCTION

The 1990 Clean Air Act Amendments (CAAA) clarify for future decades the requirements for SO2 and NO_X control. The creation of the SO2 allowance - and the ability to transfer, trade, and/or sell such allowances - provides the industry with significant flexibility in defining the least cost SO2 compliance strategy. For many utilities, an attractive option is to obtain extremely high SO2 removal efficiency (>95%) at one site - maximizing SO2 control for a given capital investment. Regarding NO_X, two factors offer potential incentive for control beyond that capable with low NO_X burners. First, the prospects of a NO_X/SO2 emissions trade - to be evaluated in terms of economic and environmental impacts in a report to Congress due January 1, 1994 - may promote significant NO_X reduction at one site, similar to that for SO2. Second, the ability to comply by averaging NO_X emissions - as proposed by Section 407 of the CAAA - provides similar incentive.

The conventional technologies used to provide significant SO2 and NO_x removal on low sulfur coals in Japan and Europe are wet flue gas desulfurization (FGD) and selective catalytic reduction (SCR). The use of SCR, although not proven for high sulfur coal due to issues relating to byproduct SO3 emissions, balance-of-plant impacts, and catalyst lifetime, is being considered by state and local regulators for new plants. Alternative technologies with less complexity, cost, and heat rate penalty could provide industry with additional compliance options and cost savings. This project supports EPRI's effort to maximize the technologies available to the industry to meet SO2 and NO_x control goals, as well as waste water and solids management requirements.

PROJECT DESCRIPTION

The objective of this project is to evaluate candidate processes for combined SO₂ and NO_x removal. The premise of the project is that processes that combine SO₂ and NO_x into one step, or that employ separate steps with synergistic interations, are preferable to FGD/SCR in terms of cost, reliability, and environmental effects.

The results of this project are not intended to endorse any specific NO_X/SO_2 processes, but rather to maximize EPRI research investment to develop, commercialize, and deploy such technologies. The results will direct investment in selected candidate processes either (1) as presently envisioned, or (2) with modifications to better meet utility needs. Results will define three possible actions:

- Full-scale process demonstration (at nominally >50 MW), based on proven performance at 1-5 MW pilot plant scale, <u>including fully integrated and</u> <u>continuous operation</u>,
- Further process development at 1-5 MW pilot plant scale, <u>including fully</u> <u>integrated and continuous operation</u>, based on bench-scale results (at several hundred acfm) that clarify the underlying chemical/physical concepts, or

• Additional bench-scale process development, addressing unresolved fundamental issues that question the process technical basis or applicability to utility systems.

To address these and other issues a technical feasibility analysis was conducted. This analysis evaluated process features in terms of the potential to meet utility needs. Economic evaluations were conducted for a limited number of processes ranked according to the technical feasibility analysis as equal or preferable to FGD/SCR. Processes not ranked equivalent to FGD/SCR were analyzed to identify improvements to increase their ranking.

PROJECT APPROACH

A process evaluation methodology was developed to rate candidate NO_x/SO2 processes by a quantitative scale in terms of potential to fulfill utility industry needs.

Candidate processes were identified by a literature search conducted in 1988 for EPRI by Battelle (1); other processes were added as identified. The initial 70 processes identified were reduced to approximately 25; in many instances the process developers had abandoned development work after identifying a key shortcoming. Also, many developers focused not on a complete process but on one step - for example gas phase SO2 or NO_X removal without consideration of practical waste water and solid management needs. Thus, in many instances a complete process as necessary for commercialization did not exist.

Developers of the processes that survived the initial screening were solicited for detailed process information. As many processes are similar in concept, several could represented by one type, to simplify the analysis. A complete technical feasibility assessment was completed for 15 of the processes.

Cost estimates have been, or are being, prepared for eight or these processes for both new plant application and for retrofit to existing plants. In addition, costs were developed for conventional and advanced versions of FGD/SCR according to the EPRI Technical Assessment Guide (3). Capital and total levelized costs were developed for a 500 MW unit firing bituminus high sulfur coal; specific premises are presented later in this paper.

EVALUATION METHODOLOGY

The purpose of the evaluation methodology is to rate each process by quantitative scores for key criteria. The evaluation methodology provides a broad-based systems perspective for evaluating technologies, rather than focusing on one or a selected number of characteristics or features. Although quantitative scores are derived, the results are by definition subjective, due to the nature of quantifying the value of a process feature.

Table 1 presents the process evaluation methodology criteria, described as follows:

<u>Retrofittability (for existing plants only)</u>. The features of a process that determine the advantages/disadvantages for retrofit into existing plant sites are considered. These include process conditions at the point of access (flue gas temperature, gas composition), the "footprint" required by the process and the subsequent area for installation, the land requirements for waste disposal, and the use of existing equipment. Also, processes for retrofit were evaluated according to two cases of SO2 and NO_X removal. These were (a) 90% and 80% for SO2 and NO_X removal, respectively, (both new and retrofit), and (b) a second retrofit case of 50% SO2 and NO_X removal. The latter was included to reflect the potential need for moderate control applications.

<u>Environmental Risk</u>. This criterion addresses relative risk posed by either air, water, or solids emissions; and risk to worker health/safety. The process features considered are (a) the fate/composition of high-volume waste from SO2 and NO_X removal (either regenerated for commercial use or treated for landfill), (b) the composition/nature of low-volume wastes or byproducts, (c) secondary gaseous emissions, and (d) risk induced by process upsets.

<u>Process Reliability</u>. Process features proposed to define reliability issues are (a) chemical complexity (number of significant chemical process steps), (b) mechanical complexity (number of significant mechanical steps), (c) sensitivity of process equipment to upsets in boiler operation, reagent feed, temperature control, etc., and (d) presence of corrosive environments (requiring exotic/costly materials of construction).

<u>Energy And Resource Requirements</u>. The energy and resource requirements, estimated based on a simplified process flow sheet developed for each process, allowed an estimate for (a) auxiliary power use (or additional power generation potential), (b) consumable reagents (lime, limestone, ammonia, etc.), (c) catalyst/sorbent consumption rates, and (d) byproduct or energy credit. These quantitative estimates used fuel, auxiliary power, and chemical cost per the EPRI TAG.

Table 2 provides an example of the manner in which points were awarded for process features, by presenting the indices for determining scores for selected Retrofittability and Environmental Risk criteria.

For each process, a total score was derived by summing the points awarded for each of the preceding criteria, according to weighting factors. The baseline assessment presumed that all criteria were equally important - and thus each category received equal weight. In addition to the baseline case, sensitivity analyses were conducted to determine if the process rating significantly changed when either Retrofittability, Environmental Risk, Process Reliability, or Energy & Resource Requirements received additional weighting. Thus, a total of 5 scores provided the basis for comparing candidate processes.

CATEGORIZATION OF NOx/SO2 PROCESSES

Six categories can be defined into which almost all combined NO_X/SO_2 processes can be assigned. Although most processes are unique, many share similar chemical processes

and physical equipment, and thus are similar in how they integrate into the balance-ofplant. Table 3 summarizes the processes considered for evaluation, and the six categories defined. The categories are described as follows:

<u>Adsorption/Regeneration</u>. This type of process (Figure 1a), representing the largest number of candidates identified, employs contacting a physical sorbent or catalyst with flue gas, which adsorbs or reacts with SO2 and NO_x. This sorbent/catalyst is physically removed from the flue gas to a regeneration reactor, where the sulfur or nitrogen species are liberated from the sorbent. Generally, the regeneration step(s) require high temperature or reducing gas (e.g., CO, H2, methane) at sufficient residence time to create a byproduct stream of concentrated SO2 or NO_x. Each absorption/regeneration process differs in regard to the type and quantity of sorbent/catalyst that must be recirculated, the location of the flue gas adsorber (before or after the air heater), the requirement for an additional particulate collector, the regeneration temperature and quantity of reducing gas, and fate of NO_x (e.g., regenerated or reduced selectively in the flue gas).

<u>Flue Gas Irradiation</u>. This category requires exposing flue gas to a high energy flux, most commonly an electron beam to generate particulates (ammonium sulfates or nitrates) for collection by an ESP or baghouse. Processes differ in terms of the method of exposing flue gas to the energy flux, and the control equipment employed to form and collect particulate.

The key features of the electron beam process are illustrated in Figure 1b. Flue gas leaves the existing particulate collector, proceeds to an evaporative spray cooler and electron beam chamber, where irradiation generates hydroxyl radicals and oxygen atoms, which react with SO2 and NO_X to form sulfuric and nitric acids. These acids react with injected ammonia to form sulfates and nitrates of ammonia, which are subsequently collected in a two-phase particulate control device. Collected solids are granulated and prepared for use as feedstock for fertilizer manufacture.

<u>Catalytic/Oxidation Reduction</u>. This process type employs two sequential catalysts to (a) remove NO_x by SCR, and (b) oxidize SO₂ to SO₃, condensing the latter as sulfuric acid for byproduct sale. Processes differ in the temperature at which each reactor operates, the location of the particulate control device, and the mechanism for acid condensation.

Figure 1c presents a schematic of one version of this process designed to follow a conventional particulate collector. A conventional SCR reactor reduces NO_X, followed by a reheating system (using auxiliary fuel) to elevate flue gas temperature and improve SO2 to SO3 oxidation reactor performance. After SO3 formation, a condenser is employed to produce a high quality sulfuric acid for resale. The heat released by the oxidation of SO2 to SO3 and the condensation of the sulfuric acid is partially recovered with a heat exchanger to reduce auxiliary fuel consumption.

<u>Wet Scrubber Additives</u>. This category employs additives in wet scrubbers (most notably lime, limestone, or dual alkali) to remove NO_x. The principle additives are iron chelate based compounds, which employ chemical properties to dissolve NO in solution,

removing the resulting compound as hydroxlyaminedisulfonates (HADS, and associated similar compounds). Processes differ in terms of the specific additive employed, the techniques for spent additive regeneration and/or recovery, and waste management practices.

<u>Dry Alkai Additives</u>. Additives have been developed that can be injected into alkalibased dry injection systems (e.g., spray dryers, in-duct processes) to effect NO_x removal. For example, sodium hydroxide has been employed with conventional spray dryers to provide modest NO_x removal that varies with the process conditions in both the dryer vessel and the particulate collector. Similar to wet scrubbing, the specific fate of NO_x removed appears to be a form of HADS. Both the HADS and sodium species in the waste present special waste management issues.

<u>Electrochemical Catalysts</u>. Catalysts that employ electrically induced polarity to accomplish electrochemical reduction of SO₂ and NO_x have been developed. The fate of SO₂ and NO_x is reduction to elemental sulfur and nitrogen; the former is condensed in low temperature heat exchangers, similar to sulfuric acid. Processes differ with respect to the form and material in which the catalyst is manufactured.

TECHNICAL FEASIBILITY EVALUATION RESULTS

The process evaluation methodology was applied to 15 of the processes in Table 3. Analyses were conducted for both new and retrofit applications (differentiated by including the Retrofittability criterion and the Case 2 [50%/50%] SO2/NO_X control goals in addition to Case 1). Total process scores were compared to those for FGD/SCR for a "baseline" case - where the criteria of Retrofittability, Environmental Risk, Process Reliability, and Energy and Resource Requirements were assigned equal weighting. In addition, four scores were derived for cases where each criterion was assigned a dominant (80% weighting) role.

The results identified five processes that consistently rated higher than FGD/SCR for the conditions cited. These processes were three absorption/regeneration (NOXSO, Copper Oxide, Zinc Oxide), one flue gas irradiation (E-beam, for retrofit only), and one catalytic reduction/oxidation (WSA-SNO_x). The features of these processes that contribute to their selection are discussed in the following.

Absorption/Regeneration

The NOXSO, Copper Oxide, and Zinc Oxide processes each share common features and thus reasons for receiving a relatively high score. All three processes scored at or near the top in Environmental Risk due to eliminating high volume waste by regenerating SO2 into a byproduct and reducing NO_X to molecular nitrogen, without producing significant secondary emissions. The combination of these two features without significant offsetting penalties in other criteria (e.g., Process Reliability) promoted a high rating.

Among these three absorption/regeneration processes, the NOXSO process received simultaneous high scores for both new and retrofit applications. A significant factor promoting a high ranking for NOXSO is the Retrofittability score, as the process requires low temperature flue gas. The Copper Oxide process requires flue gas temperature access prior to the air heater, and thus suffers in Retrofittability compared to NOXSO. However, the NO_X reduction and SO₂ regeneration steps are less complex for Copper Oxide than NOXSO or Zinc Oxide; thus the Copper Oxide process derives relatively favorable scores for Chemical and Mechanical Complexity. The Zinc Oxide process scores well in Energy & Resource Requirements, as the combination of sorbent attrition rate, unit cost, and mass recirculation rate minimizes sorbent make-up costs.

Catalytic Reduction/Oxidation

The process evaluated to represent this category, the WSA-SNO_x process, similarly eliminates high volume waste products and produces a commodity for resale. However, the Environmental Risk score is penalized by the need to manage/dispose two catalysts, the potential for secondary emissions (e.g., SO3, NO2), and possible worker exposure to sulfuric acid in the plant. The strengths of this process are the relatively few significant chemical and mechanical steps, leading to a favorable Chemical and Mechanical Complexity Score, and a favorable Energy & Resource Requirement score.

Electron Beam Process

The electron beam process scored above advanced FGD/SCR for retrofit plants only. The ease of retrofit allowed by access to flue gas after the particulate collector contributed to the Retrofittability score; in Energy & Resource Requirements production of a saleable byproduct offset a significant auxiliary power penalty. (The lower NO_X removal requirement for Retrofit Case 2 [50%] reduced auxiliary power relative to an 80% requirement.) This process did not score very high in any one category, but received moderate to good scores among all categories. The process did not rank above conventional FGD/SCR for new installations, as the retrofit score was not included and the auxiliary power penalty for achieving high NO_X removal (80%) assumed required for new plants is high.

ECONOMIC EVALUATION RESULTS

Preliminary capital and operating costs for these processes have been determined. Table 4 provides the specific design and economic assumptions employed for this analysis.

Complete process flowsheets were prepared, allowing equipment lists to be developed, and costs assigned based on budgetary bids from several equipment vendors. The uncertain development state for candidate processes necessitated that the cost analysis define the sensitivity to changes in key design variables. In this manner, costs were developed for a "baseline" design, that incorporates the best estimate for design variables, and a "sensitivity" analysis to determine the influence of uncertainty for these variables on process cost.
The premise of the sensitivity studies is that the lack of operating experience allows a significant uncertainty in process design, which may not provide commercially acceptable conditions. Historically, design premises for developing technologies have been "optimistic," in that a lack of realistic experience leads to inadequate design for factors such as contactor residence time, mass transfer, reagent reactivity, and equipment sparing. Thus, costs for the first several full-scale versions of developing processes are frequently greater than estimates derived from pilot-scale data. However, experience can lead to improve designs, which eventually can lower cost and/or improve performance. This trend has been witnessed with wet lime/limestone scrubbers, as recent design concepts are lower in cost than the earlier generation designs applied in last decade.

Combined NOx/SO2 Process Cost Discussion

Costs are presented in this paper only for the NOXSO, WSA-SNO_x, and E-beam processes; as well as for a conventional and advanced version of FGD/SCR. An advanced version of FGD/SCR credited this approach with deriving the same improvements in process control, materials of construction, and catalyst activity/performance that are assumed for candidate NO_x/SO2 processes. For example, the advanced process version assumed developing catalysts would be available in 5-7 years that provided control of the NO_x and residual ammonia available presently with 2/3 the amount of catalyst, thereby requiring a smaller reactor. The advanced FGD process employed reduced sparing and other process developments. Additional specifics of the conventional and advanced process versions are detailed in reference (2).

Figures 2, 3, and 4 present capital and operating costs for these processes, including the results of sensitivity analyses.

<u>NOXSO</u>. Figure 2a shows the NOXSO capital cost estimate of approximately \$257/kW can vary based on the design premises for particulate control, solids handling, absorber residence time, sorbent utilization, and sorbent unit costs. Specifically, the capital cost increase (or decrease) is shown for changes to (a) particulate collector design, requiring changes in specific collecting area (SCA) by +15 or -10%, (b) spare solids recirculation capacity (changes from +100 to -25% from baseline sparing assumptions), (c) file gas absorber residence time (+ 20% or -20% changes from baseline, respectively), (d) sorbent utilization (+20% and -20% changes, respectively), and finally (e) sorbent unit cost (+20% or -20% from baseline cost). These results show the design premises for particulate control, adsorber residence time, and sorbent utilization have the most significant effects on NOXSO process costs.

Figure 2b presents the results for NOXSO levelized costs, including a sensitivity analysis for the previously discussed design premises, and operating cost factors such as natural gas and sorbent attrition rate. Figure 2b shows the baseline cost estimate of approximately 11.7 mills/kWh can change by 0.5 mills/kWh or more due to each of the following: particulate control, sorbent utilization, sorbent cost, waste disposal, and natural gas consumption. The results show the influence of sorbent attrition is most significant,

and if doubled or halved from the baseline values affects levelized cost by 2.8 or 1.3 mills/kWh, respectively.

<u>WSA-SNOx</u>. Similar results for the WSA-SNO_x process are presented in Figure 3. Figure 3a shows the WSA-SNO_x capital cost of approximately \$375/kW can vary based on the design premises for particulate control, space velocity of the SCR reactor and the SO₂ oxidation catalyst reactor, and the acid condensing tower spare capacity. Specifically, the capital cost increase (or decrease) is shown for changes in (a) air/cloth ratio for the fabric filter (increase to 1.5, versus decrease to 5.5 ft/s), (b) SCR catalyst space velocity (5000 hr-1 versus 7000 hr-1), (c) SO₂ oxidation catalyst space velocity (1500 vs. 1900 hr-1), and (d) increasing (by 10%) or eliminating condensing tower spare capacity. Figure 3b shows the baseline cost estimate of approximately 10.5 mills/kWh can vary by approximately 0.25 - 0.5 mills/kWh for each of the following: SCR catalyst space velocity, SO₂ oxidation catalyst space velocity, SO₂ oxidation catalyst life, sulfuric acid condensing tower sparing, and revenue from recovered sulfuric acid.

<u>Electron Beam</u>. Results for the electron beam process are shown in Figure 4. Figure 4a shows capital cost estimates approach S400/kW, and show the influence of changes in evaporator residence time, capital cost of the electron beam generator, the successful development of an advanced two-stage low power consuming electron generator, and particulate control. For the levelized cost presented in Figure 4b, the electron beam approach requires almost 13 mills/kWh. The influence of the preceding design variables is shown, as is the effect of market value of the byproduct material.

Comparison to FGD/SCR

Figures 5 and 6 compare combined NO_x/SO2 process results with conventional and advanced FGD/SCR. The results compare baseline costs as well as a minimum and maximum range, suggested by the previous sensitivity studies. The minimum and maximum costs are based on the scenario of <u>all described design premises changing</u> <u>simultaneously to the maximum/minimum range</u>. This occurrence is not anticipated, but the range is reported to indicate the cost estimate uncertainty.

Results for the "baseline" assumptions indicate all NOx/SO2 process candidates require greater capital and levelized cost than either conventional or advanced FGD/SCR. This is attributable to the more extensive equipment required for byproduct generation equipment, heat exchangers, solid sorbent materials handling, etc., necessary to eliminate high volume waste for disposal. Only the NOXSO process has the potential to be competitive with conventional and advanced FGD/SCR on a capital cost basis.

For levelized cost, baseline estimates are not competitive with conventional and advanced FGD/SCR. However, all three combined NO_X/SO_2 processes potentially can provide competitive alternatives, depending on the validity of the design assumptions.

RESULTS APPLICATION

These results have been and will continue to be used by EPRI to direct research to maximize the number of viable combined NO_X/SO_2 control technologies. The results of this study indicate that some processes are ready for additional development at 1-5 MW pilot plant scale, while others could benefit most from from additional bench-scale development prior to more costly pilot plant work.

Pilot Plant Development

Early results from this project prompted EPRI participation in several key pilot plant activities to develop the NOXSO and SNRB processes, with Ohio Edison and other . cosponsors. These activities are described in a companion paper in this Symposium (3).

Additional Processes

These results can be used to evaluate process improvements to increase technical feasibility scores of candidate processes that, as presently envisioned do not rate equivalent or preferable to FGD/SCR. Two examples are:

Wet Chemical Scrubber Additives. This category received low scores for (a) Energy & Resource Requirements, as the excessive loss and subsequent makeup required for chelating agents contributed to a significant operating cost, and (b) Environmental Risk, as the contamination of conventional scrubber waste with both the chelating agent and the nitrogen-containing waste (possibly as a form of HADS) could complicate disposal and management of the scrubber high volume waste. A variation of this process has been evaluated with enhanced methods for recovery of chelating agent, and treatment of scrubber slurry for HADS which increases the process score to be equivalent to FGD/SCR. The economics of the wet scrubber additive combined NO_X/SO2 process with these improvements will be evaluated.

<u>Activated Carbon (Absorption/Regeneration)</u>. This process received a low score initially due to the (a) high attrition rate and makeup required for activated carbon (penalizing the Energy & Resource Requirements score), and (b) large number of chemical and mechanical individual process steps (penalizing the Chemical and Mechanical complexity score). Reducing the char consumption rate and simplifying the regeneration steps increases the total process score to be competitive with conventional and advanced FGD/SCR. A version of this process is presently being evaluated that is capable of lower char replacement costs, and with simplified regeneration or sulfur compound disposal.

At present economic evaluations are being developed for three additional absorption/ regeneration processes (Copper Oxide, Activated Carbon, and Zinc Oxide), and for the wet scrubber additive process (iron chelate with electrochemical regeneration). An economic evaluation is being conducted for the SNRB process for new plants. The SNRB process, although not scoring equivalent to FGD/SCR in the baseline case, demonstrated a favorable score when Process Reliability was emphasized (due to the small number of chemical and mechanical steps). Also, two advanced processes with limited bench-scale data exhibit potential to derive a high score (Lehigh absorption/regeneration, and IGR electrochemical); their further development will be monitored and possibly supported. Additional processes that did not initially compare well with FGD/SCR will be evaluated to define process improvements .

SUMMARY

This project evaluated the technical feasibility of initially 70 combined NO_x/SO₂ processes, for the purpose of identifying alternatives to FGD/SCR. The technical feasibility was determined through a specially-developed <u>process evaluation</u> <u>methodology</u> that evaluated candidate NO_x/SO₂ processes using vendor-supplied information. This analysis, conducted for both new and retrofit applications, identified several processes that ranked favorable to FGD/SCR. For new plants, processes in the sorbent absorption/regeneration category (NOXSO, Copper Oxide, Zinc Oxide), one from the catalytic reduction/oxidation category (WSA-SNO_x), were rated preferable to conventional and advanced FGD/SCR for new applications. For retrofits, the electron beam process scores equivalent or preferable to FGD/SCR. Other processes - such as activated carbon, wet chemical additives, and SNRB - have been evaluated to identify conditions for which their rating increases relative to FGD/SCR.

Cost estimates show all processes require higher capital cost than FGD/SCR, (\$160-200/kW) a consequence of more complex and numerous components to regenerate SO2 and NO_X into reusable byproducts, recover heat for use in plant, etc. Capital cost for combined SO2/NO_X processes were greater than FGD/SCR; sensitivity analysis showed each processes had potential for lower capital cost, equivalent to FGD/SCR for NOXSO.

Regarding levelized costs, candidate SO2/NO_x processes required higher levelized cost than FGD/SCR (8.8 mills/kWh). Similar to capital cost, each candidate process has potential for significantly lower levelized cost. Depending on the design assumptions and research results, each process could be economically competitive with FGD/SCR.

Processes that did not score favorable compared to FGD/SCR can implement process modifications to improve their rating compared to FGD/SCR.

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CRITERIA FOR THE EVALUATION METHODOLOGY

1. **Retrofitability**

- Required Point of Access to Flue Gas Stream (20%) -
- Process Land/Space Requirements (20%) -

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- Land/Space Requirements for Waste Disposal (20%) -
- Use of Existing Equipment (40%) -

2. Environmental Risk

- High Volume Waste or Byproduct Materials (60%) -
- Low Volume Waste or Byproduct Materials (10%)
- Secondary Gaseous Emissions (20%)
- Risk Induced by Process Upsets (10%)

3. Process Reliability

- Chemical Complexity (25%)
 Mechanical Complexity (25%)
 Sensitivity to Process Upsets (25%)
- Corrosive Environments (25%)

Energy_and Resource Requirements 4.

- Quantity of Energy Required
- Reagent Consumption Rates
- Catalyst/Sorbent Consumption Rates
 Byproduct or Energy Credit

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EXAMPLES OF THE SCORING PROCEDURE/POINTS AWARDED

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Retrofitability: Example: Required point of access to the flue gas stream

<u>Points</u>	Description		
10	Access required following a cold side ESP or baghouse		
5	Access required between the air heater and the particulate collection device		
3	Access required between the air heater and economizer		
1	Access required upstream of the economizer		

Environmental Risk: Example: High volume waste or byproduct materials

<u>Points</u>	Description
10	Process produces a byproduct of high purity which is always marketable
8	Process produces a byproduct for which market may be limited by seasonal or geographic factors
7	Process produces a byproduct which could potentially be sold but for which a market has not been established
6	Process produces a benign waste which is easy to handle and presents no disposal problems
5	Process produces benign waste more difficult to handle
3	Process waste contains soluble materials which could be leached from the waste
0	Process waste stream is potentially hazardous
Example:	Low volume waste or by product materials
<u>Points</u>	Description
10	Process produces no low volume wastes
8	Process produces low volume wastes which are saleable
7	Process produces low volume wastes which are easily disposed of (e.g., co-disposal with other waste streams)
6	Process produces low volume wastes which are treatable
5	Process produces low volume wastes which can be reprocessed (e.g., catalysts with valuable metals)
4	Process produces low volume waste which may present some disposal problems due to chemical/physical properties
2	Process produces a low volume waste which is hazardous
0	Process produces multiple hazardous low volume wastes

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PROCESS IDENTIFIED FOR TECHNICAL EVALUATION

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Overall Process Category	Process Name
Solid Adsorption/Regeneration	UOP/PETC Fluidized-Bed Copper Oxide Rockwell Moving-Bed Copper Oxide NOXSO Mitsui/BF Activated Coke Sumitomo/EPDC Activated Char Sanitech Nelsorbent SOx/NOx Control Lehigh University Low Temperature Battelle ZnO Spray Dryer
Irradiation of the Flue Gas	Ebara E-Beam ENEL Pulse-Energization
Wet Scrubbing	Argonne/Dravo ARGONNOX Dow Electrochemical Regeneration
Gas/Solid Catalytic Operations	Haldor Topsoe WSA-SNO _X Degussa Catalytic B&W SO _X /NO _X /RO _X /BO _X (SNRB) Parsons Flue Gas Cleanup
Dry Injection Additives	Argonne High-Temperature Spray Dryer PETC Mixed Alkali Spray Dryer Studies
Electrochemical	IGR/Helipump

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GENERAL DESIGN PREMISES FOR ENGINEERING EVALUATION

Design Premises

Application: Location: Boiler Size: Boiler Type: Plant Life: Fuel Analysis:	Utility Boiler Kenosha, WI 500 MWe Pulverized coal 30 years
C:	67.0
H:	4.6
N:	1.2
S:	3.0
0:	4.7
Cl:	0.1
Ash:	16.4
Moisture:	3.0
Firing Rate:	196 tph
Gross Heating Value:	12,360 Btu/lb
SO, Emission:	4.8 1b/MBtu
NOÇ Emission:	0.4 lb/MBtu, (0.6 lb/MBtu for retrofit)
SO, Reduction:	New - 90%, for retrofit - 90% & 50%
NO ^c Reduction:	New - 80%, for retrofit - 80% & 50%

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Economic Premises

Commercial Operating	
Date:	January 1995
Construction Period:	3 years
Discount rate:	6.2%/year
AFUDC rate:	6.2%/year
Levelized fixed	
charge Rate*:	10.6%/year
Base Inflation Rate:	0%/year
Real Escalation Rate:	
Natural Gas:	4.3%/year
Nonfuel Items:	0.0%/year
30-year Levalization	
rate:	1.0%/year

* Based on 30-year book life, 20-year tax life, 38% composite federal and state tax, and 2.0% for property taxes and insurance.



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ADVANCED FLUE GAS TREATMENT USING ACTIVATED CHAR PROCESS COMBINED WITH FBC

Hitoshi Murayama Thermal Power Department Electric Power Development Co., Ltd. Tokyo, Japan 104

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ABSTRACT

There is a process combined with the use of a fluidized bed combustion boiler (FBC) as a flue gas treatment process using activated char. This technology utilizes both features of the activated char flue gas treatment system and the fluidized bed combustion boiler. The activated char flue gas treatment system shows a high denitrification (DeNOx) performance with the injection of ammonia. This is similar to the NOx removal system (SCR) using a metal catalyst that is often used to remove low SOx concentration flue gas. The fluidized bed combustion boiler makes low SOx concentration flue gas by the in-furnace desulfurization (DeSOx).

Furthermore, the activated char flue gas treatment system has DeSOx and de-dusting performances. Combination use with the above DeNOx technology enables high-level treatment of flue gas.

The Electric Power Development Company has been entrusted by Agency of Natural Resources & Energy, Ministry of International Trade & Industry, to perform the pilot (demonstration) test of the activated char flue gas treatment system, for which laboratory testing has already been performed. This test plant has a treatment gas amount of 10,000 m³ N/h and is attached to the FBC boiler demonstration test plant (50 MW) located in our company's Wakamatsu Coal Utilization Research Center. Testing of the plant has been carried out since last year.

The results show that the test plant satisfies the targeted performance of 80 percent NOx removal efficiency, 90 percent SOx removal efficiency, and $30 \text{ mg/m}^3\text{N}$ outlet dust concentration.

We also understand that the system has several other features and are now collecting data for commercialization of the system.

INTRODUCTION

Dry type flue gas treatment technology using activated char in the thermal power plant has been under development for more than 20 years in Japan. Its demonstration test was started 10 years ago. At present, the technology is being developed for its commercialization.

This technology has the following advantages: the amount of water used is very low compared to the conventional flue gas treatment technology (when the system is used as desulfurization (DeSOx) equipment); high-level flue gas treatment is possible; and it is not necessary to consider the influence of flue gas on the downstream equipment because the system can be installed right before the stack.

The flue gas treatment process using the activated char includes the following three processes: the dry type DeSOx process for pulverized coal combustion; the dry type DeSOx and denitrification (DeNOx) process for pulverized coal combustion; and the DeNOx process using activated char (AC-DeNOx) for the fluidized bed combustion boiler (FBC).

The Electric Power Development Company (EPDC) was entrusted by the Ministry of International Trade and Industry (MITI) to perform tests for putting these three processes to practical use. This paper reports the results of tests made so far with respect to the AC-DeNOx process used for the fluidized bed combustion boiler.

ACTIVATED CHAR FEATURES

Since the activated char has a very large specific surface, it has been used widely as an air cleaning agent and waste water treatment agent since the second half of the nineteenth century.

The activated char has various performances depending on the raw materials or manufacturing method. Activated char (activated coke) used for the treatment of flue gas has the following features.

- SOx is adsorbed.
- It has catalytic capability to decompose NOx under the existence of NH3.
- In low-temperature areas (less than 100 °C), NOx adsorption reaction becomes remarkable in place of catalytic reaction.
- SOx adsorption level is higher than NOx removal reaction level in reactivity.
- Recycle use available.
- The performance improves by repetitive recycle use.

In the DeSOx reaction, SOx is oxidized and adsorbed on the activated char surface in a form of sulfuric acid as shown in Table 1. If ammonia exists in the flue gas, it is adsorbed by the ammonium hydrogen sulfate or the ammonium sulfate.

The DeNOx reaction includes the same catalytic reaction as the SCR reaction, oxidation and adsorption reaction, and the reaction with reducing material on the surface of activated char. (Refer to Table 2.) In the flue gas treatment around 140 °C in the coal fired power plant, the main reaction is the SCR reaction.

The DeSOx reaction and the DeNOx reaction hardly occur at the same time on the surface of activated char. The DeSOx reaction has priority to its occurrence. That is, in flue gas having a high SOx concentration, the activated char performs DeSOx reaction. In flue gas having a low SOx concentration, the DeNOx reaction becomes remarkable. Figure 1 shows the relationship between the SOx concentration at the entrance of the reaction tower filled with activated char and the NOx removal efficiency. It is understood that the lower the SOx concentration is, the higher the NOx removal efficiency.

The DeSOx and DeNOx performances of the activated char lower with its adsorption of SOx, etc. It therefore becomes necessary to remove the activated char with the lowered performance and to add high-performance activated char. Normally, the reaction tower structure will be the moving bed type. Furthermore, the DeSOx and DeNOx performances of activated char are regenerated for reuse because of the high cost of production. The desorption process of SOx is mainly performed in the 400 °C reducing atmosphere. Table 3 shows the reaction configuration. The SOx which is oxidized and adsorbed on the activated char is reduced to SO2. If ammonia is present, it functions as a reducing material. If there is no ammonia, the carbon of the activated char functions as a reducing material. In the latter case, the activated char becomes depleted. This will be described later.

OUTLINE OF AC-DeNOx SYSTEM

The FBC boiler has better environmental features than PCF because of its in-furnace desulferization and low temperature burning. Generally, the FBC boiler is equip with the SCR system to satisfy the emission regulations in Japan.

The Wakamatsu Coal Utilization Research Center of EPDC also has an FBC demonstration plant (50 MW) with SCR.

Fig. 2 shows the comparison between the SCR system and AC-DeNOx system. SCR is placed in front of the AH (air preheater) because it is used in about 350 °C flue gas. In this case, the compound of NH₃, SO₃ and fly ash often causes plugging of the AH and vibration in the fan. However, as the AC-DeNOx system is able to denitrate in 140 °C flue gas, it is placed just before the stack. Furthermore, SO₃ is easily caught by activated char and cannot be detected in the flue gas of the AC-DeNOx outlet. It is therefore not necessary to consider the troubles of downstream equipment.

When the flue gas temperature is low at boiler start up, in case of the SCR system, NH3 has not been injected because the catalyst surface is covered with an ammonium sulfate compound. NH3 injection can be started when the temperature of the flue gas is sufficiently high. In the case of the AC-DeNOx system, activated char also has DeNOx performance in low temperature flue gas, as already described.

This AC-DeNOx system roughly consists of the DeNOx tower and the regenerator. The type of the DeNOx tower is a moving bed type because the activated char bed catches dust and SOx. The relation between gas flow and activated char is a crossflow. In the regenerator, SOx which is adsorbed in the activated char is desorbed, and condensed SO₂ gas which contains HCl etc. is generated. The generated gas is washed with water and then blown into the bottom of the FBC furnace with compressed air. The SOx in the furnace reacts with the calcium in the FBC bed material and is removed. Therefore, the generated SO₂ gas treatment equipment does not need in AC-DeNOx system.

As stated above, the AC-DeNOx tower works as a dust collector. The method is the as same as a granular bed dust collector. The dust which was collected by the activated char bed is discharged with activated char from the AC-DeNOx tower and separated from the activated char with a vibrating sifter through the regenerat(

The features of the AC-DeNOx system are summed up as follows:

- Denitrification can be expected from boiler start up.
- It has a secondary desulfurization effect and high performance desulfurization by combination with the FBC boiler.
- It has a dust collecting function.
- It can achieve high performance flue gas treatment.
- It is not necessary to consider this influence on downstream system such as AH, as with the SCR system.

PILOT (DEMONSTRATION) TEST FACILITY

The AC-DeNOx test facility is installed in the 50 MW FBC boiler demonstration test plant at the EPDC Wakamatsu Coal Utilization Research Center. This FBC boiler is a bubbling type and the demonstration test has been continuing since 1987.

Figure 3 shows the system of the AC-DeNOx test facilities. The test flue gas is taken out in front of the SCR in the FBC plant. The temperature and the dust concentration of its gas are controlled by the gas cooler and the bag house respectively. After the gas pressure is increased by fan, and NH3 is injected, the flue gas enters the AC-DeNOx tower.

As for activated char flow, activated char which goes in the DeNOx tower moves down slowly and is discharged out of the tower by the activated char discharging conveyor. The activated char is then sent to the regenerator by the bucket conveyor. The char reactivated in the regenerator is put into the vibrating sifter to remove activated char powder and fly ash from the char. The char is again sent to the DeNOx tower. Because a small amount of activated char is lost, the lost amount is replaced.

The condensed SO₂ gas which is generated in the regenerator is washed for removing HCl etc. and then goes into the wind box of the FBC boiler.

Table 4 shows the outline of the DeNOx tower. The tower is rather large compared with the SCR reactor.

Figure 4 shows the structure of the DeNOx tower. It is divided three layers along the char flow. The first layer is the flue gas inlet layer, that is the louver layer, for the desulfurization and dust removal. The second layer is for dust removal and denitrification. The third one is for the DeNOx. The moving rate of

the three layers is different for each. The rate of the first layer is the fastest and the rates are slow in order of the second and third layers. These rates are determined according to the degree of dust collection. The average retention time of the activated char is 120 ~ 150 hrs.

The structure of the regenerator is shown in Figure 5. As shown in the figure, it is divided into two parts; the heating part and cooling part. The methods of heating and cooling are indirect for each. The middle of the regenerator between the heating part and the cooling part is for collecting generated gas.

TEST ITEMS AND TEST CONDITIONS

The first test item is to achieve the target performance shown in Table 5. The DeNOx efficiency is more than 80%, the DeSOx efficiency is more than 90%, and the dust concentration at the AC-DeNOx tower is less than 30 mg/m³N. The other test items are as follows:

- Stability of operation over a long period time
- Loss ratio of activated char
- Boiler type characteristics
- Optimal amount of moved activated char
- Others

For the test conditions, the inlet gas condition is shown in Table 6. The actual NOx and SOx concentrations are shown in Figures 6 and 7. Maximum NOx concentration is about 250 ppm and maximum SOx concentration is less than 100 ppm. In most cases these are 200 ppm and 50 ppm, respectively.

In regard to NH3 injection, NH3 reacts with SOx before reacting with NOx on activated char. Therefore, an amount of NH3 injection is also needed for the reaction with NOx and SOx. The amount of NH3 reacting with SOx is $1.2 \sim 1.7$ as mole ratio which has been obtained in laboratory tests. In these tests, NH3 is injected at a mole ratio of $1.5 \text{ NH}_3/\text{SOx}$. For removing NOx, NH3 and NOx reacts one to one. NH3 is injected by set up mole ratio.

Though other compounds may react with NH3, they are ignored. The amount of NH3 injection is determined by the following equation.

UNH3 = {C_{SOx} x 1.5 + C_{NOx} x [set up mole ratio]} x 10⁻⁶ x [flue gas volume] U_{NH3}: NH3 injection volume (m³N/h) C_{SOx}: Concentration (ppm) C_{NOx}: NOx Concentration (ppm)

TEST RESULTS

The test equipment has worked for about 3,000 hours as of this September. It has been confirmed that the target performance of this test is achieved. An example of the performance test results is shown in Table 7. Also, there has not been any serious mechanical trouble up to now.

Some factors which give influence to DeNOx efficiency were found. These factors are the partial accumulation of dust in the DeNOx tower, oxygen concentration and moisture content in flue gas.

The detailed test results are as follows.

DeNOx and DeSOx Performance

DeNOx efficiency was over the target value, 80%, in the early test run, but went down gradually. At last, the efficiency became less than 80% after a few months. There are some reasons for this phenomenon. The most important reason is the non-uniform flue gas flow in the DeNOx tower because of the partial accumulation of dust.

The reason of the partial accumulation of dust is that dust goes in the activated char layer deeply, contrary to our expectations. In the early stage, the DeNOx tower had two layers of activated char, which were the louver layer with a width of about 100 mm, and the downstream layer, 1,700 mm. The char flow rate of the front layer was fast, but the back layer was slow. Part of the dust went into the back layer so that dust accumulated in the lower level of the layer. As a result, the pressure drop of the DeNOx tower went up, flue gas distribution became bad and DeNOx efficiency dropped.

In our study, the DeNOx tower was made over into the three layers by the division of the back layer into two layers. The char flow rate of the second layer has been made faster compared with the former rate to ensure smooth discharge of dust from the DeNOx tower. The modification made improvement of the pressure drop of the DeNOx tower and DeNOx efficiency. Figure 8 shows the trend of the pressure drop before and after modification. The DeNOx efficiency has been confirmed to maintain ever 80%.

The relations between oxygen concentration, moisture content and the DeNOx efficiency are shown in Figure 9 and Figure 10, respectively. Figure 9 shows that less than 5% oxygen concentration remarkably gives influence to DeNOx efficiency. Moisture content is higher and the DeNOx efficiency is lower. By rough estimation the 1% increase of moisture content makes the DeNOx efficiency about 2% down.

Figure 11 shows the trend of DeNOx activity of activated char itself. The white circle indicates the trend of regenerated char activity. It cannot be seen as a large change, and the activity goes up only gradually. The solid circle indicates the char activity at the outlet of the DeNOx tower. There is no big difference between the regenerated char activity and the outlet of the DeNOx tower char. Though the char at the outlet of DeNOx tower is covered with fly ash, like dirty snow ball, the results indicate that it does not cause any great decrease in DeNOx efficiency. Also, much SO₂, which makes char activity decrease, was not adsorbed in the char.

There are no problems in regard to the DeSOx performance. Until now, the DeSOx 1 efficiency has been maintained at more than 90% which is the target value.

Dust Removal Performance

Before this test began, the target of dust removal efficiency was less than 30 mg/m³N. According to the test results, dust concentration at the outlet of the DeNOx tower has been less than 10 mg/m³N at all times. The inlet dust concentration was 100 ~ 240 mg/m³N. The reason why the results were much lower than the target value is that the char rate of the back layer, the flue gas outlet side layer, is set slow, so that the generation of activated char powder is reduced. In the case of other flue gas desulfurization plants using activated char, outlet dust concentration is $12 ~ 20 \text{ mg/m^3N}$. In these plants, the char rates are over four times faster than our test plant.

The analysis of the amount of unburned carbon in dust indicates that there is not such a great difference between the inlet dust and the outlet dust. That is, not so much activated char powder is generated in the back layer.

Activated Char Loss

In this system there is a certain amount of loss of activated char. There are two types of loss. The first is the mechanical loss which occurs due to abrasion between the char and the structure or of the char against itself as it circulates through the system.

The second type is chemical loss, as mentioned before, which is the carbon consumption in char at the time of deoxidizing SO3 in the regeneration.

The trend of activated char loss during testing is shown in Figure 12. This figure indicates that the activated char loss rate is less than 1% in all tests. The activated char loss rate is calculated as the percentage of weight (kg) of char supply loss against the weight (kg) of char circulation per an hour. The results are lower than our expectations. The reason is that char is not consumed so much as deoxidization material to supply sufficient ammonia in regeneration.

In our DeSOx demonstration test using activated char, commissioned by MITI, the loss rate was about 1.8%. In order for the flue gas to have more than 500 ppm SOx, there was not sufficient ammonia to deoxidize SO3. Therefore, more char was consumed. However, each plant has individual features, and it is not easy to make comparisons among different plants. All that can be said is that the AC-DeNOx plant has less char loss than the AC-DeSOx plant.

<u>Others</u>

The response of the DeNOx system to boiler start up and shut down was tested. Figure 13 shows the result of response test at boiler start up. The results indicate that the AC-DeNOx system can work early from boiler start up. The DeNOx efficiency is near 100% in the early stage, and gradually goes down with time and with the increase of flue gas volume. The minimum efficiency is 40 \sim 50%. After that, with the DeNOx tower temperature going up, DeNOx efficiency increases.

But as activated char has high heat capacity, the temperature in the DeNOx tower does not rise easily. Therefore, the DeNOx efficiency goes up slowly. This is a weak point of this system. But operation methods can cover this weak point.

There are no problems at boiler shut down. When flue gas stops, the temperature in the DeNOx tower rises easily because of char oxidization. The countermeasure of this phenomenon has been confirmed.

In regard to removal of heavy metal and halogen, some materials were measured at the inlet and outlet of the DeNOx tower. The results show that mercury is removed effectively by this system, hydrogen chloride (HCl) is removed by $50 \sim 70\%$ at 140 °C. Other materials are also removed, but as their inlet concentration level is low, the effectiveness of removal is not clearly confirmed.

CONCLUSION

The pilot (demonstration) test of AC-DeNOx technology for FBC has been good, according to expectations. As a result, this technology will be applied to the 350 MW FBC being replaced, instead of an oil-fired boiler, at Takehara Thermal Power Station No. 2 Unit.

During the remaining test period, the confirmation of long time stable operation, the performance of following boiler load change and the like are to be tested and the reliability of this technology will be confirmed.

In this paper, activated char flue gas treatment technology has been mentioned as an FBC flue gas cleaning method with high DeSOx, DeNOx and dust removal efficiency. Also, activated char is useful for removing hydrocarbon-like dioxin, heavy metal ______ and other toxic materials. In fact, in Germany, the activated flue gas treatment system is used to remove dioxin from incinerator flue gas.

Thus, activated char has several kinds of performance. There are some choices to adopt activated char flue gas system to fit the purpose of gas treatment.

To promote the use of activated char systems, the activity of activated char must be increased, and its price should be lower. Research and development is currently progressing regarding these issues.



Figure 1. Relation between Inlet SOx and NOx Removal Efficiency



Figure 2. Comparison between SCR and Activated Char DeNOx System in FBC Plant



Figure 3. Activated Char DeNOx Test Facilities

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Figure 5. Structure of Regenerator

Figure 4. Structure of DeNOx Tower

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Figure 6. SOx Emission from FBC Boiler



Figure 7. NOx Emission from FBC Boiler



Figure 8. Trend of Pressure Drop at DeNOx Tower



Figure 9. Influence of Oxygen Content in Flue Gas to DeNOx Efficiency



Figure 10. Influence of Moisture Content in Flue Gas to DeNOx Efficiency



Figure 11. DeNOx Performance Laboratory Test Results of Activated Char



Figure 13. Start up Characteristics of AC-DeNOx Pilot Plant

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DeSOx REACTION ON AC SURFACE

• 1/2 02 (g) --> 0 (ad)

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- SO₂ (g) + O (ad) --> SO₃ (ad)
- $SO_3(ad) + H_2O(g) --> H_2SO_4(ad)$
- NH3 (g) + H2SO4 (ad) --> NH4HSO4 (ad)
- NH_3 (g) + NH_4HSO_4 (ad) -- > (NH_4)₂SO₄ (ad)

Note: AC: Activated Char g: gas ad: adsorption

Table 2

DeNOx REACTION ON AC SURFACE

- Catalytic Reaction with NH3
 NO (g) + NH3 (g) + 1/4 O2 (g) --> N2 (g) + 3/2 H2O (g)
- Adsorption Reaction

 $1/2 O_2 (g) --> 0 (ad)$ NO (g) + 0 (ad) --> NO₂ (ad)

Reaction with Nitrogen Functional Group

NO (g) + 0 (ad) --> NO₂ (ad) NO₂ (ad) + NH = C (surface) --> N₂ (g) + OH (ad) + O - C (surface)

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Note: AC: Activated Char g: gas ad: adsorption

REGENERATION REACTION ON AC SURFACE (high temp. & reduction condition)

- $(NH_4)_2SO_4$ (ad) --> $2NH_3$ (g) + H_2SO_4 (ad)
- H_2SO_4 (ad) --> SO_3 (ad) + H_2O (g)
- $3SO_3$ (ad) + $2NH_3$ (g) --> $3SO_2$ (g) + N_2 (g) + $3H_2O$ (g)
- $(\cdot 2SO_3 (ad) + C --> 2SO_2 (g) + CO_2 (g))$
- $2NH_3(g) + 60 C(surface) --> H_2(g) + 0H(ad)$
- NH₃ (g) + 0 C (surface) --> NH \approx C (surface) + H₂O

Note: AC: Activated Char g: gas ad: adsorption

Table 4

Specifications of AC-DeNOx Test Plant

ltem	Specification	
Туре	Cross flow moving bed	
Reactor Volume (effective)	25m3	
Space Velocity	400 1 <i>/</i> h	
Gas Volume	10,000m3N/h	
Gas Temperature	140 C	

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Target Value of Pilot Test

Items	Target Value
DeNOx Efficiency	More than 80%
DeSOx Efficiency	More than 90%
Outlet Dust Concentration	Less than 30 mg/m3N
Pressure Drop (DeNOx Tower)	Less than 150mmAq

Table 6

Inlet Flue Gas Condition

item	Value	
Flue Gas Volume	10,000m3N/h	
Gas Temperature	140 C	
NOx Conc.	200ppm	
SOx Conc.	50ppm	
Dust Conc.	200mg/m3N	
HCI Conc.	10ppm	
HF Conc.	5ppm	

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Performance Test Results of AC DeNOx System

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Items	Target Values	Test Results
Inlet NOx (ppm)	200	153
OutletNOx (ppm)	40	26
NOx efficiency (%)	80	83
Slip NH3 (ppm)	30 or less	12
Inlet SOx (ppm)	50	12
Outlet SOx (ppm)	5 or less	< 5
SOx efficiency (%)	90	>90
Inlet dust (mg/m3N)	200	119
Outlet Dust (mg/m3N)	30 or less	5

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COMBINED SO2/NO_x CONTROL USING FERROUS·EDTA AND A SECONDARY ADDITIVE IN A LIME-BASED AQUEOUS SCRUBBER SYSTEM

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ABSTRACT

Integration of NO_x control into existing flue-gas desulfurization (FGD) systems addresses site-specific control requirements while minimizing retrofit difficulties. Argonne has studied the use of metal-chelate additives, such as ferrous • EDTA in various wet FGD chemistries, to promote combined SO₂/NO_x scrubbing. A major process problem is oxidation of the iron to the ferric species, leading to a significant decrease in NO_x-removal capability. Argonne discovered a class of organic compounds that, when used with ferrous • EDTA in a sodium carbonate chemistry, could maintain high levels of NO_x removal. However, those antioxidant/reducing agents are not effective in a limebased chemistry, and a broader investigation of antioxidants was initiated. This paper discusses results of that investigation, which found a practical antioxidant/reducing agent capable of maintaining NO_x removals of about 50% (compared with about 15% without the agent) in a lime-based FGD chemistry with Fe(II) • EDTA.

INTRODUCTION

A number of technologies are available to remove either sulfur dioxide (SO_2) or nitrogen oxides (NO_x) from flue gas. However, integrated technologies that can simultaneously control both species could offer significant advantages, such as lower capital and operating costs, better system operability and reliability, and possibly lower resource consumption and waste volumes. The construction of complete integrated systems will be of interest for new utility plants and industrial applications, as well as for existing sites that currently have minimal pollution control. On the other hand, opportunities to incorporate integrated pollution-control measures into existing flue-gas cleanup (FGC) systems will be particularly important for operators of SO₂ scrubbing systems who are faced with the need to add additional control of NO_x .

Argonne National Laboratory (ANL) has been conducting research on combined SO_2/NO_x control technologies for the U.S. Department of Energy (DOE) since 1981. Much of that work has emphasized techniques for the retrofit of NO_x control to both wet and dry (spray drying) scrubber systems, particularly in high-sulfur coal applications. This paper reports the results of recent work with combinations of chemical additives designed to promote the economic removal of NO_x in wet flue-gas desulfurization (FGD) systems using a lime-based chemistry.

Some metal chelates, such as ferrous ethylenediaminetetraacetate [Fe(II) • EDTA], promote NO_x removal because they quickly react with dissolved nitric oxide (NO), forming the complex Fe(II) *EDTA * NO. The coordinated NO can react with sulfite and bisulfite ions, freeing the ferrous chelate for further reaction with NO. This synergism makes separate regeneration of the Fe(II) • EDTA to release the NO unnecessary. A significant process problem is oxidation of the iron in the additive to the inactive, ferric state. This oxidation occurs both by direct reaction with dissolved oxygen and by reaction with species produced from decomposition of the Fe(II) • EDTA • NO complex. In some cases, addition of another chemical, specifically an antioxidant and/or reducing agent, has been effective in counteracting the harmful effects of ferrous oxidation. Recently (1), we have published our first studies performed with Fe(II) • EDTA combined with an antioxidant/reducing agent in a sodium-carbonate chemistry. However, these antioxidant/reducing agents were not as effective in a lime-based chemistry, and a broader investigation of antioxidants was initiated.

In this paper, we compare results obtained for $Fe(II) \cdot EDTA$ alone in sodium carbonate with results obtained in a lime-based scrubber chemistry. We also present results obtained in a lime-based chemistry with $Fe(II) \cdot EDTA$ and various antioxidant/reducing agents singly and in combination. We have found an effective antioxidant/reducing agent capable of maintaining NO_x removals of about 50% (compared with about 15% without the agent) in a lime-based FGD chemistry with Fe(II) $\cdot EDTA$. The control of SO₂ is not impaired, and may in fact be improved, by the additive.

EXPERIMENTAL PROCEDURE

A flow diagram of the laboratory-scale scrubber used for this research is shown in Figure 1. The scrubber vessel itself is approximately 3 in. in diameter and uses a "disk and donut" design internally to promote gas-liquid contacting. In addition, a sieve plate is placed at the bottom of the scrubber to provide some liquid holdup in the column. By adjusting the fractional open area in the plate, one can adjust pollutant removals for a given liquid recirculation rate. That rate can be varied between about 300 and 1400 mL/min, with typical values for the experiments reported here ranging from 300 to 500 mL/min. The "flue gas" (blended from bottled gases) feed rate was approximately 100 standard liters per minute, yielding liquid to gas ratios (L/G) of about 20-40 (gal/min)/(1000 ft³/min). Instrumentation from Beckman is used to continuously monitor the following flue-gas components: oxygen (O₂), carbon dioxide (CO₂), NO, nitrogen dioxide (NO₂), and SO₂.

Recently, several modifications were made to the scrubber system that are not included in earlier descriptions (1, 2). The previously used glass humidifier was replaced with an all-metal steam generator. A precision metering pump feeds water to a metal coil immersed in an oil bath at 125°C at a rate sufficient to humidify the feed-gas stream to a water vapor content of about 8%. Two sampling points are used for feedgas analysis. One is placed upstream of the water-vapor addition to the feed stream and is used primarily to set up the feed-gas mixture. The other is placed immediately upstream of the feed-gas injection point into the scrubber column and is the primary feed-gas sampling location after a scrubbing experiment is started.

The initial experiments in hydrated lime, Ca(OH)2, consisted of a statistically designed series of runs to test the effects of variations in feed gas O_2 concentration from 2-6%, feed gas SO_2 concentration from 1000-3000 ppm, and Fe(II) • EDTA (additive) concentration from 0 to 0.067 M. We set the baseline conditions without Fe(II) • EDTA so that the SO2 removal would be about 90%. This required the use of a sieve plate at the bottom of the scrubber having an open area of 9.8%. A liquid recirculation rate of 500 mL/min was needed for 90% SO2 removal and resulted in a liquid level of 33-36 cm in the scrubber column. An initial amount of lime equivalent to 0.08 moles/L was added to all scrubbing solutions. The initial pH varied from about 10 without Fe(II) • EDTA to about 7.5 with Fe(II) • EDTA. During the experiments, the pH was controlled with a 10 wt% lime slurry at 6.5 after dropping to that level. Temperature in the scrubbing solution holding tank was maintained at 50°C. A 20% excess of EDTA was used in all formulations of the Fe(II) \cdot EDTA additive. The flue gas was prepared by first preparing a base mixture of gases containing 14.5% CO₂, the desired O₂ concentration, and the balance as nitrogen (N₂). Pollutant gases were added as follows: NO₂ was set first at 50 ppm, NO was added at a previously set level of 450 ppm, and, finally, the prescribed amount of SO₂ was added.

Subsequent experiments that were conducted to investigate secondary additives (antioxidant/reducing agents) used similar conditions so that they could be compared with the previous series and earlier work with sodium carbonate. The pollutant gas concentrations were 3000 ppm for SO_2 , 450 ppm for NO, and 50 ppm for NO_2 . The other constituents were 8% moisture, 14.5% CO_2 , 6% O_2 , and the balance N_2 . The liquid circulation rate was varied from about 250 mL/min to 400 mL/min in order to maintain the liquid level in the scrubber at the same 33-36 cm above the sieve plate. The different rates reflected changes in the properties of the scrubber liquor. Concentrations of 0.067 M for Fe(II) •EDTA and 0.033 M for the secondary additives were used. Initial pH values varied from about 5 to 7.5 for different additive combinations. All tests were batch runs that lasted from one to two hours.

RESULTS AND DISCUSSION

The statistically designed experiments showed that the only variable that had a significant effect on both NO and NO_x removal in a Ca(OH)₂ chemistry was the additive, Fe(II) •EDTA. The magnitude of this effect over baseline conditions was found to steadily decline, from zero time, at 5-, 10-, 30-, and 60-min intervals from +26% to +2%. The SO₂ variable had a small positive effect, while the O₂ variable had a small negative effect on both NO and NO_x removal at those same intervals (<±5% in all cases).

In both chemistries studied to date, NO_x removal with Fe(II) EDTA alone can be characterized generally by an initial decline to a minimum value, which then either rises slightly or stabilizes at an apparent equilibrium value. We believe that this behavior is due predominantly to initial oxidation of ferrous EDTA to ferric EDTA and removal of free Fe(II) EDTA by formation of the complex Fe(II) EDTA NO, followed by a slight increase in regeneration rate of Fe(II) EDTA, and finally, a stabilization of the ferrous EDTA concentration. Overall, the initial set of experiments with Fe(II) EDTA in Ca(OH)₂ gave NO_x removals that degraded much more rapidly than had been the case in sodium carbonate. The reason for this different behavior in the two chemistries is explored later in this paper. However, given the well-known problem of ferrous ion oxidation in such systems, it was decided to investigate combinations of Fe(II) EDTA and antioxidant/reducing agents.

Experiments reported previously (1) demonstrated improved NO_x removal in a sodium-carbonate chemistry with Fe(II) •EDTA when a secondary organic additive was present. When one of the same compounds (pyrogallol) was tried in a lime chemistry with Fe(II) •EDTA, however, little if any improvement was observed. This is shown in Figure 2, where performance with the secondary additive was actually worse early in the run and only marginally better at longer times. In contrast to this behavior, in sodium carbonate it was found that after 90 min of scrubbing, NO_x removal had dropped to 32% with Fe(II) •EDTA alone; with Fe(II) •EDTA and pyrogallol, after 90 min, NO_x removal had increased slightly to 64%. (1).

To help understand why the pyrogallol was not effective in a lime chemistry, we decided to conduct a more detailed comparison of the performance of $Fe(II) \cdot EDTA$ for combined SO_2/NO_x removal in both lime and sodium carbonate chemistries. We first noted a significant difference in SO_2 removal behavior when comparing performance with and without the additive $Fe(II) \cdot EDTA$. In sodium carbonate, SO_2 removal without $Fe(II) \cdot EDTA$ was set at about 90% by adjusting the liquid level in the column and was found to decrease slightly, to about 87-83%, with $Fe(II) \cdot EDTA$ added. In contrast, SO_2 removal in lime was again set to about 90% without $Fe(II) \cdot EDTA$, but it was found to increase dramatically, to about 99\%, with the additive.

Next, we compared NO_x removals under similar conditions for both of these chemistries, as shown in Figure 3. Differences in the conditions for these two experiments were as follows (sodium carbonate versus lime): feed gas nitrogen dioxide, 75 ppm versus 50 ppm; feed gas O_2 , 5.4% versus 6.0%; and excess EDTA, 1% versus 20%. Note that previous work in sodium carbonate showed little difference in NO_x removal when unmixed nitrogen dioxide levels of 0-150 ppm were used (1). We also found that O_2 concentration variations in the range of 4-8% had little effect on NO_x removal (1).

Finally, a 20% excess of EDTA should have had a beneficial effect on NO_x removal, because a 20% excess of EDTA has been found to *decrease* the rate of oxidation of Fe(II) by dissolved oxygen, compared with the rate for a stoichiometric Fe(II) •EDTA solution (3). Important conditions that were identical were the concentration of SO₂ in the feed gas, scrubbing solution pH, liquid level in the scrubber column (33-36 cm), and initial concentration of Fe(II). The important feature to note in comparing the two curves in Figure 3 is that the NO_x removal declines much more rapidly in the lime chemistry than in the sodium-carbonate chemistry, reaching its minimum value after about 45 min.

To assess the role of oxygen in this different behavior, experiments were performed with the additive $Fe(II) \cdot EDTA$ in both chemistries without O_2 in the feed gas. The results for NO_x removal from these tests are shown in Figure 4. Although a comparison between the runs with and without O_2 for each chemistry shows considerable differences, it is noteworthy that NO_x removal is still significantly worse in the lime chemistry than in the sodium-carbonate chemistry. The obvious conclusion is that another effect, besides oxidation from flue-gas O_2 , is responsible for the lower NO_x removal with $Fe(II) \cdot EDTA$ in lime as compared with the removal in sodium carbonate. A plausible explanation for this effect is the much reduced solubility of sulfite ions in a lime environment as compared with a sodium environment. In fact, sodium sulfite is about 10,000 times more soluble than calcium sulfite. The importance of this fact lies in the proposed scrubbing mechanism for NO

by Fe(II) • EDTA. As described in the literature (4), the principal reaction is presumed to be the equilibrium reaction shown below:

Fe(II) \cdot EDTA²⁻ + NO <---> Fe(II) \cdot EDTA \cdot NO²⁻

The regeneration of the complex Fe(II) \cdot EDTA from Fe(II) \cdot EDTA \cdot NO has been postulated to occur by complex reactions with sulfite (SO₃²⁻) and/or bisulfite (HSO₃⁻) (<u>5</u>). The kinetics of these reactions have been shown to be dependent on the total S(IV) concentration (i.e., concentration of SO₃²⁻ + HSO₃⁻). Hence, the rate at which "fresh" Fe(II) \cdot EDTA can be regenerated in order to maintain a high NO removal depends on the concentration of sulfite plus bisulfite. From this point of view, therefore, the simple fact of the lower solubility of sulfite and bisulfite in a lime system would lead to a lower NO_x removal than in a pure sodium-containing system.

The investigation of antioxidant/reducing agents was resumed with the study of several new candidate compounds combined with Fe(II) • EDTA in Initial screening results with several different antioxidant lime. candidates are shown in Figure 5. As can be noted from the figure, one antioxidant had little effect on NO_x removal, some gave improved NO_x removal, and one actually gave worse NO_x removal. Figure 6 shows results for NO_x removal obtained with the best candidate investigated thus far, sodium ascorbate, with various Fe:ascorbate ratios. With an Fe:ascorbate ratio of 2:3, NO_x removal after one hour is about three times higher than with Fe(II) • EDTA alone (49% versus 15%). This level of removal could be sustained for about 30 min. In order to understand the mechanism by which the ascorbate species improved NO_x removal, we performed an experiment with Fe(II) • EDTA and sodium ascorbate in lime, but without O_2 in the feed gas stream. The result for this test is compared in Figure 7 with the test for Fe(II) • EDTA alone without oxygen As can be seen from Figure 7, even without O_2 , addition of in lime. sodium ascorbate leads to a great improvement in NO_x removal when compared with Fe(II) • EDTA alone. This result implies that ascorbate is performing another role besides that of simple antioxidant. It could be that ascorbate ions may be involved in regeneration of Fe(II) • EDTA from the complex Fe(II) • EDTA • NO and/or that ascorbate can reduce ferric • EDTA Further work on the role of ascorbate ions in the to ferrous•EDTA. overall mechanism is in progress.

Before we describe the results obtained on some combined antioxidant systems (i.e., two added chemicals) with Fe(II) \cdot EDTA in a lime-based scrubbing system, it is of interest to note a change we made in the experimental system. During the course of the combined chemical work, we noticed that in some systems, we had to lower our recirculation rate to unrealistically low levels in order to maintain the liquid level in the scrubber column at 33-36 cm above the sieve plate. Because of this, we changed the sieve plate to one having 10.3% open area and found that we could now achieve 90% SO₂ removal with a circulation rate of 510 mL/min and a liquid level 28-31 cm above the sieve plate. One interesting effect we found when making this change in liquid level can be seen in Figure 8, which compares NO_x removal for scrubbing solutions having an Fe:ascorbate ratio of 1:1 for the liquid levels of 33-36 cm and 28-31 cm. Overall, the differences are rather small. However, at the lower liquid level, we were able to maintain a constant NO_x removal

of 42% for 50 min with no decline observed after a total running time of 100 min. This may indicate a situation where the oxidizing and reducing effects have been balanced. This potentially significant result needs to be confirmed by repeating these conditions and running the experiment for a longer period.

From an economic perspective, the most interesting combination of secondary additives was sodium ascorbate and urea. Urea itself had no noticeable effect on NO_x removal when used with $Fe(II) \cdot EDTA$ alone. However, as shown in Figure 9, when urea is added to the scrubbing solution along with sodium ascorbate, NO_x removal improves over that obtained with the same amount of ascorbate alone. Also, Figure 10 shows that urea with ascorbate can even perform better than a greater amount of ascorbate alone (i.e., some ascorbate can be replaced with urea to obtain a NO_x -removal performance comparable with that of the original amount of the more expensive ascorbate). The optimum ratio of urea to ascorbate is yet to be determined.

CONCLUSIONS

In this paper, we have shown the following important results in regard to combined scrubbing of SO_2/NO_x in an aqueous scrubber system:

- Fe(II) EDTA additive alone improves SO₂ removal from about 90% to 99% in a lime-based scrubber chemistry.
- NO_x removal in a lime-based chemistry declines much more rapidly than in a sodium chemistry either with or without oxygen in the feed gas.
- Ascorbate ions can markedly improve $\rm NO_X-removal$ performance in a lime-based chemistry either with or without oxygen in the feed gas.
- Partial replacement of ascorbate with less expensive chemicals (such as urea) appears to be possible.

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Figure 1. Flow diagram of laboratory aqueousscrubber system



Figure 2. $NO_{\rm X}$ removal in hydrated lime with ${\rm \dot{F}e\,(II)\,\bullet EDTA}$ alone or Fe(II) ${\rm \bullet EDTA}$ and pyrogallol



Figure 3. $NO_{\mathbf{x}}$ removal with the additive Fe(II)+EDTA in both sodium carbonate and hydrated lime chemistries



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Figure 4. $NO_{\bf X}$ removal for Fe(II)+EDTA without oxygen in both sodium carbonate and hydrated lime



Figure 5. Screening test results for several antioxidant candidates in a lime-based scrubber chemistry



Figure 6. NO_X removal for various initial ratios of Fe(II):sodium ascorbate in a lime-based scrubber chemistry



Figure 7. NO_x removal with Fe(II) •EDTA and with or without sodium ascorbate and no oxygen in the simulated flue gas



Figure 8. NO_x removal for Fe(II) EDTA with sodium ascorbate at two different scrubber liquid levels



Figure 9. NOx removal with or without urea at the same Fe:sodium ascorbate ratio and with a scrubber liquid level of 33-36 cm



Figure 10. NO_x removal for Fe(II) •EDTA with sodium ascorbate and with or without urea and with a scrubber liquid level of 28-31 cm

RECENT DEVELOPMENTS IN THE PARSONS FGC PROCESS FOR SIMULTANEOUS REMOVAL OF SO_X and NO_X

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ABSTRACT

The Parsons Flue Gas Cleanup (FGC) Process was developed to remove 99-plus percent of both SO_x and NO_x from coal-fired boiler flue gas.

The Parsons process consists of three key process steps. Two of the steps, H_2S recovery and sulfur production, use commercially proven technologies; the third, hydrogenation, is an adaptation of commercial experience to permit processing particulate-containing flue gases dilute in SO_x and NO_x .

Bench scale and pilot scale units have been built for testing of the key SO_X-NO_X hydrogenation step. Bench scale results confirm the ability to remove 99-plus percent of both SO_X and NO_X . Recent pilot plant tests have demonstrated that the catalytic hydrogenation reactor is capable of removing 99-plus percent of SO_X and 92 to 96 percent of NO_X from coal-fired boiler flue gas.

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INTRODUCTION

The objective of the Parsons Flue Gas Cleanup (FGC) Process is simultaneous removal of 99-plus percent SO_X and NO_X from coal-fired boiler flue gases. The Parsons FGC Process is unique for the following reasons:

- It is capable of simultaneously removing 99-plus percent of SO_x and NO_x.
- It is a regenerable process.
- It produces salable elemental sulfur.
- It is an adaptation of technology that has been successfully used in some 70 commercial plants treating sulfur plant tail gases.
- The process economics are essentially informative to the amount of sulfur in the coal.

The technology has under gone continuing development for the past few years. This paper will describe the process configuration, and the latest results of the bench scale and the pilot scale test rograms.

PROCESS DESCRIPTION

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The Parsons FGC Process includes the following process steps:

- Simultaneous catalytic reduction of sulfur oxide (SO_x) to hydrogen sulfide (H_2S) , nitrogen oxides (NO_x) to elemental nitrogen (N_2) , and residual oxygen to water in a single reduction step.
- Recovery of H₂S from the hydrogenation reactor effluent gas.
- Production of elemental sulfur from H₂S-rich gas.

A process block flow diagram and a process flow sketch for a typical Parsons FGC plant are presented in Figures 1 and 2.

Boiler operation is controlled to produce a flue gas with low residual oxygen content. The controlled-oxygen content flue gas feed to the FGC plant exits the boiler's economizer, passes through a multicyclone assembly where large ash particles are removed, and is then mixed with steam-methane reformer gas and sulfur plant recycle tail gas to form the feed to the catalytic hydrogenation reaction module where the SO_x , NO_x , and residual oxygen are reduced. A proprietary honeycomb catalyst is mounted in the flue gas duct to permit passage of flue gas particulates with low pressure drop and nil fouling tendency. The hydrogenation step is an extension of the Beavon Sulfur Removal (BSR) process, developed jointly by Parsons and Unocal in the early 1970's, to treat particulate containing flue gas. Seventy BSR plants have demonstrated the commercial reliability of the hydrogenation, H_2S recovery, and sulfur production steps in tail gas plants.

The hot hydrogenator effluent is used to preheat the boiler combustion air in a "nil-leak" heat pipe, or equivalent, air preheater. Essentially all of the remaining ash is then removed from the cooled flue gas in the electrostatic precipitator and the ash-free flue gas is fed to a direct-contact desuperheater. Here, the flue gas is cooled and a small amount of water is removed by condensation. Blowdown from the desuperheater circulating aqueous stream is filtered to remove traces of fly ash and is subsequently steam stripped to remove dissolved H_2S ; it can then be disposed of by sewering.

The cooled effluent flue gas from the desuperheater enters an absorption column containing an H_2S -selective solvent. The process (FLEXSORB) is licensed by EXXON. Essentially all of the H_2S and a portion of the CO_2 in the flue gas is absorbed by the solvent. The absorber effluent gas, containing less than 10 ppmv H_2S , is vented to the atmosphere through a stack mounted atop the absorber. The effluent stack gas is saturated with water vapor; reheat, as required, added to the absorber effluent to reduce the length and frequency of occurrence of a steam plume.

The H_2S -enriched solvent leaves the bottom of the absorber and enters the regenerator where it is heated and steam stripped to release the acid gases from solution. The H_2S -containing off gas exiting the top of the regenerator is sent to a Recycle Selectox sulfur plant which converts the H_2S to elemental sulfur; this process is licensed jointly by Parsons and Unocal. The salable bright yellow elemental sulfur is collected as a liquid product and the tail gas is recycled to the hydrogenation reactor for further sulfur recovery.

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PROCESS DEVELOPMENT

The development of the Parsons FGC Process has included both the bench scale and the pilot scale programs. Because the H_2S recovery via selective amine and Recycle Selectox sulfur production technologies are both commercial proven, the objective of the development project was to confirm the applicability of the hydrogenation process in treating coal-fired boiler flue gas.

Bench Scale Development

The objective of the bench scale work was to develop a catalyst system and to establish reaction conditions to meet defined performance criteria. From 1987 till 1990, the University of Delaware (UOD), Center for Catalytic Science and Technology, conducted more than 150 bench scale test runs. Two of the tested catalyst systems achieved 100 percent conversion of both SO_x and NO_x , and the third catalyst system achieved 100 percent conversion of SO_x and 98% conversion of NO_x , at reactor temperature of $600^{\circ}F$ and space velocity up to 5000 hr⁻¹. These three preferred proprietary catalyst active ingredients were prepared on ceramic honeycomb substrates for the 1990 pilot test.

Pilot Scale Development

<u>Pilot Plant Design</u>. The performance of the catalytic hydrogenation reactor has been tested in a pilot plant designed to process a flue gas slipstream from boiler No. 6 of the St. Marys Municipal Power Plant located in St. Marys, Ohio. Boiler No. 6 has a nameplate capacity of 10 MW and burns high sulfur, eastern Ohio bituminous coal. The objective of the pilot plant is to confirm the high percentage SO_x-NO_x reduction capability reported by the bench scale work. The coal characteristic and flue gas composition for the St. Marys pilot plant design are given in Table 1 and 2. A pilot plant flow diagram is presented in Figure 3. Figure 4 is a photograph of the pilot plant installed at the St. Marys Municipal Power Plant.

In the pilot plant, a 10,000-scfh (maximum) power plant boiler slipstream is fed to a cyclone for large particulate removal and then to a fabric filter for further removal of particulates. The flue gas is preheated and intimately mixed with a reducing gas produced by controlled sub-stoichiometric combustion of natural gas in oxygen. The oxygen content of the flue gas is reduced in the reaction furnace. The reaction effluent gas is cooled in a waste heat boiler. The system permits bypassing a portion of the reaction furnace product to permit accurate control of the feed temperature to the hydrogenator. Two hydrogenator vessels are installed, which can be operated singly, in parallel, or in series. Instrumentation was provided to determine the hydrogenator product composition using effluent analyzers to measure concentrations of H_2S , SO_2 , NO_x , CO, H_2 , and O_2 . The pilot plant product is incinerated in the power plant boiler combustion zone prior to returning to the power plant stack.

<u>Pilot Plant Operation and Results</u>. The pilot plant was commissioned during the 1989 Phase I campaign. In its initial operations, it successfully achieved 90plus percent SO_X and 85-plus percent NO_X reductions using proprietary honeycomb substrate catalysts. Equipment performance and control instrumentation problems were defined during the Phase I campaign.

The pilot plant was modified in 1990. The modifications were aimed at improving equipment and instrument performance. Also, operating and analytical procedures were refined. Subsequent Phase II test results showed that the system achieved SO_x reduction of 99-plus percent and NO_x reduction of 92 to 96 percent.

The University of Delaware prepared three different proprietary honeycomb substrate catalyst systems for the pilot plant test. One modified commercial catalyst system from another supplier was also tested at the pilot plant. Catalyst charge consisted of two cubic feet of ceramic honeycomb substrate catalyst inserted into a catalyst rack with dimensions of 12" X 12" X 26" in height. The St. Marys pilot plant was operated 24 hours a day, 7 days a week.

A 6-week test was performed using a proprietary honeycomb substrate catalyst A. The SO_x and NO_x conversions remained high and steady throughout the entire test period. The SO_x and NO_x conversions as a function of the average reactor bed temperature operating at a space velocity of 2,500 hr⁻¹ are plotted in Figure 5.1 and 5.2, respectively.

Another important independent variable studied during the pilot test runs was excess hydrogen and its effect in SO_x and NO_x conversions. Figure 5.3 and 5.4 are plots showing the SO_x and NO_x conversions as a function of excess hydrogen at the reactor outlet. As it is shown in Figure 5.3, the high SO_x conversion (99-plus percent) is essentially independent of the amount of excess hydrogen provided to

the reactor. The high NO_x conversion is somewhat dependent on the amount of excess hydrogen. As shown in Figure 5.4, the NO_x conversion decreased from 97-plus percent at about 1.0 mole percent hydrogen at the reactor outlet to 94-plus percent at about 0 mole percent hydrogen.

A summary of the key results for catalyst A follows:

Pilot Plant Test Results - Catalyst A

SO _x reactor inlet, ppmv	2,000-3,000
SO _x reactor outlet, ppmv	0-20
SO _x conversion, %	99+
NO _x reactor inlet, ppmv	300-600
NO _x reactor outlet, ppmv	10-30
NO _x conversion, Z	92-96
Space velocity, Hr	up to 3,000
Average reactor temperature, ^o F	up to 730

When the test was completed, the catalyst blocks were examined for the effects of particulate on honeycomb openings. All catalysts blocks were found to be essentially clean and free of particulate plugging.

Another test was also completed using a different catalyst system designated as catalyst B. The test results of catalyst B were very similar to catalyst A in SO_x and NO_x conversions.

The conversions of SO_x and NO_x remained high and steady throughout the entire test period. Figure 6.1 and 6.2 are plots showing SO_x and NO_x conversions versus average reactor temperature, respectively, operating at a space velocity of 3,000 hr⁻¹. The slope of the SO_x conversion curve is much steeper than the NO_x conversion curve. This implies that the SO_x reduction is more temperature dependent than the NO_x reduction.

Correlations between excess hydrogen at the reactor outlet and the reduction of SO_X and NO_X are shown in Figure 6.3 and 6.4, respectively. As in the case of catalyst A, the SO_X conversion for catalyst B is essentially independent of the amount of excess hydrogen at the reactor outlet. However, the NO_X conversion is somewhat dependent on the amount of excess hydrogen. The NO_X conversion decreased from 95-plus percent at about 1.0 mole percent hydrogen at the reactor outlet to 90-plus percent at about 0 mole percent hydrogen.

A summary of the key results for catalyst B follows:

Pilot Plant Test Results - Catalyst B

SO, reactor inlet, ppmv	1,800-2,800
SO, reactor outlet, ppmv	0-20
SO _x conversion, %	99+
NO, reactor inlet, ppmv	300-600
NO, reactor outlet, ppmv	10-30
NO, conversion, %	92-96
Space velocity, hr ⁻¹	up to 4,000
Average reactor temperature, ^o F	up to 810

The effect of high particulate loading in the flue gas on the performance of ceramic honeycomb substrate catalyst was examined during the last 2 days of test runs. During the high dust loading test, the Gore-tex membrane/Teflon B fiberglass fabric filter bag house was completely bypassed. No changes in the performance of catalytic SO_x and NO_x reductions were observed during the high dust loading test. At the end of the catalyst B test run, the reactor was open for inspection. The honeycomb catalyst blocks were examined and the openings were found to be free of particulate plugging.

Operating parameters were also defined during the pilot test runs to convert 100 percent of the incoming SO_x to H_2S in the catalytic reactor with zero elemental sulfur formation, since the presence of elemental sulfur at the reactor effluent would cause solids deposition and potential plugging problems in the transfer lines and equipment.

CONCLUSION

Based on the bench scale and the most recent Phase II pilot plant test results, it is concluded that:

- The bench scale tests confirm that 99-plus percent conversion of both SO_x and NO_x is possible for properly controlled conditions and preferred catalyst selection.
- Two different preferred proprietary honeycomb substrate catalyst systems produced 99-plus percent conversion for SO_x and 92 to 96 percent conversion for NO_x in the pilot test.
- The honeycomb substrate catalyst system provided minimum pressure drop and was capable of allowing passage for particulates without plugging the openings during the high dust loading test.

- Pilot plant tests demonstrated that very low excess reductant (H₂) was required to achieve high conversions of SO_x and NO_x. This can significantly reduce the hydrogen gas requirement and subsequently the capital and operating costs of the FGC plant.
- Operating parameters were defined to achieve 100 percent reduction of S0₂ to H₂S. No elemental sulfur was formed in the reactor.
- The pilot plant operating experience gained regarding system chemistry, equipment and instrument performance will provide the basis for the demonstration and commercial scale plant design and operation.

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TABLE 1 St. Marys Pilot Plant Coal Characteristic - Ultimate Analysis

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Component	<u>WtZ</u>
Moisture	12.0
Carbon	57.5
Hydrogen	3.7
Nitrogen	0.9
Sulfur	4.0
Chloride	0.1
Ash	16.0
Oxygen	<u>5.8</u>
	100.0

Btu/1b	HHV (wet)	10,100
Sulfur	content, 1bs/10 ⁶ Btu	3.96

TABLE 2 St. Marys Pilot Plant Flue Gas Composition

Component	<u>Mol Z</u>
Nitrogen	73.4
Oxygen	3.25
Water Vapor	9.2
Carbon Dioxide	13.8
Sulfur Dioxide	0.35
Nitrogen Oxides	600 ppmv
Ash	10,615 ppmv

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Figure 1. Parsons FGC Process Block Flow Diagram



Figure 2. Parsons FGC Process Flow Sketch



Figure 3. Parsons FGC Process Pilot Plant Flow Diagram



Figure 4 - Photo of Pilot Plant Installed at St. Marys, Ohio



Figure 5.1 - Catalyst A - Reactor Temperature vs. SO_X Conversion



Figure 5.2 - Catalyst A - Reactor Temperature vs. NO_X Conversion



Figure 5.3 - Catalyst A - Excess H_2 vs. SO_X Conversion



Figure 5.4 - Catalyst A - Excess H_2 vs. NO_X Conversion



Figure 6.1 - Catalyst B - Reactor Temperature vs. SO_X Conversion



Figure 6.2 - Catalyst B - Reactor Temperature vs. NO_X Conversion


Figure 6.3 - Catalyst B - Excess H_2 vs. SO_X Conversion



Figure 6.4 - Catalyst B - Excess H_2 vs. NO_X Conversion

Session 6A

WET FGD OPERATING ISSUES

PILOT-SCALE EVALUATION OF SORBENT INJECTION TO REMOVE SO, AND HC1

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ABSTRACT

This paper presents the results of a pilot plant test program conducted at the Electric Power Research Institute's (EPRI) High Sulfur Test Center (HSTC) as part of EPRI Research Project 2250-3 to investigate the feasibility of injecting dry alkaline materials into flue gas upstream of the ESP for removal of gaseous SO_3 and HCl.

Four sorbents were tested: commercial hydrated lime; high-surface-area hydrated lime; commercial-grade sodium bicarbonate (NaHCO₃); and activated alumina. Conditions which were varied during the test program included the sorbent injection rates, flue gas flow rate, temperature, ESP specific collection area, and SO₃ and HCl concentrations.

Test results showed that the SO_3 removal was greater than the HCl removal for all sorbents and process conditions evaluated. For a given sorbent, the most important parameter for SO_3 removal was the sorbent injection rate, which agrees well with the predictions from a simple mathematical model. For SO_3 removal, the commercialgrade NaHCO₃ and the regular and high-surface-area hydrated limes performed about the same when compared on a weight basis. However, at high injection rates, the hydrated limes degraded the operation of the ESP, causing both the outlet opacity and outlet mass loading to increase. The operation of the ESP improved when NaHCO₃ was injected compared to baseline operation. The injection of activated alumina did not appear to affect the operation of the ESP, but the sorbent was relatively unreactive towards SO_3 and HCl.

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INTRODUCTION

The results of a test program to evaluate the technical feasibility of removing sulfuric acid vapor (H_2SO_4) and hydrochloric acid (HCl) vapor from flue gas by injection of dry sorbents are presented in this paper. The testing was performed at the Electric Power Research Institute's (EPRI) High Sulfur Test Center (HSTC) located at the New York State Electric and Gas' Kintigh Station near Barker, New York. The testing was sponsored under EPRI Research Project 2250-3. Additional funding for the sorbent injection study presented in this paper was provided by Kansas City Power & Light Co. and Louisville Gas & Electric.

Sorbent injection technology involves the injection of a dry alkaline sorbent into a flue gas duct upstream of a particulate control device (e.g., ESP, baghouse, or particulate scrubber). The application of this technology has the potential to reduce stack plume opacity resulting from condensed sulfuric acid droplets in the stack exit gas. The presence of these very fine droplets (ranging from about 0.1 to 0.5 micron) can significantly affect visual opacity.

The application of sorbent injection technology can also remove vapor-phase HCl. For utilities operating wet FGD systems, removing HCl upstream of the scrubber can reduce the soluble chloride concentration of the scrubber recirculation liquor. This has the potential to improve scrubber performance (e.g., removal efficiency, limestone utilization) and to reduce the corrosion tendencies of scrubber materials of construction. If this technology could be successfully applied to new FGD systems, the use of less expensive materials of construction may be possible.

The current study was a follow-on to an earlier evaluation of this technology by EPRI, performed at the HSTC. Although very limited in scope, the earlier study suggested that removal of H_2SO_2 and HCl was feasible and that some of the operating

variables that may affect removal efficiency included the type of sorbent, the addition rate of the sorbent, the sorbent duct residence time, and the gas temperature at the point of injection. The primary objective of the current study was to perform a more exhaustive evaluation of sorbent injection technology in an attempt to more fully characterize the process.

CHEMICAL REACTIONS

Although the SO₃ in the flue gas at the process conditions existing at the HSTC is actually present primarily as sulfuric acid vapor (H_2SO_4) , it is more convenient to discuss the chemical reactions as if the SO₃ is the true chemical species. Therefore, the term SO₃ is used throughout this paper in place of H_2SO_4 .

$$SO_3(g) + Ca(OH)_2(s) ----> CaSO_4(s) + H_2O(g)$$
 (1)

$$2HC1 (g) + Ca(OH)_2 (s) ----> CaCl_2 (s) + 2H_2O (g)$$
 (2)

$$SO_3$$
 (g) + 2NaHCO₃ (s) ----> Na₂SO₄ (s) + H₂O (g) + 2CO₂ (g) (3)

$$3SO_3(g) + Al_2O_3(s) ----> Al_2(SO_4)_3(s)$$
 (5)

6HCl (g) +
$$Al_2O_3$$
 (s) ----> $2AlCl_3$ (s) + $3H_2O$ (g) (6)

In addition to the above reactions, all cf the sorbents have the potential to react with SO_2 and CO_2 , both of which are present in flue gas. These reactions are not expected to have a significant effect on the tests at the temperatures evaluated. Therefore, they are not addressed in this paper.

While the above reactions are known to proceed and produce relatively stable products, it was not known whether the overall rates would be sufficient to remove SO_3 and/or HCl in a cost-effective manner at typical flue gas conditions.

TEST METHODOLOGY

Process Diagram/Description

A simplified process flow diagram for the pilot unit showing the configuration used for the current test program is presented in Figure 1. Flue gas was extracted approximately isokinetically from the outlet duct on the Kintigh Station boiler for use at the HSTC. This test program was conducted on the HSTC 4-MW spray dryer/ESP pilot unit flow path. The flue gas passed through the spray dryer vessel (which was not in operation during this program) and then proceeded to the outlet duct where sorbent injection occurred. The flue gas then passed through a five-field ESP for sorbent and fly ash removal. For most of the tests, only the first three fields were energized for an SCA of about 300 ft²/kacfm. A few tests were also conducted with two fields for an SCA of 200 ft²/kacfm. After the ESP, the flue gas was returned to the Kintigh Station ductwork.

The normal sulfur content of the coal fired at Kintigh (2.8%) produces a flue gas SO_2 concentration of about 1600 to 1800 ppmv and a SO_3 concentration of about 10 to 15 ppmv.

The chloride content of the Kintigh Station's coal (0.1%) produces a flue gas HCl concentration of about 50 to 55 ppmv. For most of the current tests, the inlet HCl concentration remained at the baseline level, but for a few tests, it was increased to approximately 100 ppmv by spiking the flue gas with anhydrous HCl.

The flue gas SO_3 concentration was varied for many of the tests by spiking with SO_3 . The SO_3 was produced by passing an SO_2 /air mixture over a vanadium catalyst at 800°F. The SO_2 content of the SO_2 /air mixture was changed to alter the amount of SO_3 that was injected into the gas stream. The SO_3 was injected into the flue gas just upstream of the spray dryer vessel.

The gas flow rate and temperature at the outlet of the spray dryer vessel were controlled to their desired setpoints using a variable-speed fan and an electric heater. The flue gas SO_2 and O_2 concentrations were measured at the spray dryer inlet, the spray dryer outlet, and the outlet of the ESP to determine if measurable SO_2 removal occurred and to correct the measured concentrations and calculated removals for air inleakage into the system.

Sorbent was gravimetrically fed into small hoppers and then pneumatically conveyed into the flue gas downstream of the spray dryer vessel. A small weight loss feeder with a self-contained hopper was used for the low sorbent flow rates (3 to 50 lbs/hr). A 4-inch weigh belt and a sorbent silo were used for the higher flow rates (32 to 160 lbs/hr) and for overnight tests.

Gas Sampling

The SO₃ concentration in the flue gas was determined by a controlled condensation technique. This technique involved pulling a sample of flue gas through a heated filter, then through a glass condenser which was maintained at 140°F. This temperature was below the SO₃ dewpoint but above the water dewpoint. As a result, SO₃ and not water condensed on the walls of the glass condenser. Condensation appeared as a visible "fog" in the condenser. The gas sample then entered a set of impingers designed to remove gaseous HCl and water vapor. The sample then exited through a pump and a dry gas meter.

For this study, the process inlet and outlet flue gas streams were sampled simultaneously for at least 30 minutes, which was more than adequate to observe the condensation of SO_3 in the condenser. At the end of the sampling time, condensed SO_3 was recovered by rinsing the condenser with about 60 mL of distilled water into previously weighed sample bottles. The SO_3 concentrations in the flue gas streams were determined by analyzing the samples for sulfate (by ion chromatography) and by recording the amount of gas sampled (i.e., from the dry gas meter readings).

The HCl concentrations in the inlet and outlet flue gas streams were determined by two methods. For most tests, the impinger solutions from the inlet and outlet flue gas samples were analyzed for chloride by ion chromatography. An infrared HCl monitor was also used to continuously measure the HCl concentration in the flue gas at the outlet of the ESP. This monitor was checked with span gases and found to be quite accurate over the concentration range of interest (less than 150 ppmv). The HCl concentrations measured by the impingers did not agree well with those measured by the monitor. However, from past experience with the monitor on the spray dryer system, it is believed that the HCl concentrations determined by the monitor better represent the true HCl concentrations in the flue gas. This monitor has shown that the HCl concentration in the flue gas at the inlet to the HSTC is normally about 52 ppmv when the Kintigh power plant is near full load. Since all of the current

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tests were performed when the power plant was close to full load, the removal of HCl across the pilot system was determined using the ESP outlet concentration measured by the HCl monitor and an assumed inlet concentration of 52 ppmv.

The spiked flue gas was sampled for SO_3 and HCl just downstream of the spray dryer vessel but upstream of any sorbent injection. Sampling at this location supplied the inlet SO_3 and HCl concentrations (i.e., before any sorbent injection). The outlet concentrations were measured by sampling at two locations: immediately upstream of the ESP; and downstream of the ESP and induced draft fan. By sampling simultaneously at all three locations, which was done for a selected number of tests, one could determine the SO_3 and HCl removal occurring across the flue gas ductwork and across the combination of the ductwork and the ESP.

Reagent Properties

Four reagents were tested: commercial hydrated lime; a special high-surface-area hydrated lime; commercial-grade $NaHCO_3$; and activated alumina. Samples of each reagent were taken twice each day when that particular sorbent was being injected into the ductwork. Selected samples were analyzed for specific surface area (using a one-point BET method) and for sorbent particle size. A summary of the reagent properties is presented in Table 1.

Experimental Conditions

The experimental conditions for the current study are summarized in Table 2. Most of the tests were conducted at an ESP inlet temperature of $315^{\circ}F$ and an inlet flue gas flow rate of 13,600 acfm. For almost all of the tests, only the first three fields of the five-field ESP were energized. At that flue gas rate, operation with three fields yielded a specific collection area of about 300 ft²/kacfm. Throughout the program, the first field was rapped every 5 minutes, the second every 10 minutes, and the third every 20 minutes. The last two fields, which were not energized, were rapped every 20 minutes.

Most of the tests lasted less than 2 hours. For these tests, the system was allowed to equilibrate for about 15 minutes after the sorbent flow was initiated prior to beginning data collection. The equilibration time period was chosen based on data from the continuous HCl analyzer which sampled the gas exiting the ESP. These data showed that the HCl concentration stabilized about 15 minutes after the sorbent injection rate was changed.

DISCUSSION OF RESULTS

This section discusses the results from the current program. First, a theoretically based model developed to aid in data interpretation is discussed, then the measured results are discussed in light of the model.

Mathematical Model Development

The results of this program are best interpreted by a theoretically based model which was developed for predicting SO_3 removal as a function of operating conditions. With this model, SO_3 removal can be predicted for other locations and other operating conditions.

At the high reagent ratios tested in this program $[e.g., Ca(OH)_2-to-SO_3 molar ratios ranging from 2 to over 40], it is likely that the rate-controlling step for SO_3 removal was the diffusion of SO_3 from the bulk gas to the sorbent particles. Therefore, a gas diffusion model was developed to compare the measured SO_3 removal to that predicted by the model and to see if any knowledge could be gained by exercising the model for a variety of conditions.$

The development of the model assumed:

- A large excess of reagent was present, relative to the amount of SO₃ removal;
- All of the resistance to mass transfer occurred in a thin film surrounding the particle;
- The competing reactions of HC1, SO_2 , and CO_2 with the sorbent particles were not important;
- The sorbent particles were spherical with smooth external surfaces (i.e., internal or pore surface areas did not contribute to the overall reaction rates at the relatively low sorbent conversion efficiencies);
- The average particle diameter accurately approximated the true distribution of sorbent particle diameters;
- The particles were well dispersed in the flue gas at all times;

- There was no net velocity between the particles and the flue gas; and
- Constant temperature and pressure were maintained.

Since the particles were assumed to be well dispersed in the flue gas, the problem could be reduced to a single particle associated with some amount of flue gas. Therefore, the modeling process involved calculating the volume of flue gas per particle, then calculating the rate of diffusion, or flux, of SO_3 to that particle.

In its general form, the flux of SO_3 to the sorbent particle is given by:

$$N_{s03} = k_g \cdot A \cdot C_t \cdot (y_{s03 \text{ bulk}} - y_{s03 \text{ surf}})$$
(7)

where:	N ₅₀₃	= the flux of SO ₃ to the sorbent particle (gram moles SO ₃ /sec);
	k _g	<pre>= gas-phase mass transfer coefficient (cm/sec);</pre>
	A	external surface area of the particle (cm ²);
	C,	= concentration of flue gas (gram moles total gas/cm ³);
	Y _{SO3 bulk}	mole fraction of SO ₃ in the bulk gas (moles SO ₃ /total moles gas); and
	y _{so3 surf}	= mole fraction of SO_3 at the sorbent's surface

Since the model assumes that the rate-controlling step for the SO_3 removal process is the diffusion of SO_3 through a thin film surrounding the sorbent particle, the concentration of SO_3 at the surface of the particle must be zero and the flux expression is reduced to:

$$N_{so3} = k_g \cdot A \cdot C_{so3 \text{ bulk}} = k_g \cdot \pi \cdot d_p^2 \cdot C_{so3 \text{ bulk}}$$
(8)

where: d_p = diameter of sorbent particle (cm); and $C_{so3 bulk}$ = concentration of SO₃ in the bulk flue gas (gram moles SO₃/cm³).

The above equation can be rearranged and solved analytically to give:

Percent SO₃ Removal = 100
$$\left[1 - \exp\left(\frac{-2\pi \cdot D_{BO3} \cdot M}{p_p \cdot d_p^2 \cdot G} t\right)\right]$$
 (9)

where: $D_{sn3} = H_2SO_4$ (v) diffusion coefficient (cm²/sec);

- M = sorbent injection rate (g/sec);
- p_p = particle density (g/cm³);
- G = total gas flow rate (actual cm³/sec);
- t = reaction time (sec).

A very important parameter in this equation is the diameter of the sorbent particle. The model assumes a single particle size, but all of the sorbents showed a distribution of particle sizes. To correctly model the SO_3 removal data, the model would have to integrate the removal occurring for each of the particle sizes. Since this was beyond the scope of this study, an average value for the particle diameter was used. Furthermore, the aerodynamic particle size (i.e., the actual agglomerated particle size in the ductwork) is more important for modeling the SO_3 removal process. The SO_3 removal data seemed to closely fit the diffusion model if a particle diameter of 10 microns was assumed. As shown in Table 1, this assumed diameter does not differ greatly from the average diameter determined from the particle size distribution data.

The time for the reaction between the sorbent and the flue gas is also an important parameter in the modeling equation. Since the flue gas flow rate, duct length, and duct diameter were well known for the current study, it was possible to accurately determine the reaction time for the sorbent in the ductwork. However, since most of the particles were removed in the first field of the ESP, it is difficult to predict the total reaction time of the particles with the flue gas. For the modeling results presented in this study, it was assumed that the particles continued to react with the flue gas in the ESP for a time equal to one-half of the flue gas residence time in the first field of the ESP (i.e., 1.32 or 2.31 seconds, depending upon the flue gas flow rate).

Another important parameter in the above equation is the diffusion coefficient for SO_3 . Since the SO_4 is present as gaseous H_2SO_4 under typical flue gas temperatures

and flue gas moisture levels, the diffusion coefficient was estimated by calculating the diffusion coefficient of H_2SO_4 in nitrogen at the temperature and pressure of the flue gas stream. The diffusion coefficient was calculated to be 0.169 cm²/sec at 315°F using the method of Fuller, et al. (<u>4</u>). The diffusion coefficient would increase with the absolute temperature of the flue gas (e.g., the diffusion coefficient was calculated to be 0.183 cm²/sec at 350°F), so the model predicts higher SO₃ removal at higher temperatures.

Sorbent Addition Rate - SO, Removal

For a given particle size, flue gas flow rate, and reaction time, the diffusion model predicted that the only other important parameter for SO_3 removal is the sorbent addition rate. This rate determines the number of particles injected into the flue gas, and therefore, the volume of total gas surrounding each particle. The model assumed that there was no effect of sorbent type. The experimental results from the current test program agree fairly well with this model as shown in Figure 2.

The data for the commercial-grade NaHCO₃ and the regular and high-surface-area hydrated limes (Figure 2) show that the observed SO₃ removal agrees fairly well with the model predictions at moderate sorbent injection rates. However, the model tends to overpredict SO₃ removal at very high sorbent injection rates and to underpredict SO₃ removal at low sorbent injection rates. For activated alumina, the model seems to overpredict SO₃ removal at nearly all injection rates. There are plausible explanations for the deviations from the model.

At very high sorbent injection rates, it is likely that the assumption of welldispersed sorbent particles is much less valid than at low injection rates. Therefore, the model will tend to overpredict SO_3 removal. This is also supported by the fact that the measured SO_3 removal never reached 100%, even at very high sorbent injection rates.

At lower sorbent injection rates, the diffusion model tends to underpredict SO_3 removal across the system. We speculate that this may result from some SO_3 removal being caused by condensation of H_2SO_4 at cold spots in the ESP. Since the ESP is a pilot-scale unit, it has more external surface area per unit volume than a full-sized unit. As a result, cold spots in the ESP are much more important on a

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pilot-scale unit than on a full-scale unit. The background SO_3 removal across the pilot ESP was quantified by simultaneously measuring the SO_3 concentrations at the system inlet and outlet when no sorbent was injected into the ductwork. The background removal ranged from 10% to 30% and seemed to increase with the inlet SO_3 concentration. This observation is consistent with the background SO_3 removal since higher inlet SO_3 concentrations create higher dew point temperatures, resulting in higher SO_3 removal.

Activated alumina is known to readily agglomerate, which, as for high injection rates with the other sorbents, tends to increase the effective particle diameters and lower the actual SO_3 removal. Thus, the model's overpredictions of the SO_3 removal for activated alumina could be rationalized but not proven.

Sorbent Addition Rate - HCl Removal

Figures 3 and 4 show the HCl removal data for the four sorbents at a gas temperature of 315°F. These data are quite different from the SO_3 removal data for several reasons:

- The magnitude of the HCl removal was less than that for the SO₃ removal.
- The effect of sorbent type on HCl removal was more pronounced than for SO_3 removal when the sorbents were compared on a mass basis (Figure 3). Comparing the data on a reagent ratio basis caused most of the data to collapsed onto one curve (Figure 4).
- The shape of the removal versus sorbent injection rate curve was more linear.

These data suggest that HCl removal was not limited by gas-phase diffusion. Some other mechanism evidently controlled HCl removal. The data were not sufficient to prove which mechanism controlled the overall reaction, but it is easy to fit the data if one assumes that the overall reaction was controlled by the kinetics of a first-order reaction between the sorbent and HCl. The curves shown in Figures 3 and 4 were the results of fitting a first-order reaction rate expression to the data.

Inlet SO, Concentration

For a given sorbent mass injection rate, the diffusion model predicted that there was no effect of inlet SO_3 concentration on the percent SO_3 removal for the sorbent injection process. The data taken in this test program appear to agree with this prediction. However, for a given *reagent ratio* (i.e., moles sorbent/moles SO_3), the data show that the percent SO_3 removal was higher for higher inlet SO_3 concentrations (Figure 5). This trend was also predicted by the diffusion model and can be explained by noting that, for the same reagent ratio, more particles must be injected into the flue gas for the higher inlet SO_3 concentrations than for the lower concentrations. Therefore, less gas volume is associated with each particle at high inlet SO_3 concentrations, and the distance that the SO_3 has to diffuse to reach the sorbent particles is reduced.

Flue Gas Temperature

Another objective of this test program was to evaluate the effect of flue gas temperature on SO_3 and HCl removals for the sorbent injection process. Most of the experiments were completed at a flue gas temperature of 315°F (ESP inlet temperature). Additional tests were performed at 350°F at the same sorbent residence time.

The data from the tests showed no significant effect of flue gas temperature on SO_3 and HCl removal levels. The diffusion model predicted a slight increase in the SO_3 removal when the temperature was increased to 350°F because the diffusion coefficient of H_2SO_4 increases with temperature. It is likely, however, that in this pilot-scale system, the predicted increase in SO_3 removal was negated by the decrease in SO_3 removal due to cold spots in the ESP. The cold spots become less effective as the gas temperature is increased.

Sorbent Residence Time

The effect of sorbent residence time on the SO_3 removal level was investigated by injecting the sorbent into the flue gas at a location closer to the ESP inlet (Figure 1). Injecting at this point decreased the duct residence time from 2.0 to 1.3 seconds and the total (duct plus ESP) estimated residence time from 3.3 to 2.6 seconds. Figure 6 shows the effect of changing the sorbent injection location on the SO_3 removal obtained with the commercial hydrated lime. No significant effect

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of changing the total residence time from 3.3 to 2.6 seconds was observed. Any change in SO₃ removal with residence time was apparently within the ability to measure the SO₄ removal, which was estimated to be $\pm 5\%$.

Sorbent Surface Area

The data from the current study show that the high-surface-area hydrated lime performed no better than the commercial-grade hydrated lime, even though the high-surface-area hydrated lime had almost twice the surface area (35 vs. 20 m²/g). In addition, the activated alumina had a very high surface area (170 m²/g) but was much less reactive towards SO₃ and HCl. Sodium bicarbonate had the lowest surface area of all the sorbents tested (3 m²/g), but it performed as well as the hydrated limes. However, the sodium bicarbonate thermally decomposes in the flue gas to form higher-surface-area sodium carbonate; the measured value of about 3 m²/g probably understates the actual reactive surface area of the reagent after it is injected into the flue gas. Even so, data from the literature (<u>1</u>) indicate that the surface area of the thermally decomposed NaHCO₃ is probably much less than those of the other sorbents.

The apparent lack of dependance upon sorbent specific surface area agrees with the predictions of the diffusion model. The model states that the internal surface area of a sorbent particle is not important since the SO_3 removal process is assumed to be limited by the diffusion of SO_3 from the bulk gas to the external surface of a sorbent particle.

EFFECT ON ESP OPERATION

One goal of this test program was to determine the effects of sorbent injection on ESP operation. The injection of alkaline sorbents into the flue gas upstream of the ESP can affect the operation of the ESP due to the increased mass loading, changes in the overall particle size and resistivity, and the removal of SO_3 which is a known ESP conditioning agent.

The following measurements were made for baseline (i.e., fly ash only) and sorbent injection conditions:

Voltage-current relationships for each field of the ESP;

- Continuous flue gas opacity measurements at the outlet of the ESP; and
- Flue gas mass loadings at the outlet of the ESP.

Most of these measurements were conducted when three of the ESP fields were energized, corresponding to a specific collection area (SCA) of 300 $ft^2/kacfm$. Some measurements were performed when only two ESP fields were energized (SCA of 200 $ft^2/kacfm$) to simulate a smaller ESP. The results of these measurements are discussed below.

Results of ESP Testing

Early in the program, it was observed that injecting hydrated lime at high flow rates (greater than 2.2 lb/hr/1000 acfm) had adverse effects on the operation of the ESP. This was first evidenced by strong sparking in the first field of the ESP. If the power to the first field was turned off to stop particle collection in the first field, sparking immediately started in the second field of the ESP.

At lower hydrated lime injection rates (less than 2.2 lb/hr/1000 acfm), the severity of the sparking was diminished, but the voltage-current relationships in the first field were still altered. The corona current in the first field was much lower when the hydrated lime was injected than the during fly-ash-only conditions. Since the lower corona current probably indicated a low particulate collection efficiency in the first field, it was speculated that the second and third fields would exhibit the same behavior as the first field if the sorbent injection continued for an extended period of time.

Several overnight tests were performed to investigate the effect of hydrated lime injection on the ESP for a longer time period. The ESP outlet opacity and outlet mass loading are summarized in Table 3 and illustrated in Figure 7. Figure 7 shows that the ESP outlet opacity increased when hydrated lime was injected at high flow rates (greater than 2.2 lb/hr/1000 acfm). Figure 8 compares the voltage-current relationships in the absence of sorbent injection with those for the injection of a large amount of hydrated lime. These data were taken after the hydrated lime had been injected continuously for about 36 hours. The data show that the hydrated lime drastically reduced the operating current in the first two fields and produced back-corona in the third field. The current may be reduced to very low levels in all fields if the sorbent were to be injected for a longer time.

The results from the outlet mass loading tests (Table 3) tend to agree with the outlet opacity measurements and appear to support the observation that ESP performance deteriorates over time when large amounts of hydrated lime are injected into the flue gas. For example, the outlet mass loading increased from 0.025 lb/MBtu under fly-ash-only conditions to 0.068 lb/MBtu after hydrated lime was injected at 50 lb/hr/1000 acfm for approximately 48 hours. However, for the same injection rate of hydrated lime, another outlet mass loading test showed a lower-thanbaseline outlet mass loading of 0.019 lb/MBtu. Data collection for this test began approximately 1 hour after the start of the hydrated lime injection and lasted for approximately 10 hours. As shown in Figure 7, the ESP outlet opacity during this time period was relatively low until the very end of the mass loading test. About 11 hours after the start of the hydrated lime injection, the outlet opacity increased to the relatively high level. The outlet opacity remained at this level while the other mass loading test was conducted (the 0.068 lb/MBtu test). These data indicate that the performance of the ESP degrades with time when hydrated lime is injected at high injection rates.

The ESP outlet opacity returned to the baseline level soon after the sorbent injection was turned off. When the sorbent injection was restarted at a lower rate (1.0 lb/hr/1000 acfm), the opacity did not increase. However, as shown in Table 3, the mass loading at the ESP outlet appeared to increase even at this low sorbent injection rate.

The sparking problems and the drastic altering of the voltage-current relationships were not apparent when either activated alumina or NaHCO₃ were injected into the flue gas stream. The outlet opacity also remained fairly constant while these sorbents were injected into the flue gas. In fact, the ESP outlet mass loading test which was performed while NaHCO₃ was injected showed that the efficiency of the ESP improved compared to that for fly-ash-only conditions. This result was somewhat expected because sodium compounds are known conditioning agents for ESP's due to their relatively low resistivity.

FULL-SCALE IMPLEMENTATION

The data from this study suggest that it is possible to reduce SO_3 levels and plume opacity by injecting either hydrated lime or sodium bicarbonate into the flue gas. These sorbents were equivalent for SO_3 removal when compared on a mass basis. Costs for injecting these sorbents for SO_3 removal and plume opacity reduction were estimated for a 300-MW, base-loaded power plant. To achieve an 80% reduction in flue gas SO_3 levels from a moderate initial level (e.g., 20 ppm), about 7500 tons per year of either sorbent would have to be injected. For hydrated lime reagent at \$65/ton, this would result in an annual sorbent cost of about \$500,000, which is equivalent to about 0.2 to 0.3 mil/kWh. For sodium bicarbonate reagent at \$200/ton, the annual sorbent cost would rise to about \$1.5 million, which is equivalent to 0.7 to 0.8 mil/kWh. For either sorbent, a permanent sorbent storage and injection system would be estimated to cost between \$500,000 and \$750,000.

The injection of these sorbents would slightly increase the volume of solid waste produced by the plant. For a case with a 2.8% sulfur content and 8% ash content in the coal, the sorbent injected would represent about 4% to 5% of the dry weight of the combined ash and FGD sludge stream produced. Note that this represents about twice the amount of hydrated lime generally used in cases where it is added to the combined ash/FGD sludge stream for stabilization. In such cases, it may be possible to eliminate lime addition to the sludge if hydrated lime is used for SO₃ control. Thus, for this circumstance, the net reagent cost for SO₃ control by hydrated lime injection would be about half that of the estimate above, or only about \$250,000 per year for the example case.

The only drawback to using hydrated lime may be the potential adverse effects on ESP performance. The magnitude of these effects will likely be site specific and will depend greatly on the hydrated lime injection rate required. While sodium bicarbonate could be used instead to avoid any potential adverse effects on the ESP, for the example case described above, the sodium bicarbonate reagent would be at least three times more expensive than hydrated lime reagent. Also, the addition of highly water-soluble sodium salts to the solid waste stream from the plant may be undesirable.

CONCLUSIONS

Based on the results from the current test program, the following conclusions can be drawn:

- The injection of alkaline sorbents will remove SO₃ and, to a lesser extent, HCl from power plant flue gas streams. However, care must be taken to avoid ESP outlet particulate emission problems caused by certain sorbents.
- For all of the sorbents tested, the removal of HCl was much less than the removal of SO₂.
- For SO₃ removal, the commercial-grade NaHCO₃, the commercial-grade hydrated lime, and the high-surface-area hydrated lime all performed about the same when compared on a weight basis. The activated alumina was less reactive than these sorbents, even though it had a much higher specific surface area.
- The SO₃ removal results from the current study agree fairly well with the predictions of a simple gas-phase diffusion mathematical model. This model predicted that the most important parameters for SO₃ removal were the particle size of the sorbent, the sorbent injection rate, and the sorbent residence time in the flue gas.
- The injection of large amounts of hydrated lime caused the ESP outlet opacity and mass loading to increase. The voltage-current relationships for the ESP were also significantly altered.
- A permanent sorbent storage and injection system would cost between \$500,000 and \$750,000 for a 300-MW, base-loaded power plant. The annual sorbent costs for obtaining 80% removal of a 20 ppm SO₃ concentration in this plant would be about \$500,000 (0.2 to 0.3 mil/kWh) and \$1.5 million (0.7 to 0.8 mil/kWh) for hydrated lime and sodium bicarbonate, respectively.

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Table 1

SUMMARY OF REAGENT PROPERTIES

Sorbent	<u>_Ca(OH)</u> 2	<u>Ca(OH)</u> 2	NaHCO3	<u>A1₂03</u>
Grade	Commercial	High Surface	Commercial	Activated
Source	Chemical Lime	Chemical Lime	Kerr McGee	Alcoa
Average Surface Area (m²/g)	20	35	3	170
Avg. Particle Diameter (µm)	14	12	11	. 7

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Table 2

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	<u>Lowest Value</u>	<u>Base-Case Value</u>	<u>Highest Value</u>
Gas Flow Rate (acfm)	7,700	13,600	13,600
Gas Temperature (°F)	305	315	350
Inlet SO ₃ (ppmv)	10	24	40
Inlet HCl (ppmv)	52	52	100
Duct Residence Time (sec)	1.0	2.0	3.5
Total Residence Time (sec) [®]	2.3	3.3	5.7

SUMMARY OF EXPERIMENTAL CONDITIONS

"Assuming particles are collected in the first half of the first ESP field.

Table 3

SUMMARY DATA FROM ESP OUTLET MASS LOAD TESTS

Sorbent Type	Sorbent Flow (lb/hr/1000_acfm)	ESP Outlet Loading <u>(lb/MBtu)</u>
Fly Ash Only		0.027
Fly Ash Only		0.025
Fly Ash Only		0.048ª
Ca(OH) _z (1 hr after sorbent flow initiated)	3.7	0.019
Ca(OH) ₂ (48 hrs after sorbent flow initiated)	3.7	0.068
Ca(OH) ₂	2.3	0.084ª
Ca(OH) ₂	1.0	0.065ª
NaHCO ₃	3.7	0.009

*Performed with only two fields energized.



Figure 1. Pilot Unit Configuration for Sorbent Injection Experiments



Figure 2. Experimental and model results for SO_3 removal by injection of NaHCO₃, conventional hydrated lime, high-surface-area hydrated lime, and activated alumina. The model assumes a 3.28-second reaction time. All data are at a gas temperature of 315°F.



Figure 3. Experimental and model results for HCl removal by injection of NaHCO₃, conventional hydrated lime, high-surface-area hydrated lime, and activated alumina. Sorbents are compared on a mass basis. All data are at a gas temperature of 315° F.



Figure 4. Experimental and model results for HCl removal by injection of $NaHCO_3$, conventional hydrated lime, high-surface-area hydrated lime, and activated alumina. Sorbents are compared on a reagent ratio basis. All data are at a gas temperature of 315°F.



Figure 5. Effect of inlet SO₃ concentration on SO₃ removal for conventional hydrated lime. The model assumes 10 μ m particles and a 3.28-second reaction time. All data are at a gas temperature of 315°F.



Figure 6. Effect of sorbent residence time on SO₃ removal for commercial-grade hydrated lime. The model assumes 10 μ m particles. All data are at a gas temperature of 315°F.



Figure 7. Effect of hydrated lime injection on flue gas opacity as measured at the ESP outlet.



Figure 8. ESP current-voltage relationships for baseline and hydrated lime injection conditions. Data for hydrated lime conditions were taken after hydrated lime injection had been in progress for 48 hours at 3.7 lb/hr/1000 acfm.

CONTROL OF ACID MIST EMISSIONS FROM FGD SYSTEMS

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ABSTRACT

Acid mist emissions can be a significant problem at power plants burning highsulfur coal and using wet scrubbers for flue gas desulfurization (FGD). The acid mist, which is formed by condensation of sulfuric acid vapor within the scrubber system, can be a major contributor to particulate emissions. Since the acid mist is predominantly submicron in size, it avoids capture in conventional mist eliminator systems, and it scatters light very effectively. This can result in excessive visible emissions in some cases.

Improved control of acid mist emissions can be achieved by replacing or augmenting the conventional mist eliminators with a wet electrostatic precipitator (WESP). This paper describes a two-phased study performed to determine the degree of control that can be achieved with this approach. Phase I was a study of the electrical operation of a lab-scale WESP collecting an acid mist from a coal combustion pilot plant equipped with a spray chamber. The results of this study were used to develop and validate a computer model of the WESP. In Phase II, measurements were made at two utility scrubber installations to determine the loadings of acid mist, fly ash, and scrubber carryover. These measurements were used as input to the model to project the performance of a retrofitted WESP.

INTRODUCTION

Acid mists can be a major source of corrosion problems and visible emissions at power plants that burn high-sulfur coals and are equipped with wet flue gas desulfurization (FGD) systems. When flue gas is rapidly cooled in an FGD system, the SO_3 is condensed along with water vapor to form an ultrafine mist of sulfuric acid. The mist droplets are so small that they escape collection in the scrubber and the mist eliminators (MEs) (1). When discharged into the atmosphere, these fine droplets scatter and absorb light very effectively, sometimes resulting in excessive visible emissions. The presence of the acid mist in the flue gas can also be a contributing factor in excessive corrosion of the ducting and the stack liner downstream from the MEs. If a wet electrostatic precipitator (WESP) is used to replace or augment the MEs, the acid mist loading can be substantially reduced, along with the associated corrosion problems.

Under contract to the Department of Energy/Pittsburgh Energy Technology Center (DOE/PETC), Southern Research Institute investigated the use of a compact WESP to control acid mist emissions. The project was primarily directed toward acid mist emissions from wet FGD systems, although other sources of acid mist could be controlled by this approach. The goal of this investigation was to assess the improvement in acid mist control that was possible by using a WESP to replace or augment the existing MEs in an FGD system. The project was organized in two Phases. Phase I was initiated in August 1988 and completed in November 1989. It involved laboratory and pilot-scale studies of the WESP concept, along with the development of a WESP computer model. Phase II was completed in April 1991 and involved field measurements at utility FGD installations, projections of WESP performance, and development of a WESP demonstration plan.

PHASE I OBJECTIVES

The primary objectives of the Phase I effort were to (1) determine the ability of a compact WESP to collect the fine acid mist, (2) determine the effect of fly ash loading on mist collection efficiency, and (3) develop and validate a computer model of the WESP to help interpret test results and extrapolate results to full-scale applications. The second objective was included because the fly ash loading leaving the scrubber can vary widely, depending upon the performance of the upstream particulate control device. Also, a very high loading of submicron fly ash could adversely affect WESP performance by space charge suppression of the corona current.

PHASE I APPROACH

The approach used in Phase I of this project was to first fabricate a laboratory-scale WESP that could be used to determine the expected WESP fractional collection efficiency and provide data for validating a computer model of the WESP. Since it was anticipated that the volatile acid mist could present sampling difficulties, initial testing was done with a nonvolatile simulant oil, di-2-ethylhexyl sebacate (DES). A sketch of the WESP setup used for these tests is shown in Figure 1. After successful completion of these tests, the WESP was modified and connected to a pilot-scale combustion system to allow testing on an actual acid mist. The acid vapor was generated by firing either SO_2 -doped natural gas or a combination of SO_2 -doped natural gas with coal. This was done to allow testing of the WESP on the mist alone and the mist in combination with a fly ash loading typically encountered downstream from a scrubber. The acid mist was formed by passing the flue gas through a spray humidification chamber to simulate condensation in the scrubber system. A sketch of the modified WESP setup used in the pilot combustor tests is shown in Figure 2.

The data obtained from the tests with the DES and the actual acid mist were used to validate the computer model after each series of tests. The validated computer model was then used to make projections of WESP performance in a utility retrofit situation.

LABORATORY TESTS WITH SIMULANT OIL

The WESP setup used in these tests consisted of a tubular WESP made from a 1/8-inch diameter wire suspended along the axis of a 8-inch diameter galvanized metal tube. The energized length of wire was 3.5 feet. For the laboratory tests, air was drawn through the WESP system at a nominal flowrate of 100 cfm, resulting in a WESP specific collecting area (SCA) of about 74 $ft^2/kacfm$. This may be compared to a typical fly ash precipitator having an SCA of 250 to 350 $ft^2/kacfm$. Thus, these tests were designed to simulate a very compact WESP design.

The DES oil was atomized using a Sonic Development ST-47 nozzle operated at an air pressure of 88 psig and an oil pressure of 12 psig. This typically produced an aerosol with a mass mean diameter of about 4 μ m. Although this is somewhat coarse for an acid mist, it provided an adequate concentration of submicron particles for reliable size-resolved efficiency measurements.

Collection efficiency as a function of particle size was determined from cascade impactor measurements made at the inlet and outlet of the WESP. Typical results obtained from these measurements are compared with the results of two alternate computer models, a current-specific model (2) and a current-seeking model (3), in Figure 3. For the particle size range resolved in these tests, the collection efficiency varied from about 97% for submicron particles to 99.8% for 10 μ m particles. These results were extremely encouraging and showed good agreement with one of the two models initially considered.

The current-specific model was found to give better agreement with the WESP performance data, because it allowed input of both the applied voltage and the operating current. The current-seeking model predicts the current based on the applied voltage and the particulate space charge. The equation that is used for this is valid only in the region near corona onset (i.e., at relatively low voltage and current). The current-seeking model does not do a good job of predicting performance in this case since the actual voltage and current (60 kV and 270 μ A/ft²) are far from the region of corona onset (about 30 kV and near-zero current).

PILOT COMBUSTOR TESTS WITH ACTUAL ACID MIST

For these tests, the WESP was connected to a pilot-scale coal combustion facility equipped with a spray humidification chamber to serve as a source for the condensed acid mist. The acid mist was generated by firing SO_2 -doped natural gas in the combustor and condensing the resulting acid vapor into a fine mist in the spray humidification chamber. Since this resulted in a saturated flue gas entering the WESP, it was necessary to make extensive modifications to the WESP setup to avoid electrical tracking along the highvoltage insulator. As shown in Figure 2, a hot-air purge system was installed to keep the high-voltage insulator dry, and a mist eliminator was added to prevent the carryover of large unevaporated droplets into the WESP. The hot purge air typically accounted for about half of the totai gas flow through the WESP. Since the mist eliminator would collect mostly large particles, it had little effect on the acid mist fraction.

As in the laboratory tests, the size-dependent efficiency of the WESP was determined by cascade impactor measurements at the inlet and outlet of the WESP. Since the hot purge air was added downstream from the inlet sampling location, the inlet loadings had to be corrected for this dilution. Blank impactor runs were performed with each set of runs to ensure that no artificial weight gains resulted from flue gas interaction with the impactor substrate material. The impactor substrates were also acid washed to neutralize any alkaline sites that might adsorb SO₂ and cause a spurious weight gain.

Prior to each set of impactor runs, a measurement of the gas-phase SO_3 level by the controlled condensation method was made to assure constant conditions. To cover a range of acid mist concentration, two series of tests were conducted at nominal SO_3 levels of 25 ppm and 47 ppm. For these two series of tests, the average inlet mass loadings of acid mist were 8.6 mg/acm (0.0038 gr/acf) and 16.3 mg/acm (0.0071 gr/acf). These loadings were lower than expected for complete condensation of the acid, possibly due to removal of some of the acid vapor in the spray chamber. Nevertheless, the loadings showed the expected variation with SO_3 level. A summary of the test results is given below.

<u>Test Parameter</u>	Low_SO3	<u>High SO₃</u>
Initial SO ₃ concentration, ppm	25	47
Inlet mass loading, mg/acm (gr/acf)	8.59 (0.0038)	15.3 (0.0071)
Inlet mass median diameter, µm	1.9	1.5
WESP applied voltage. kV	68	68
ESP current density, µA/ft ²	251	196
Specific collecting area, ft ² /kacfm	48.9	40.3
Collection efficiency, %		
Smaller than 1 µm	87.4 to 92.9	62.1 to 83.0
Smaller than 5 μ m	88.5 to 93.0	71.4 to 91.8

These results show that the WESP is capable of good control efficiencies at an SO_3 level of 25 ppm. However, the WESP performance degrades at the higher SO_3 level of 47 ppm. Although this is partly attributable to a slight difference in the specific collecting area, the primary factor is the reduction in current density from 251 to 196 μ A/ft², a reduction of 22%. This results from the increased particulate space charge and the concomitant suppression of corona current.

The space charge effect could be seen very dramatically in the voltage-current characteristics of the WESP, as illustrated in Figure 4. At an applied voltage of 50 kV, the operating current with no acid mist present was about 1.1 mA, compared to a current of about 0.4 mA with 25 ppm of SO_3 (8.6 mg/acm of acid mist). With 47 ppm of SO_3 (16.3 mg/acm of acid mist), the current was further reduced to about 0.35 mA at 50 kV. In actual practice, it may be possible to compensate for this effect to some degree by increasing the applied voltage. As shown in Figure 4, the voltage was actually increased to over 80 kV without sparkover, but this was not considered to be a realistic operating point for a commercial WESP.

It should be noted that all of the WESP testing with an actual acid mist was done with a much lower SCA than that used in the laboratory tests with the DES aerosol (40 to 49 versus 74 $ft^2/kacfm$). This was done to provide a more realistic simulation of a very compact WESP that could be retrofitted onto a scrubber. This difference in SCA, combined with the reduced current densities (196 to 251 versus 270 μ A/ft²), account for the lower collection efficiencies with the acid mist. The reduced current densities are a result of the space charge effect, which is more pronounced with acid mist due to the larger number of fine particles (1.5 to 1.9 versus 4 μ m mass median diameter).

PILOT COMBUSTOR TESTS WITH MIST AND FLY ASH

Since a dramatic space charge effect was evident in the mist-only results, additional tests were conducted to examine any further degradation in WESP performance that might be caused by fine fly ash particles. This was accomplished by co-firing the SO_2 -doped natural gas with a small quantity of coal to simulate the mass loading of fly ash in flue gas leaving a scrubber. The total thermal input into the combustor was maintained constant so there would not be a significant change in the temperature profile. With coal burned at a rate of 2 lb/hr and SO_2 -doped natural gas fired at a rate of 970 cfh, the flue gas entering the spray chamber contained about 45 ppm of SO_3 , and the inlet mass loading averaged about 27.6 mg/acm (0.012 gr/acf). This is comparable to recent measurements made by Flakt, Inc., at a scrubber installation of Seminole Electric, where an average loading of 28.8 mg/acm (0.0126 gr/acf) was reported (1).

Assuming that the ratio of the acid mist mass loading to the SO_3 level was the same as in the two mist-only tests, the inlet loading of acid mist may be estimated to be 15.6 mg/acm (0.0068 gr/acf). By difference, the inlet loading of fly ash is about 12.0 mg/acm (0.0052 gr/acf). With a coal containing 10% ash, this loading of fly ash would correspond to an upstream control efficiency (in the primary ESP or baghouse and scrubber) of about 99.7%, yielding a mass emission rate of about 0.013 lb/MMBtu, based on fly ash only. The total mass emission rate, including acid mist, would be about 0.03 lb/MMBtu. The total particulate mass would be composed of about 57% acid mist and 43% fly ash. Based on the measured mass median diameters (mmds) of the mist (1.5 μ m) and the mist/fly ash combination (2.2 μ m), the mmd of the fly ash is estimated to be 3.1 μ m. This case is believed to be a reasonable simulation of a precipitator/scrubber installation operating in compliance with the 1979 NSPS (4). The results of this test are summarized below; the results of the high-SO₃ mist case are also included for comparison.

<u>Test Parameter</u>	Mist Only <u>High SO₃</u>	Nist Plus <u>Fly Ash</u>
Initial SO ₂ concentration, ppm	47	45
Inlet mass loading, mg/acm (gr/acf)	16.3 (0.0071)	27.6 (0.012)
Inlet mass median diameter, µm	1.5	2.2
WESP applied voltage, kV	68	45
WESP current density, $\mu A/ft^2$	196	64
Specific collecting area, ft ² /kacfm	40.3	42.5
Correction erriciency, &	60 1 to 00 0	62 A to 77 1
Smaller than 1 µm		03.4 to //.1
Smaller than 5 µm	/1.4 to 91.8	DD.1 TO //.6

Comparison of the mist-plus-ash case and the mist-only case shows a striking degradation of the electrical operating conditions with fly ash present. With fly ash in the system, it was not possible to maintain the same applied voltage that was used in the mist-only case. Intermittent sparking resulted in excessive tripping of the power supply and limited the applied voltage to about 45 kV. It may have been possible to operate at a higher voltage, but this would have required frequent resetting of the power supply, which may have compromised the outlet impactor data. In actual practice, the use of a spark-rate controller may partially alleviate this problem.

The presence of the fly ash appears to produce a larger performance degradation in the 1 to 5 μ m size range than in the submicron size range. Since a very small mass fraction of the fly ash is submicron (typically less than 1 to 2%), it would not be surprising to see similar submicron collection efficiencies for the two cases, if the electrical operating conditions were similar. However, the degraded electrical conditions apparently limited the maximum submicron collection efficiency to 77.1%, compared to 83.0% for the mist only. For all particles smaller than 5 μ m, the cumulative collection efficiency was reduced from a maximum of 91.8% to 77.6% with fly ash present.

PHASE II OBJECTIVES

The primary goal of the Phase II work was to refine the projections of WESP performance by using data from two utility FGD installations. This required SO_3 and particle size measurements, along with chemical analyses, to determine the loadings of acid mist, fly ash, and scrubber solids downstream from the two scrubbers. These measurements provided the data needed to project WESP performance using the computer model developed in Phase I. A secondary objective was to estimate the effect of the WESP on opacity relative to the baseline configuration (scrubber with ME only). Another major objective of Phase II was to develop plans for a follow-on demonstration of the WESP concept at utility sites, if warranted.

SITE SELECTION

The first task under Phase II was to select the test sites for the field measurements. It was preferred that the two sites have substantially different levels of SO_3 in the flue gas, so that the effect of acid mist loading could be examined. A high SO_3 concentration was desirable at one of the sites, so that the effects of space charge corona suppression could be further analyzed using the computer model. It was also considered desirable to avoid the selection of two sites with the same types of boilers, scrubbers, and MEs, so that the results would be applicable to a wider range of equipment types. Based on these considerations, two sites were ultimately selected.

Site 1 was a 700-MW, cyclone-fired unit equipped with a combination venturi/ spray tower FGD system. The FGD system consisted of six scrubber modules, five of which were normally in operation. At the exit of each tower, the gas was discharged at a right angle and flowed horizontally through two vertical mist eliminators. Because of severe corrosion of the reheater tubes, the reheater had been removed, and the unit had been converted to wet-stack operation. The combination of a high sulfur content (3.2% nominal) and high iron content in the ash, along with the high-temperature cyclone firing, was reported to produce a very high SO_3 concentration at this site (5).
Site 2 was a 575-MW, pulverized coal-fired unit equipped with a venturi rod/spray tower FGD system. Each of the four scrubber modules was equipped with a horizontal mist eliminator mounted directly above the spray tower, so that the gas flow through the mist eliminator was vertically upward. Just above the mist eliminator was an in-line tubular reheater. Previous data obtained at this site (6) suggested that the SO₃ concentration would be lower than at Site 1, although the nominal coal sulfur content was about the same as at Site 1. The lower conversion of SO₂ to SO₃ at Site 2 is presumably associated with the different boiler type and the lower iron content of the ash.

SO2/SO3 DATA

Table 1 gives a summary of the SO_2 and SO_3 concentrations measured ahead of the scrubber at both sites. There is essentially no difference in the SO_2 concentrations measured at the two sites, but the SO_3 concentration is significantly higher at Site 1, for the reasons already discussed. If the reported amounts of SO_3 were completely condensed in the form of sulfuric acid (H_2SO_4) , this material alone could account for a mass loading of about 0.03 gr/dscf at Site 1 or about 0.02 gr/dscf at Site 2. At Site 1, this would be sufficient to account for over 85% of the particulate mass measured at the ME outlet by the cascade impactors. At Site 2, it would be sufficient to account for about 70% of this mass. However, chemical analyses of the impactor samples (discussed later) reveal that the H_2SO_4 actually accounts for only 40 to 45% of the particulate mass at Site 1 and about 57 to 62% of the particulate mass at Site 2. This suggests that some of the SO_3 or sulfuric acid is removed in the scrubber and ME system.

To investigate the question of SO_3 removal across the scrubber, outlet SO_3 measurements were made at Site 2. To determine the amount of SO_3 removed, the sampling probe was heated to convert all of the H_2SO_4 back to SO_3 . Measurements were also made with the probe at flue gas temperature (about 160°F after reheat) to verify that all of the SO_3 was condensed. These measurements confirmed that all of the SO_3 was condensed at this point (residual below the

detection limit of 0.3 ppm) and that the amount of condensed H_2SO_4 was equivalent to an SO_3 concentration of 6 ppm. After correcting the inlet and outlet SO_3 concentrations to the same O_2 levels, the removal of SO_3 across the scrubber was calculated to be 28%. Allowing for this loss, the acid mist would be expected to account for about 61% of the outlet particulate mass at Site 1 and about 50% of the outlet particulate mass at Site 2. Chemical analyses of the impactor samples revealed 40 to 45% H_2SO_4 at Site 1 (about 16 to 20% less than calculated from the gas-phase SO_3 concentration) and 57 to 62% H_2SO_4 at Site 2 (about 7 to 12% more than calculated). The lower H_2SO_4 recovery at Site 1 may indicate that the SO_3 removal was higher than at Site 2 (removal measurements were made at Site 2 only). The slightly higher recovery at Site 2 could be attributable to other sulfates in the ash.

TOTAL AND SUBMICRON MASS LOADINGS

Particle size and mass loading measurements were made at both sites using University of Washington Mark V cascade impactors that were heated to avoid condensation within the impactor. At Site 1, these measurements were made at the ME inlet and outlet with either one or two MEs in place. This provided an analysis of the size-dependent collection efficiency of the MEs to compare to the projected performance of the WESP. Normally, the FGD system at Site 1 operates with two MEs in series. However, a WESP supplier (ABB Flakt, Inc.) recommended that one of the MEs be removed if a WESP were to be retrofitted. Therefore, measurements were made with both one and two MEs in place. Surprisingly, there was very little difference in the cumulative mass loadings measured with either one or both MEs in service. Therefore, only a single value is reported for the outlet mass loading.

At Site 2, measurements were made at the ME outlet and the reheater outlet. Only the ME outlet data are of interest for a WESP retrofit. It would not make sense to retrofit a WESP after the reheater, because the evaporation across the reheater would make the droplets finer and possibly more difficult to collect. These measurements were made at the request of the host utility to assist them in correlating the measured emissions with opacity. Table 2 presents the average total and submicron mass loadings obtained at both sites at each sampling location. As expected, the mass loading was very large ahead of the MEs (13.7 gr/acf), and this mass was dominated by particles larger than 1 μ m. The mass mean diameter (MMD) of this material was estimated to be 44 μ m. Downstream from the MEs, the mass loading was much lower, and the particulate mass was predominantly submicron in size. The cumulative submicron mass loading was slightly higher at Site 1 than Site 2 (0.022 versus 0.021 gr/acf), although the cumulative submicron percentage was lower at Site 1 than Site 2 (87% versus 95%). Thus, Site 2 appears to have a finer distribution on the basis of submicron mass percentage, but it actually presents less challenging conditions for a WESP retrofit than does Site 1, because the absolute loading of submicron particles is lower at Site 2. This small difference in submicron mass translates into a large difference in the number concentration of submicron particles, which is critical in terms of space charge effects.

CHEMICAL COMPOSITION

The cascade impactor samples were analyzed to determine the weight percent of H_2SO_4 , fly ash, and scrubber solids as a function of particle size. The analytical methods and procedures for calculating the weight percent of each component are detailed in the Phase II final report (7). To provide a sufficient quantity of sample for analysis, selected impactor stages were combined, yielding four size fractions: (1) larger than 8 μ m, (2) 1 to 8 μ m, (3) 0.1 to 1 μ m, and (4) smaller than 0.1 μ m. Figure 5 shows the H_2SO_4 content increases with decreasing particle size. At Site 2, this same trend was evident down to the 0.1 to 1 μ m fraction, but the fraction smaller than 0.1 μ m contained slightly less acid than the 0.1 to 1 μ m fraction, as indicated below.

<u>Size fraction, µm</u>	<u>H₂SO₄, Wt_%</u>	Scrubber <u>Solids, Wt%</u>	Fly <u>Ash, Wt%</u>
Less than 0.1	56.9	0.4	42.7
0.1 to 1	61.8	2.2	36.0
1.0 to 8	47.1	11.2	41.7
Larger than 8	27.3	72.7	0

WESP PERFORMANCE PROJECTIONS

The WESP computer model developed in Phase I was used to make performance projections for WESPs retrofitted at the two test sites discussed above. For the Site 1 projections, the mass loading and size distribution measured with one ME in place were used, since that configuration was recommended by a WESP supplier. For the Site 2 projections, the measurements made at the ME outlet were used. In each case, projections were made with two sets of electrical conditions, corresponding to the best and the worst conditions achieved in the Phase I pilot testing.

	Predicted collect	ion_efficiency, %
Electrical conditions	<u>Site 1</u>	<u>Site 2</u>
45 kV and 72 nA/cm^2	84.9	97.5
60 kV and 114 nA/cm^2	96.2	98.7

The lower efficiencies for Site 1 are entirely attributable to the higher loading of fine particles and the resulting space charge effects. For both cases, the SCA was 50 ft²/kacfm; the gas velocity was 20 ft/sec; and the tube length was 10 ft.

For Site 1, the baseline opacity, with both MEs in place, was 42 to 60% (as determined by a trained smoke reader after dissipation of the steam plume). The projected opacity after the WESP retrofit described above was 11 to 19% with the worst electrical conditions and 8 to 14% with the best electrical conditions. For Site 2, baseline opacity data were not available, but the projected opacity (after the WESP retrofit) was substantially lower than at Site 1 (1.5 to 3% with the worst electrical conditions and less than 1.5% with the best electrical conditions). These results strongly suggest that the WESP retrofit could maintain opacity below 20% at both of the sites investigated.

FOLLOW-ON DEMONSTRATION

Based on the results of Phase I and Phase II, a follow-on demonstration of the WESP concept appears to be justified. Therefore, preliminary planning for a follow-on demonstration has been undertaken. Two approaches have been considered: (1) Installation of a prototype WESP on a full-scale scrubber module and (2) construction of a smaller, mobile WESP demonstration unit that could

be tested at various utility sites. Although the full-scale unit would be preferable in some respects, the ability to test a wide range of conditions is a key factor favoring the mobile unit. One possible embodiment of a mobile unit is shown in Figure 6. This unit would handle a gas flow of about 10,000 acfm at 125°F (about 5-MW equivalent) and would fit on a standard 40 to 50 ft trailer. The design would include provisions to test different types of discharge electrodes as well as different types of collecting tubes. Provisions would also be made for real-time monitoring of the gas flow, temperature, voltage, current, and opacity. Test parameters for the WESP demonstration program would include: coal type, SO_3 /acid mist loading, fly ash and scrubber solids loadings, size distribution, scrubber type, ME type, electrode types, and cleaning methods and frequencies.

There is no definite source of funding for the WESP demonstration unit at this time. However, the Department of Energy, the Electric Power Research Institute, several utilities, and a major WESP supplier have expressed considerable interest in this concept. Recognizing the potential benefits to the utility industry and the potential market for WESP technology, the utilities and the WESP supplier have agreed in principal to share a portion of the project costs. During the initial portion of the proposed follow-on demonstration, an economic analysis of the WESP technology would also be done. This analysis would address existing WESP technology as well as various advanced concepts in discharge electrodes and materials of construction.

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Table 1.

Summary of S0₂/S0₃ Measurements

	<u>Site 1</u>	<u>Site 2</u>
Average SO, Concentration, ppm	2100	2200
SO ₂ Concentration Range, ppm	2000 to 2260	2190 to 2210
Average SO, Concentration, ppm	19	11
SO, Concentration Range, ppm	13 to 25	9 to 13
Average S0,-to-S0, Ratio	0.009	0.005
SO ₃ -to-SO ₂ Ratio Range	0.0065 to 0.011	0.004 to 0.006

Table 2.

Total and Submicron Mass Loadings

	<u>Mass_Loading, gr/acf</u>	
	<u>Total</u>	Submicron
Site 1 - ME Inlet	13.7	0.026 (0.2%)
Site 1 - ME Outlet	0.025	0.022 (87%)
Site 2 - ME Outlet	0.022	0.021 (95%)
Site 2 - Reheater Outlet	0.011	0.010 (91%)



Figure 1. Sketch of WESP Setup Used in Laboratory Tests with Simulant Oil.



Figure 2. Sketch of Modified WESP Setup Used in Pilot Combustor Tests with Actual Acid Mist.



Figure 3. Comparison of WESP Fractional Collection Efficiency Measured Using Simulant Oil with Predictions of Two WESP Computer Models.



Figure 4. Comparison of WESP Voltage-Current Curves Obtained With and Without Acid Mist.



Figure 5. Sulfuric Acid Content of Particle Size Fractions at Site 1



Figure 6. Sketch of Mobile WESP Pilot Unit for Demonstration Program

MANAGING AIR TOXICS:

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STATUS OF EPRI'S PISCES PROJECT

by

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INTRODUCTION

The US Environmental Protection Agency (EPA) has historically regulated air toxics (hazardous air pollutants) under Section 112 of the Clean Air Act. To date, EPA has established emission standards for 8 hazardous air pollutants (arsenic, asbestos, benzene, beryllium, mercury, radionuclides, coke oven emissions and vinyl chloride). The US electric utility industry was not determined to be a source category requiring regulation for any of the eight chemicals. Of the eight, radionuclides were the last species for which EPA established hazardous emissions standards. In this instance, EPA determined that the risks associated with electric utility fossil fuel power plant emissions were sufficiently low that they should not be regulated. However, the 1990 Clean Air Act Amendments require a new evaluation of the electric utility industry emissions of hazardous air pollutants (1). This paper summarizes the key features of the air toxics provisions of the Clean Air Act Amendments, describes EPRI's activities on the subject, and provides some preliminary insights from EPRI's research to date.

1990 CLEAN AIR ACT AMENDMENTS

The Clean Air Act Amendments of 1990 greatly expanded EPAs rulemaking authority over hazardous (toxic) air pollutants. The Act contains a list of 190 chemicals (Table 1) that would be subject to control. Other substances may be added to the list by the EPA Administrator if they present adverse environmental effects. It requires sources, with exception of utility sources, that emit 10 tons or more per year of any one pollutant, or 25 tons or more per year of any combination, to apply Maximum Achievable Control Technology (MACT). Although not clearly defined, MACT is the maximum degree of reduction of hazardous pollutants that the Administrator determines is achievable. Consideration would be given to the cost and feasibility of control, energy impacts, and environmental factors. For existing sources, MACT may not be less stringent than the average emission limit achieved by the best performing 12% of existing sources in categories containing 30 sources or more. After applying MACT, a residual risk analysis will need to be performed to determine if additional controls are warranted.

Five studies which affect electric utilities are mandated: a 3-year study to address the hazards to public health associated with emissions from fossil-fuel power plants (after compliance with the acid rain provisions of the Act); a 4 year evaluation of mercury emissions, their effect on human health and the environment, and the availability and cost of potential control technology; a 3 year mercury study conducted by the National Institute of Environmental Health Sciences to define health and environmental thresholds for mercury; and, a 3-year study of atmospheric deposition rates, impacts on public and environmental health and water quality effects of air toxics on the Great Lakes and coastal water bodies; and a study on residual risk methods. EPA is directed to regulate the utility industry for

air toxics only if its 3 year study indicates that such regulation is necessary and appropriate.

Although the electric utility industry is not the primary focus of the air toxics provisions in the Clean Air Act Amendments, the potential financial implications are enormous. The Edison Electric Institute has estimated that compliance costs could be as high as \$7.8 billion per year (2). This is the case despite recent EPA studies which have shown that emissions of potential cancer-causing substances from electric utility boilers pose insignificant risks – less than 1 excess cancer per year in a population of over 200 million (3). EPA's study included arsenic, selenium, hexavalent chromium, cadmium and formaldehyde emitted from both coal and oil-fired boilers.

As the basis for this risk assessment, EPA used available air toxic emissions factors from the literature (4). However, the values used are of uncertain quality with many acknowledged limitations. Quality assurance procedures were not performed, nor do the authors of the EPA report endorse the emission factors as representative. Variations in trace element levels in coal, the design and operating parameters of boilers and control devices, and uncertainty in sampling and analytical methodologies for detecting trace pollutants all contribute to the uncertainty.

More recent analyses of these data and data gathered since completion of the EPA study generally support lower emission factors than those recommended in the EPA report (especially for chromium, manganese, and nickel). Also, the EPA study only focused on those chemicals classified as potential carcinogens. The list of 190 hazardous air pollutants also includes chemicals that are noncarcinogenic such as hydrochloric acid (HCl).

EPRI AIR TOXICS ACTIVITIES

To help the electric utility industry better understand emissions of potentially toxic chemicals from fossil fuel power plants, EPRI initiated the PISCES (Power Plant Integrated Systems: Chemical Emissions Study) project in mid-1988. PISCES is multi-media in perspective; that is, the study evaluates the presence and fate of chemicals in air, water and solid waste discharges (Figure 1). This approach is being taken so that the effects of controls on air emissions, for example, can be assessed with full knowledge of the impacts on other plant process streams (i.e., solids and wastewaters).

The project involves the collection and review of existing data regarding the source, distribution, and fate of chemicals in both conventional and advanced fossil-fuel fired power systems. It consists of several major products and activities including: a relational database of information gathered from the literature and other sources; a computerized power plant systems model to track the pathways of chemical substances and quantify emissions; a field monitoring program to measure emissions of 24 chemicals in utility flue gas at plants employing a variety of emission control technologies; an emission control technology engineering reference manual; an analytical methods guideline for measuring trace chemicals in utility process and discharge streams; and comprehensive, multimedia risk assessment (Figure 2). Other EPRI air toxics research currently underway or

planned, although not described in this paper, includes an evaluation of potential health effects (e.g., arsenic, nickel) associated with utility emissions; a comprehensive study of mercury cycling, analytical techniques, and ecosystem impacts; and an investigation of the atmospheric transformations of selected chemical species such as mercury.

The PISCES Database

The project to date has focused on information collection for conventional coal-, oil-, and gas-fired power plants. Over 500 chemicals have been identified in power plant process streams. Approximately 80 of these 500 were selected for additional data search on regulatory limits and health effects. In general, more and better data tend to be available for inorganic species in liquid and solid process streams than for air toxics. Further, lesser amounts of data are available for inorganic species in gaseous process streams and organic species in all media.

To date, the PISCES database contains more than 150 megabytes of information, including 80,000 records of reported quantity data. Detailed descriptions of the database have been reported elsewhere (5, 6). The PISCES database allows users to assemble data from a largely fragmented body of open literature and other sources on chemicals in power plant process streams. With this vehicle, one can organize the data to explore relationships between chemicals, process streams, and one or more systems or plant components.

An example of information derived from the interim database is shown in Figure 3, depicting the concentration of nickel in various fly ashes. These curves represent the probability of finding nickel less than a specific concentration for four fuels. The highest concentration is in oil-fired power plant ash. Figure 4 compares the concentration of mercury in various fuels. Based on data in the PISCES database, the fuel with the highest variability is oil.

Using other information in the database, one can determine the fate of certain classes of chemical species within the power plant. For example, comparing the concentration of chromium in coal with that found in the fly ash indicates that a large proportion of chromium is captured with the particulate matter (Figure 5). This would suggest that highly efficient particulate control devices, such as electrostatic precipitators (ESPs) and baghouses, would remove chromium from power plant flue gas streams quite efficiently. In fact, EPRI field studies have shown that chromium concentrations in the stack are quite low.

Conversely, available data for mercury indicates that most of this volatile element remains in the flue gas following an ESP (Figure 6).

The PISCES database is currently available only through EPRI. In late 1991, a subset of the database on emissions and plant parameters will be available to EPRI member companies on diskettes. The large database is expected to be placed on a CD-ROM system in 1992.

Monitoring Chemical Species

Evaluating potentially toxic emissions is critically dependent on the ability to sample and measure these chemical species, especially when a vast majority of those listed in the new Clean Air Act Amendments only appear in trace amounts in plant process streams. Without the requisite understanding of a method's capabilities and limitations, misleading results are not only possible, but highly probable.

To furnish utilities with interim guidance, EPRI has produced a compendium of available methods for measuring trace substances in a variety of process streams, including flue gas. The document will contain information on precision and detection quantification limits, where available. This information should help utilities establish and conduct sampling programs based on the most up-to-date methods, and assist them in understanding the limitations of the various measurement methods. This compendium is currently in draft form and should be published in early 1992.

Future PISCES efforts will involve both laboratory development as well as field evaluation studies of specific methods for measuring important chemicals in fuels and flue gas. Of particular interest is improved sampling techniques for mercury and benzene and speciation of important trace elements such as arsenic and chromium. A long range goal (1995-1997) is development of a continuous air toxics monitoring system for key chemical species.

Control Technology Engineering Reference Manual

Based on information in the PISCES database, a Control Technology Engineering Reference Manual will be prepared to assist utilities in determining the performance of various emission control devices in removing trace chemicals, if risk assessment supports the need for controls. These documents will not only provide emission factor estimates but also insights into the mechanisms involved in chemical removal. For example, the role of temperature, ESP size and performance, and the concentration and form of trace elements in the coal will be discussed (if known) in terms of their impact on emissions and removal. An initial state-of-the-knowledge document is planned for mid-1993.

The major issue in predicting control technology performance for air toxics removal is lack of data. Although the number of available data points for plant emissions of various chemical species is quite large, the number of paired data sets — inlet and outlet — on any given control device is sparse. For example, the PISCES database has no performance data for nickel or chloride removal by fabric filters. Figure 7 illustrates this same point for chromium. There are 51 data points for high dust gas (inlet to ESP) but only 5 data points on emitted gas. This data paucity has been a critical factor in EPRI initiating the Field Chemical Emission Monitoring (FCEM) program in association with EPRI member companies.

Field Monitoring

The PISCES Field Chemical Emission Monitoring (FCEM) program began in May 1990 with the collection of data on 24 chemicals (Table 2). Emissions and discharges

are being measured from several control technologies, including cold-side ESPs, fabric filters (conventional and pulse-jet), low-NOx burners, postcombustion NOx systems, spray dry FGD, and wet lime/limestone FGD. Plant mass balances are being performed for each metal and inorganic chemical to define their sources, pathways, and the way they partition in the plant system. Therefore, all appropriate liquid and solid waste streams are sampled in addition to the flue gas. A variety of coal-types combustion systems are included in the program. and Bituminous, subbituminous, and lignite coals are included. Combustion sources include wall-, tangential-, and cyclone-fired boilers and fluidized bed systems. Also, oil- and gasfired power plant emissions have been examined for a smaller subset of air toxics. The acquisition of new, high quality data from current utility operations, using improved sampling and analytical procedures, will upgrade the database and provide performance information for the Control Technology Engineering Reference Manual.

Preliminary data from EPRI's field monitoring study are just becoming available. One facility sampled was a midwestern U.S. power plant equipped with an ESP and wet limestone scrubber burning a western subbituminous coal. The FGD system at the time was operating with 24% flue gas bypass. The data indicate that, with the exception of mercury and chloride, over 90% of each chemical was removed with most showing over 95% removal. Mercury removal was difficult to accurately determine since it is present in such low concentrations in the clean flue gas (less than 0.0002 mg/Nm³). EPRI is currently working on an improved sampling and analytical procedure for mercury for use at future test sites.

To date, EPRI has sampled at six power plant sites. Approximately 10 more sites will be sampled through 1993. In addition, the US Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) will begin a complementary program in 1992 at approximately 10 more locations. DOE PETC will sample for the same 24 chemicals as the EPRI FCEM program and will also use the same sampling and analytical protocol.

Systems Model

The power systems model, just released for limited utility testing, provides either deterministic or probabilistic estimates of chemical emissions in the gaseous, liquid, and solid waste process streams from a specified power plant configuration. Stream conditions for coal-fired plants are characterized for fifteen plant subsections (Table 3) which are used to configure a plant for an analysis. Major plant flow rates are quantified based on internal mass and energy balance calculations for a specified plant size, equipment design, and fuel choice. To operate the model, users must specify inputs such as power system design parameters, performance characteristics, emission constraints, fuel properties, and pollution control performance measures. The pollution control performance measures can be acquired in one of two ways. Utilities may have site specific performance data on environmental control devices based on operating experience. Or, from the chemical composition data contained in the PISCES database, partitioning factors for various chemical species between solid, liquid, and gaseous streams can be derived for a device if sufficient data exist. The development of this model is motivated by utilities' desire to better understand the relationship between their power plant designs/operating factors, choice of fuels and emissions of potentially hazardous or toxic species. An important application of this model will be in characterizing the chemical composition of various power plant emission streams such as collected fly ash, bottom ash, FGD by-product, ash pond effluents, and stack gases.

The probabilistic feature of the model allows incorporation of uncertainty in calculating emissions of various chemicals. This uncertainty can stem from the variability of specific chemicals in the fuel, plant operations, and sampling and analytical variability and uncertainty (e.g., precision, accuracy, bias). This feature of the model allows utilities to assess the likelihood of emitting a substance at a specific rate with a given confidence level. In other words, the model estimates cumulative probabilities, depicting the median likelihood of observing a given emissions rate. Such estimates may be used to evaluate the overall emissions of a specific plant. Further discussion of the model and examples of its results in case studies are reported elsewhere (7, 8, 9, 10). An interim version of the model for conventional coal-, oil-, and gas-fired power plants will be available for EPRI utility member testing in late 1991.

MANAGING HCI AND MERCURY

As debate on the air toxics provisions of the Clean Air Act Amendments has progressed, two chemicals have received significant attention -- hydrochloric acid and mercury. Due to inorganic chlorides in coal, hydrochloric acid emissions will generally exceed 10 tons per year for most power plants in the US. Based on an average (0.12%) chloride content in bituminous coals, a 500 MW! power plant without an FGD (flue gas disulfurization) system would emit about 1400 tons per year of HCl. Plants equipped with FGD systems would have substantially lower emissions (over 90% removal).

Mercury, on the other hand, is emitted in relatively small quantities. Uncontrolled emissions from a typical 500 MW plant would be about 500 pounds per year. Actual emissions are less given that current environmental control technology does remove some mercury. Utility emissions of mercury are relatively small; that is, the annual contribution from U.S. fossil-fuel fired electric utility boilers represents roughly 2 percent of the 6 million kilograms global mercury budget and less than 4 percent of global anthropogenic emissions (11, 12). The following discussion is a summary of the state-of-knowledge regarding the emissions and control of HCl and mercury.

Hydrochloric Acid

Chloride concentrations vary widely in US coals, from virtually unmeasurable quantities to over 0.5% (13). Generally, eastern high-sulfur coals have higher chloride concentrations than western subbituminous and lignite coals. During combustion in the furnace, over 95% of the chloride in the coal is initially released, primarily (90%) in the form of gaseous HCl. There is little interaction between the gaseous HCl and the ash. HCl will deposit onto the fly ash only below 60 degrees Celsius (140 degrees Fahrenheit), the acid dewpoint for HCl. This is true regardless

of the pH of the fly ash. Data indicate extremely low to nondetectable levels of chloride in fly ash from lignite, bituminous, and subbituminous coals. HCl reacts quickly in the atmosphere with ammonia and calcium and is generally not detected beyond 10 kilometers (several miles) from the stack.

HCl emissions are also not a major health concern. For a power plant emitting 200 tons of HCl per year with a stack height at GEP (good engineering practice), ground level concentrations over a one-hour maximum average would be less than 1 microgram/cubic meter under adverse meteorological conditions. This is negligible compared to the threshold limit value for occupational health effects of 7000 micrograms/cubic meter.

<u>Mercury</u>

Mercury levels in U.S. coals vary from about 0.01 to 8 ppm (14, 15). Typical values, however, are about 0.24 ppm for Appalachian coals, 0.14 ppm for Interior Eastern coals, and 0.21 ppm for Illinois Basin coals (16). Mercury is probably emitted primarily in its elemental form, but it could also be in one of its many combined forms.

The literature is quite confusing regarding mercury emissions from coal-fired power plants. First, it is not always clear whether the measured mercury was total, vapor phase, or that condensed on particulates. Secondly, the sampling and analytical methods used may have been unreliable. Finally, most data available on mercury removal are from the municipal waste incinerator industry where mercury concentrations are higher by several orders of magnitude than in utility flue gas.

A literature review by Smith (17) showed mercury removals ranging from 10% to 50% through fabric filters or ESP's. This reference also reported that FGD systems removal spans a large range, from 20 to 95%. In contrast, the current EPRI PISCES database indicates about 20 to 90% removal for cold-side ESPs (5 data points) and 85 to 90% for fabric filters (3 data points). The primary reason for these large ranges is the sampling and analytical variability discussed earlier.

A recent study of a coal-fired power plant in Japan showed approximately 33% mercury removal in the particulate control system (cold-side ESP), 36% by the FGD system (wet lime), while the remainder was vented up the stack (18). The same study cited another coal-fired plant with a hot-side ESP and an FGD system with 25% flue gas bypass around the scrubber. The data in this situation showed virtually no removal in the ESP, 26% removal in the FGD system, with the remainder vented up the stack. It appears from these data that temperature plays an important role in mercury emissions. The likely explanation is that mercury is condensing on coal ash particles at the lower temperatures and remaining volatile at the higher temperatures common in a hot-side ESP.

Several recent papers have reported that mercury can be removed from municipal waste incinerator flue gas through use of chemical additives. Joy Technologies (19) reported that use of an additive in a spray dryer system improved mercury removal as did operation at lower exit gas temperatures. Joy's data show that a spray dry/baghouse combination operating on a municipal waste incinerator removed

69% of the total mercury without the additive and from 91% to 95% with the additive. The spray dry/ESP combination removed from 27% to 66% of total mercury without the additive and from 78% to 86% with the additive. The higher removals were observed at the lower exit gas temperatures. Although the additive was not specified, it is assumed to be activated carbon. Use of activated carbon has been reported by others with similar results (20, 21, 22, 23).

Another paper by several Japanese authors reported 95% to 100% mercury removal through use of a wet lime FGD system on flue gas of a municipal waste incinerator (24). Here, an oxidizing agent (sodium hypochlorite) was added to the scrubber to solubilize the mercury. The mercury was then removed from the scrubber waste water through a reduction, volatilization, condensation, and mercury separation process.

Another chemical removal method for mercury is sodium sulfide scrubbing (25). The sodium sulfide combines with both vaporous mercury and mercuric chloride to form mercuric sulfide. Mercuric sulfide is a stable compound. Reported removal efficiencies for a municipal waste incineration flue gas are between 73% and 88%. No cost data were reported.

Condensing wet scrubbers may also achieve over 90% mercury removal (26). However, to achieve this level of mercury removal, the mercury must be in the form of mercuric chloride (which is soluble) rather than vaporous mercury which will require use of an additive (such as sodium sulfide) for removal.

Another adsorption mechanism for mercury removal has been reported from Germany (27). In this instance, a reactor designed for NOx removal following an FGD system also indicated removals of virtually all of the mercury present in the flue gas. These tests were conducted at pilot scale on a municipal waste incinerator plant using lignite coke as the absorbent material.

The foregoing discussion indicates some of the uncertainties regarding mercury emissions and control. It should be emphasized that the highest removals reported have been accomplished on municipal waste incinerator flue gas, not flue gas from the coal-fired power plants where mercury concentrations are lower by several orders of magnitude. The ultimate fate of mercury is also undefined. That is, the form of the mercury in the solid or liquid by-product is not known, nor is whether the mercury revolatilizes once the solid by-products are landfilled. One author reported that 10 to 15% of the mercury in fly ash evaporated at room temperature over a period of 14 days (28).

Most of the older mercury emissions data reported in the literature are suspect given the difficulties in mercury sampling and analysis. Since mercury amalgamates with many metals, it is ubiquitous in many laboratories and thus contaminates samples. It does appear that the more recently reported data using better sampling techniques and analytical methods are reducing some of this uncertainty. However, the EPRI FCEM program is pointing to the need for further improvements in mercury sampling and analysis in utility flue gas streams.

RISK ASSESSMENT

EPRI is also conducting studies aimed at improving our understanding of what happens to air toxics after they leave the power plant stack. The goal is to develop knowledge aimed at helping answer the central question around which the whole air toxics issue revolves: What risk does the emission of these substances from power plants pose to public health and to the environment?

A key step toward answering that question is finding out which substances are of most concern. As stated previously, 190 substances have been designated as hazardous air pollutants in the new Clean Air Act Amendments. However, since most of these substances are not emitted by utility power plants or are emitted only in extremely small quantities, EPRI is trying to substantially narrow the list to a few priority substances that warrant detailed risk analysis.

Assessing the potential health risks of toxic substances in the environment is a demanding task. There is a big difference between a large, direct exposure in a short time – such as could occur, for example, if a tank containing a toxic substance ruptured near people – and exposure to a minute, diluted amount of the same substance over many years. Also, humans can be exposed to substances by different routes: inhalation, absorption through the skin, or ingestion of food and water containing the substances. Exposure to a single substance may result in a number of different physiological responses. To further complicate matters, the substances emitted from power plant stacks may be chemically transformed in the atmosphere by exposure to sunlight and water vapor or may be transformed by their interaction with the ecosystem. These transformed substances may be either more or less toxic than what was originally released from the stack. All of this must eventually be taken into account in risk assessment.

EPRI has developed a set of methodologies and is applying a series of computer models using data developed in other EPRI research programs, including the PISCES project, to determine human health risks from air toxics emissions.

The first of the models, the Air Emissions Risk Assessment Model (AERAM), is used to represent individual sources of air toxics. It uses a set of modules to calculate plant emissions, the transport and dispersion of emissions in the atmosphere, human exposures, and, ultimately, the human health risks from a particular power plant. By varying input data on fuel characteristics and the efficiency of pollution control technologies, the user can evaluate the impact of various control options on potential health risks.

Another model, called AirTox, expands on the capabilities of AERAM. It permits multiple decisions on controls to be analyzed and provides information on a range of outcomes, including cost. AirTox also allows utilities to explicitly incorporate uncertainties in such factors as ambient concentrations of substances, utility emissions, control efficiency, and the relationship between exposure and health effects. The model can help a utility put in perspective its contribution to air toxics emissions and evaluate the implications of changes in emission levels over time. EPRI and individual utilities have used these tools to conduct risk assessments for several carcinogens emitted from a variety of utility sources to determine the relative contribution from each chemical to the risk posed by each source. To date these analyses have considered only the inhalation exposure route to air emissions.

A comparison benchmark for risk was used in these analyses: an incremental lifetime cancer probability (LCP) of one in one million. This value is one of several criteria used in regulatory reviews nationwide, representing the LCP experienced by a "theoretical" individual exposed for seventy years to the maximum air concentration of all toxins under consideration. Such an exposure defines the Maximum Exposed Individual, or MEI.

Test versions of AERAM and AirTox are available to EPRI member utilities; a new methodology is being developed that will expand on these models to allow consideration of exposure routes besides inhalation. Called RiskPISCES, this multimedia risk evaluation model will link existing models for multiple exposure pathways and will perform a screening evaluation of multiple chemical species under a common framework to identify significant species; these species will then be subjected to detailed risk analyses.

The results of EPRI's risk assessment studies will be used in the compilation of a Comprehensive Risk Evaluation (CORE) to be completed in early 1993. The CORE effort will provide utilities and decision-makers with EPRI's best assessment of the human health and environmental risks posed by fossil fuel-fired power plants.

CONCLUSIONS

Electric utility flue gas emissions are generally well controlled and will be even more so after complying with the acid rain provisions in the 1990 Clean Air Act Amendments. However, the new Clean Air Act Amendments require several detailed studies of the risks associated with the combustion of fossil fuels. Based on these studies, the U.S. EPA will make a determination whether further controls beyond the acid rain provisions are necessary.

Ongoing studies by EPRI, U.S. DOE and others will provide information to assist in this evaluation of air toxics. These studies, including emissions characterization and risk assessment, will provide valuable input to EPA's studies of air toxics. With these efforts to acquire better quality data, the electric utility industry will be in an improved position to evaluate EPA's conclusions on hazardous air pollutants from fossil fuel-fired power plants.

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FIGURE 1

POWER PLANT INTEGRATED SYSTEMS: CHEMICAL EMISSION STUDIES

FIGURE 2

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FIGURE 3



FIGURE 4



FIGURE 5



FIGURE 6

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PISCES Database Records Chromium - ESP/FGD Emitted gas 5 High dust gas FGD Inlet gas 51 BOILER FGD ESP Coal STACK 505 Limestone **Collected** particulate 43 FGD Solids Bottom ash 51 570 358

FIGURE 7

TABLE 1 1990 CLEAN AIR ACT AMENDMENTS LIST OF CHEMICALS

Acetaldehyde Acetamide Acetonitrile Acetophenone 2-Acetylaminofluorene Acrolein Acrylamide Acrylic acid Acrylonitrile Allyl chloride 4-Aminobiphenyl Aniline O-Anisidine Asbestos Benzene (including benzene from gasoline) Benzidine **Benzotrichloride** Benzyl chioride Biphenyl Bis(2-ethylhexyl) phthalate (DEHP) Bis(chloromethyl)ether Bromoform 1.3-Butadiene Calcium cyanamide Caprolactam Captan Carbaryl Carbon disulfide Carbon tetrachloride Carbonyl sulfide Catechol Chloramben Chlordane Chlorine Chloroacetic acid 2-Chloracetophenenone Chlorobenzene Chlorobenzilate Chloroform Chloromethyl methyl ether

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Chloroprene Cresols/Cresylic acid (isomers and mixture) o-Cresol m-Cresol p-Cresol . Curnene 2,4-D, salts and esters DDE Diazomethane Dibenzofurans 1,2-Dibromo-3-chloropropane Dibutylphthalate 1,4-Dichlorobenzene(p) 3,3-Dichlorobenzidene Dichloroethvl ether (Bis(2-chloroethyl) ether) 1.3-Dichloropropene Dichlorvos Diethanolamine N,N-Diethyl aniline (N.N-Dimethylaniline) Diethyl sulfate 3,3-Dimethyl benzidine Dimethyl carbamoyl chloride Dimethyl formamide 1,12-Dimethyl hydrazine Dimethyl phthalate Dimethyl sulfate 4,6-Dinitro-o-cresol, and salts 2,4-Dinitrophenol 1,4-Dioxane (1,4-Diethyleneoxide) 1,2-Diphenylhydrazine Epichlorohydrin (1-Chioro-2,3 epoxypropane) 1.2-Epoxybutane Ethyl acrylate Ethyl benzene N-Nitroso-N-methylurea

TABLE 1 CONTINUED

Ethyl carbamate (Urethane) Ethyl chloride (Chloroethane) Ethylene dibromide (Dibromoethane) Ethylene dichloride (1,2-Dichlorethane) Ethylene glycol Ethylene imine (Aziridine) Ethylene oxide Ethylene thiourea Ethylidene dichlonde (1,1 -Dichlorethane) Formaldehvde Heptachlor Hexamethylphosphoramide Hexane Hydrazine Hydrochloric acid Hydrogen fluoride (Hydrofluoric acid) Hydrogen sulfide Hydroquinone Isophorone Lindane (all isomers) Maleic anhydride Methanol Methoxychlor Methyl bromide (Bromomethane) Methy chloride (Chloromethane) Methyl chloroform (1,1,1-Trichloroethane) Methyl ethyl ketone (2-Butanone) Methyl hydrazine Methyl iodide (lodomethane) Methyl isobutyl ketone (Hexone) Methyl isocyanate Methyl methacrylate Methyl tert butyl ether 4.4-Methylenedianiline Naphthalene Nitrobenzene 4-Nitrophenol 2-Nitropropane

N-Nitrosodimethylamine N-Nitrosomorpholine Parathion Pentachloronitre series ne (Quintobenzeñe) Pentachlorophenol Phenoi p-Phenylenediamine Phosgene Phosphine Phosphorus Phthalic anhydride Polychlorinated biphenyls (Aroclors) 1,3-Propane sultone beta-Propiolactone Propionaldehyde Propoxur (Baygon) Propylene dichloride (1,2-Dichloropropane) Propylene Oxide 1,2-Propylenimine (2-Methyl aziridine) QuinolineQ Quinone Styrene Styrene Oxide 2.3.7.8-Tetrachlorodibenzo p-dioxin 1.1.2.2-Tetrachloroethane Tetrachiorethylene (Perchlorethylene) Toluene Titanium tetrachloride 2.4-Toluene diamine o-Toluidine Toxaphene (chlorinated campene) 1.2.4-Trichlorobenzene 1,1,1-Trichloroethane Trichloroethylene 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol Triethylamine Trifluratin 2,2,4-Trimethylpentane

TABLE 1

CONTINUED

Vinyl bromide Vinyl chloride Vinylidene chloride (1,1-Dichloroethylene) Xylenes (isomers and mixture) o-Xylenes m-Xylenes p-Xylenes Antimony Compounds Arsenic Compounds (inorganic including arsine) Beryllium Compounds Cadmium Compounds Chromium Compounds Cobalt Compounds Coke Oven Emissions Cyanide Compounds Glycol ethers Lead Compounds Manganese Compounds Mercury Compounds Fine mineral fibers Nickel Compounds Polycylic Organic Matter Radionuclides (including radon) Selenium Compounds

TABLE 2

CHEMICALS FOR PISCES FIELD EMISSIONS MONITORING

INORGANICS

Ammonia	Lead
Arsenic	Manganese
Barium	Mercury
Beryllium	Molybdenum
Cadmium	Nickel
Chlorine/Hydrochloric Acid	Phosphorus/Phosphate
Chromium	Radionuclides (U-238
Cobalt	Selenium
Copper	Vanadium
Cyanide	Fluorine/Hydrofluoric acid

ORGANICS

Benzene Formaldehyde **Polynuclear Aromatics** Toluene

TABLE 3

POWER PLANT SUBSECTIONS FOR THE POWER SYSTEMS EMISSIONS MODEL

- 1. Coal Handling and Storage System
- 2. Boilder and Steam Cycle System
- 3. Spray Dryer FGD System
- Particulate Collection System
- Particulate co......
 Wet FGD System
 Arb Pond System
- 7. Landfill/Sludge Disposal System
- 8. Wastewater Treatment System
- 9. Main Condenser System
- Recirculating Cooling Tower System
 Recirculating Cooling Pond System
- 12. Auxiliary Cooling System
- 13. Plant Makeup Water System
- 14. Plant Service Water System
- 15. Miscellaneous Plant Systems

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RESULTS OF MIST ELIMINATOR SYSTEM TESTING IN AN AIR-WATER PILOT FACILITY

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ABSTRACT

Mist eliminator system (MES) problems are a major cause of FGD system outages, resulting in additional operating and maintenance costs. The Electric Power Research Institute (EPRI) is sponsoring an ongoing research program under RP 2250-3 to determine the cause of MES problems and to evaluate potential solutions. The program is currently focused on testing commercial MES configurations in a specially designed air-water pilot facility. The facility has been designed to test with either vertical or horizontal gas flow over a range of mist loadings and gas velocities.

This paper presents test results that relate the effects of gas velocity and mist loading on carryover. The effect of washing on carryover is also discussed. To date, eight commercial mist elimination systems for vertical gas flow have been tested: two single-stage designs, four two-stage designs, and two three-stage designs. Horizontal gas flow testing was conducted with a two-stage design.

Five of the eight vertical-flow MES designs had no measurable carryover at a mist loading of 1.5 gpm/ft² and a gas velocity of 12.5 ft/sec. Multiple-stage, vertical-flow designs that had one or more stages of peaked chevron ME's were found to operate better at extremely high velocities (roughly 16 to 19 ft/sec). The MES design with horizontal gas flow also operated very well at high mist loadings (up to 3.0 gpm/ft²) and gas velocities (up to 28 ft/sec).

INTRODUCTION

Mist eliminator system (MES) problems are a major cause of FGD system outages and frequently result in additional operating and maintenance costs as well as duct buildup and particulate emission problems. The Electric Power Research Institute (EPRI) is sponsoring an ongoing research program (RP 2250-3) to determine the causes of MES problems and to evaluate potential solutions.

Past work performed under this program has focused on characterizing MES problems at full-scale FGD systems and identifying potential solutions. As a result of that effort, a mist eliminator (ME) troubleshooting guide was developed and published by EPRI to assist utilities in solving ME problems. However, full-scale testing is often difficult and expensive. Also, the potential solutions are not always applicable to other FGD systems because of site-specific factors. The full-scale testing did identify two areas for further research, and a test program was created to investigate these research needs in an air-water pilot facility. The first area was the accuracy and suitability of different measurement methods which have been used in the field to determine mist loading to the MES, the amount of carryover, and the source of carryover. Results of research in this area were presented in a paper at the 1990 SO, Control Symposium (New Orleans).

The second research area identified was definition of the operating limits of various MES configurations. Determining the operating limits of these configurations in relation to gas velocity, mist loading, and wash intensity is needed to identify and develop solutions to MES problems and to design ME systems for new and retrofit applications.

This paper describes the air-water pilot facility and discusses the results from testing the operating limits of several MES designs. The test work included an evaluation of nine pilot-scale MES designs intended to simulate commercial fullscale ME systems. The designs differ in the number of stages used and the direction of the gas flow (eight vertical and one horizontal gas flow systems). All of the systems simulated are currently employed in existing FGD systems.

The following sections discuss the air-water pilot facility, MES configurations simulated, tests performed, and test results. The conclusions at the end of this paper summarize significant findings and discuss the impact of the results on the operation of ME systems in utility FGD systems.

PILOT TEST FACILITY DESCRIPTION

The air-water pilot facility was constructed by NELS Consulting and is located at their offices in St. Catharines, Ontario, Canada. The facility, illustrated in Figure 1, is very versatile in the number and type of mist elimination systems which can be tested. The entire facility is constructed out of Plexiglass®; this allows complete observation of the tests and simplifies the installation of mist eliminator stages and test ports. The facility can be used to test single or multiple mist eliminators with either vertical or horizontal gas flow. The mist eliminators can be tested over a range of gas flow rates and mist loadings. Mist eliminator washing can also be simulated. The pilot facility can be used to determine the effect of liquid and/or gas maldistribution on MES performance. Direct measurements which can be made in the test facility include the carryover rate and pressure drop across the mist eliminator stages. This information, when coupled with visual observations, can be used to determine the operating limits of various MES configurations. The test capabilities of the pilot facility are presented in Table 1, and a physical description of the test facility is provided below.

Air flow for testing is provided by one to three fans, depending on the air flow rate required. From the fans, the air passes through a louver damper for control of the flow rate. The air then proceeds to the bottom of the vertical gas flow test section where a set of vanes distribute and orient the gas flow for the vertical test section. The air passes through the vertical section of the facility and then through a set of perforated plates for redistribution before entering the horizontal flow test section. The duct widens out after the horizontal test section, and the air proceeds through a final mist eliminator to remove all of the entrained mist. The air then flows through a venturi for measurement of the flow rate before re-entering the fans. This flow arrangement recirculates the air and keeps it saturated, preventing evaporation which could make accurate measurement of carryover difficult at low carryover rates.

The vertical gas flow test section is approximately 25 ft high and has a 3-ft by 6-ft cross-section. One to three stages of mist elimination devices (e.g., chevrons, bulk entrainment separators, impingement trays, etc.) can be tested in the vertical section. The disengagement zone above the last mist eliminator stage can be varied from 0 to 4 ft; a zone of 2 ft was used for the tests reported in this paper. Mist for the vertical test section is generated by an array of nozzles which spray cocurrently with the gas flow. The nozzle pressure is varied to change the mist loading. Extensive calibration testing has been done to correlate the mist loading with the nozzle pressure and gas flow rate. Tests of mist eliminator washing are performed with a separate set of nozzles spraying directly on the ME face to be washed. All of the mist eliminator faces can be washed alone or in combination.

The horizontal gas flow test section is approximately 11 ft long and has a crosssection that is 8 ft high by 2.25 ft wide. One or two mist eliminator stages can be tested in this section. Mist generation and mist eliminator washing are both achieved by spraying directly on the mist eliminator with a nozzle array. All of the mist eliminator faces can be washed alone or in combination.

Gutters and drains are located in both the vertical and horizontal test sections to allow the direct measurement of carryover. Pressure transducers are used to measure the pressure drop across the venturi and the mist eliminator stages. The

transducers are connected to a computerized data acquisition system, allowing continuous monitoring and recording of the gas flow rate and pressure drop across the mist eliminators. Nozzle pressures for the mist loading and mist eliminator wash headers are also measured and recorded as a part of the tests.

MES DESIGNS SIMULATED

Vertical-Flow ME Systems

Figure 2 presents the profiles of the various chevron ME blades and the spacing between the stages for the MES configurations which were simulated in the air-water pilot facility. The blade and stage spacings are intended to be representative of full-scale installations of these MES configurations. The B&W three-stage design, which is not shown in Figure 2, is identical to the B&W two-stage design with the addition of a perforated plate located 6 ft below the first chevron stage. Each design is described in more detail below.

The ABB two-stage RC/HP MES is the same design that was formerly offered by Peabody and is currently in use in a few Peabody FGD systems. Since ABB's acquisition of Peabody, the RC/HP MES has become ABB's current offering for new FGD systems. The first stage of the RC/HP MES consists of a two-pass rough cut (RC) chevron ME with a blade spacing of 2 inches; the blades are oriented horizontally (perpendicular to the gas flow). The RC ME is followed by a four-pass high performance (HP) chevron ME that has a blade spacing of 1.5 inches. The HP ME was tested in two orientations: 1) with the blade axes horizontal; and 2) with the blade axes at a 2.5° angle from horizontal. The HP ME was tested in both orientations since the slight incline was originally included by Peabody as part of the design to improve performance. The lower face of the HP ME is located 62 inches above the lower face of the RC ME. Both ME's have a slightly extended (1.5 inches) gas-straightening section on the trailing edge of the chevron blades.

The Munters one-stage MES (T-272) is used in a few General Electric Environmental Systems, Inc. (GEESI) FGD systems. This MES consists of one horizontal stage of two-pass chevron ME modules with a blade spacing of 1.75 inches. The T-272 ME modules have an extended gas-straightening section (2 inches) on the trailing edge of the chevron blades.

The B&W ME chevrons tested have been used in several B&W FGD systems. However, the use of a perforated plate for a BES and the stage spacings used are representative of an early B&W MES design. In FGD systems more recently installed, a perforated plate is used as a tray for SO₂ removal (not as a BES), and the ME stages are spaced farther apart. The B&W MES tested uses two identical stages of chevron ME's; each stage has three passes and a 3-inch blade spacing. The stages are oriented horizontally. The chevron ME's have a small lip (0.5 inch) at the trailing edge of the blades. The pilot-scale simulation of the B&W two-stage MES used a spacing of 48.5 inches between the bottom of the first chevron ME stage and the bottom of the second chevron ME stage.

The three-stage B&W MES tested is identical to the two-stage B&W MES, except that a perforated plate (25% open area) located 6 ft below the first chevron ME stage is used as a BES. As mentioned above, a perforated plate was used as a BES only in older B&W designs. A perforated plate BES is not currently being installed in

newer B&W FGD systems; B&W now selects ME systems based on customer specifications and competitive bidding between the various ME manufacturers.

The Koch ME chevrons are relatively recent additions to the ME market and have been used or proposed for use in a few retrofit and new FGD systems. The Koch one-stage MES (Flexichevron VIII-3-1.5) has three passes, 1.5-inch blade spacing, and an extended gas-straightening section (1.5 inches) on the trailing edge of the chevrons. The blades are oriented horizontally.

The two-stage Koch ME system (Flexichevron VIII-1-2.5 followed by VIII-3-1.5) has been retrofitted in one commercial FGD system and proposed for use in several retrofit and new FGD systems. The first stage of this MES, the VIII-1-2.5, has the same blade profile as the VIII-3-1.5, but the blade spacing is about 2.5 inches. The spacing between the stages of the Koch two-stage MES in full-scale applications has varied. The spacing used in the pilot-scale simulation of the Koch two-stage design was 66 inches from the bottom of the first stage to the bottom of the second stage. This spacing was chosen based on similar spacings for other two-stage designs.

The Munters two-stage MES (T-8B followed by T-271) has been used in many Research Cottrell (RC) FGD systems. The T-8B is a peaked two-pass chevron ME with an open construction, a blade spacing of 1.5 inches, and no lip on the trailing edge of the blade. The blades of the T-8B are oriented at an angle of 45° to horizontal. The second stage is a T-271 ME identical to the T-272 mentioned above except that the blade spacing is 0.875 inch.

Figure 3 presents a more detailed drawing of the Munters two-stage design. The peaked BES modules are arranged so that the gas exits at opposite angles on each side of the peak. The pilot-scale simulation of the Munters two-stage system used T-8B modules with a span of 36 inches so that the modules would fit in the 3-ft by 6-ft vertical gas flow section of the pilot facility. The full-scale T-8B modules are normally available in spans of 38 inches. As shown in Figure 3, the T-8B ME modules have vertical plates spaced about 4.75 inches apart. These plates provide a support for the chevron blades. They also cause any water which has collected on the blade above the plate to drain off the blade and back into the absorber tower. The drainage length down a full-scale T-8B profile is limited to roughly 6.75 inches because of the vertical plates. The specially fabricated, 36-inch span, T-8B modules used in the pilot-scale simulation did not significantly affect the drainage of the T-8B ME design and allowed them to be tested in the vertical test section without modifying the pilot facility.

The ABB three-stage MES is commonly found in Combustion Engineering (CE) FGD systems and may be otherwise known as the CE ME design. ABB has stopped offering this MES in new FGD systems in preference to the RC/HP MES mentioned before. This MES consists of a stage of 45° angled slats used as a bulk entrainment separator (BES), followed by two stages of peaked, two-pass chevron ME modules. The spacing between the bottom of each stage and the bottom of the next stage is 2 ft. Both the BES and the peaked chevron ME modules have 3-inch blade spacings. The peaked chevron ME modules are angled at approximately 30° from horizontal and have a small lip (0.5 inch) on the trailing edge of the chevrons.

Figure 3 shows another view of the ABB three-stage design. Because of the peaked design, there were a few special considerations in the design of the MES testing.

As shown in Figures 2 and 3, the ABB three-stage MES uses BES slats and peaked twopass chevron ME modules. The gas exits the ME stages at an angle of approximately 45°. The slats and peaked chevron ME modules do not have an extended section at the trailing edge of the profiles to straighten the gas. Additionally, the drainage length for the chevrons is approximately 55 inches on each side of the peak for full-scale modules. Since drainage is considered important in the evaluation of carryover, it was necessary to preserve the full drainage length of the ABB peaked modules. Therefore, they were modified to fit into the 3-ft by 6-ft vertical test section. Because of these two factors (the exit angle of the gas and the length of the legs of the peaked ME's), a new angled gas flow section of the pilot facility was built to test the ABB three-stage MES design. This angled flow section was designed specifically to follow the path of the gas exiting the BES slats and peaked chevrons.

Figure 4 shows a schematic of the angled flow section which replaced the vertical gas flow test section in the pilot facility. As shown, only one side of the peaked ME modules was used. Pilot facility structural constraints prevented testing of a full peak (total span of roughly 8 ft, 2 inches). The angled flow section of the pilot facility had a horizontal cross-section of 16 ft^2 .

The disengagement zone for the ABB three-stage MES simulation was 2 ft vertically above the highest point of the second stage of peaked ME modules. At this point, the tower cross-section decreased drastically, speeding up the velocity of the gas and entraining any droplets which passed through the disengagement zone. A disengagement height of 2 ft was used to be consistent with the other vertical-flow ME systems tested.

Although the ABB three-stage MES design was simulated in an angled flow portion of the pilot facility, it is actually used as a vertical-flow mist eliminator in fullscale systems. To better simulate the design, angling the pilot facility ducting was done to prevent extreme maldistribution of the gas and mist caused by the exit angles of the BES and peaked chevron ME's.

Horizontal MES

Figure 5 shows the Munters two-stage horizontal-flow MES tested as part of this program. This MES design is normally found in Kellogg FGD systems and consists of a T-130 ME followed by a T-125 ME. The chevrons of the two stages have sinusoidal-shaped profiles. The blades are oriented vertically and have channels for mist drainage. The two stages are identical except for the blade spacing, 1.2 inches for the T-130 (first stage) and 1 inch for the T-125 (second stage). In full-scale systems, the spacing between the two stages is generally determined by the amount of room needed for wash headers. The same spacing (61 inches) was used in the pilot-scale simulation. Prefabricated ME modules like those used in full-scale systems were used for the pilot-scale simulation, and each horizontal-flow ME had a separate box to drain liquid from the ME blades. The drain boxes allow the ME loadings to be measured directly with the same system of drains used to measure the carryover.

Upon inspection at the pilot facility, it was found that the blades of the horizontal ME modules, both the T-130 and T-125, were manufactured incorrectly. They were slightly shorter than those normally installed in the field, resulting in a small gap inside the top frame of the modules which was not normally present according to Munters. The shorter blades did not affect the surface area of the ME presented to the gas flow. To correct the problem, a $Plexiglass \bullet$ plate was used to block off the gap at the top of the ME blades. The plate kept gas and mist from entering the frame space.

TESTING

Measurement Methods

For the vertical-flow ME systems tested, carryover is defined as any liquid which made it through the 2-ft disengagement zone, which is the distance between the top of the last ME stage and the point where the tower cross-section starts narrowing. This liquid was physically collected with a system of gutters and drains and weighed. For the Munters two-stage, horizontal-flow MES, a disengagement zone was not applicable. All liquid which made it past the second ME (T-125) was physically collected and weighed.

Carryover results are presented in this paper as a function of gas velocity. For the vertical-flow ME systems simulated, the gas velocity was based on the horizontal cross-sectional area taken up by the chevrons. For the horizontal-flow MES design, the prefabricated frames were slightly different in size. Therefore, the gas velocity was based on the average facial area of the two chevron stages.

For vertical-flow ME systems, the mist loading to the first stage was calibrated prior to testing any of the ME systems. This was done by collecting and measuring the amount of mist which reached the level of the lowes: stage without any ME's in the tower. A system of gutters and drains was installed especially for the purpose of collecting the mist.

Mist loading to the Munters two-stage, horizontal-flow MES was generated by nozzles spraying directly on the ME, evenly covering the chevrons. The mist loading was measured directly during testing with the system of drains and drain boxes shown in Figure 5 by physically collecting and measuring all liquid which impacted on the first ME as well as any that passed through it.

Tests Performed

Dry and wet pressure drop data were collected as part of this program. However, the pressure drop results are not presented in this paper due to space limitations.

Tests to determine the carryover as a function of the mist loading and gas velocity were performed on each MES. Gas velocities of approximately 7 to 20 ft/s were used for the vertical-flow ME tests, and velocities of approximately 7 to 28 ft/s were used for the horizontal-flow ME test. Most of the ME systems were tested at mist loadings of 0.6, 1.5, and 3.0 gpm/ft². However, some systems which performed better were tested at higher loadings to define their operating limits.

As part of this program, the mist loading that could be expected at the inlet of a MES in a full-scale FGD system was predicted. The estimate was based on the terminal velocity of droplets produced from two common commercial spray nozzles used in full-scale FGD systems. The estimate predicted that potential mist loadings to the inlet of a MES could range from approximately 0.1 to 7.3 gpm/ft² at velocities from 6 to 14 ft/s, assuming a liquid-to-gas ratio (L/G) of 100 gal/kacf. This estimate

did not take into account droplet coalescence or droplet wall impingement, which could lower the mist loading to the MES. Mist loadings to the entrance of a MES are also believed to depend on several other site-specific factors (e.g., distance from last spray header to first ME, L/G, etc.). Mist loadings of about 0.5 gpm/ft² have been measured at two full-scale FGD systems; however, the measurements were taken just downstream of structures which could have acted as BES's. A mist loading range of 0.6 to 3.0 gpm/ft² was chosen for this test program to cover the potential range of mist loadings that might be present in a full-scale FGD system.

The nozzles used in the air-water pilot unit were considerably smaller than those used for FGD slurry in a full-scale plant. However, essentially all of the droplets from the smaller nozzles were still greater than 50 microns in diameter. With these size droplets and the velocities used in the pilot unit, all of the MES designs tested should be capable of extremely high droplet removal efficiencies, according to information supplied by the manufacturers. The majority of the carryover observed in the air-water pilot facility was due to re-entrainment of droplets from the ME blades, not droplet penetration.

In the case of the Munters two-stage, horizontal-flow 323, both the overall system (T-130 followed by T-125) and the individual stages were lasted to determine the carryover rate. The individual stages were tested at a mist loading of 1.6 gpm/ft² so that their relative performance could be compared.

The majority of the carryover tests were repeated two or three times consecutively without changing conditions to ensure that consistent results were obtained. For each MES, a number of repeatability tests were also performed in which the conditions were changed and then returned to the desired settings.

Evaporation was not a concern in the test facility because of the closed-loop design of the system. However, some condensation did occur when testing the vertical-flow ME systems. Tests to quantify the condensation were performed, and the effects of condensation have been accounted for in all results presented here. Condensation was not a problem in the horizontal flow tests because of a lack of ductwork prior to the carryover collection point.

Wash testing was performed to determine the effect of different wash intensities on the carryover from the ME systems. Since this program was performed in an airwater system, the wash tests were designed only to test the effect of the wash rate on carryover, not the effect of the wash rate on ME cleanliness. In the majority of the wash tests, a base mist loading of about 1.5 gpm/ft² was maintained throughout the wash testing. Wash schemes were designed to simulate existing full-scale systems. Each ME was washed on the face (upstream or downstream) where it is normally washed in full-scale FGD systems. For two- and three-stage ME systems, the wash sequencing was also duplicated. For example, in some systems, the first and second ME's are washed at the same time, while in other systems, they are washed at separate times.

As with the carryover testing, repeatability tests were performed regularly. Wash durations were varied depending on the length of time required to see an effect on the carryover rate. In most cases, the ME's were washed from approximately 1 to 10 minutes with steady state generally achieved very quickly based on visual observations. Gas velocities for wash tests generally bracketed the normal operating velocity of each MES. The range of wash rates tested included those typically used in commercial FGD systems. For seven of the eight vertical-flow systems, these included wash rates of roughly 0.7 gpm/ft^2 , 1.7 gpm/ft^2 , and one higher loading (3.0 to 4.7 gpm/ft^2). However, as for the carryover tests, MES designs with higher capacities were washed at higher-than-normal loadings and velocities to determine their operating limits.

Considerations for Evaluating Carryover Values

The velocities reported in this paper are based on the cross-sectional area of the pilot facility occupied by the chevron blades. The superficial velocity based on the overall cross-section of an FGD tower would be considerably lower (20% to 30%) than the actual velocity of the gas going through the MES. This is due to the MES support structure present in the tower which blocks off some of the cross-sectional area. Therefore, it is important that the effects of support structure on the gas velocity through the MES be taken into account when applying the results reported here to full-scale systems.

The point at which carryover becomes significant can depend on particulate emissions and/or solids and slurry buildup in downstream ductwork. The significance of carryover also depends on the particular MES design. For example, horizontal-flow MES designs generally operate at a higher velocity than vertical-flow MES designs. Therefore, a horizontal-flow MES will clean a larger volume of gas per unit of surface area. The carryover and wash testing results presented in this paper are in units of gpm/ft² of ME surface area in the plane perpendicular to the gas flow. The point at which carryover becomes significant is based on the total volume of gas treated and the mist eliminator surface area. Since horizontal-flow MES designs, a horizontal-flow MES could have a higher carryover rate (in gpm/ft²) and still perform better than a vertical-flow MES with a lower carryover rate in relation to the total volume of carryover.

Following are some examples of simplified calculations showing the general method used to determine the value at which carryover becomes significant for a full-scale FGD system.

Carryover That Could Cause Significant Particulate Emissions:

Assumptions

- Particulate emissions of 0.015 lb/MMBtu (half of the most recent NSPS limit) caused by slurry carryover are significant.
- For the purpose of this estimation, all slurry carryover is assumed to be carried out the stack, and carryover from washing is assumed to cause insignificant particulate emissions.
- 10% suspended solids and 50,000 ppm dissolved solids in slurry.
- 10 ft/s superficial velocity in tower and 12.5 ft/s actual velocity through MES (20% blockage by supports)--typical velocities for vertical-flow MES designs.

Based on these assumptions, the point at which carryover becomes significant from a particulate emissions standpoint is 0.0004 gpm/ft². If the MES was designed to work at a tower superficial velocity of 20 ft/s (25 ft/s actual velocity through the MES) as is typical for horizontal-flow MES designs, the value at which slurry carryover becomes significant from a particulate emissions standpoint would increase to 0.0009 gpm/ft².

Carryover That Could Cause Significant Duct Buildup:

Assumptions:

- The same assumptions as in the previous example plus the following.
- 3 inches of dry solids buildup on the floor of the duct in six months is significant. This is equivalent to 18.8 lb of dry solids per square foot of duct floor.
- For the purposes of this estimation, all slurry carryover is assumed to deposit on the floor of the duct, and carryover from washing is assumed to cause insignificant duct buildup.
- 300-MW unit with 0.871 x 10⁶ acfm at 130°F.
- 150 ft of duct with a 15-ft by 15-ft cross-section.
- Solids on duct floor have dry bulk density of 75 lb/ft³.

Based on these assumptions, the point at which carryover becomes significant from a duct buildup standpoint would be 0.0001 gpm/ft^2 . Three inches of dry solids puts a weight load of 18.8 lb/ft^2 of duct floor on the ducting.

Again, if the MES worked at a superficial velocity of 20 ft/s (25 ft/s actual velocity through the MES), twice the slurry carryover would be required before it becomes significant from a duct buildup standpoint in the example case. The actual point at which carryover becomes significant depends on the specific FGD system concerned. For instance, in the above example, if the slurry that landed on the duct floor was not drained and did not evaporate, 21.5 inches, weighing 125 lb/ft^2 of duct floor, would build up in six months with the 0.0001 gpm/ft² carryover rate. This could shift the point at which carryover becomes significant.

The above estimations show only the factors that must be considered when deciding how much carryover is significant. Clearly, some of the carryover would be emitted from the stack, and some would land on the ductwork, rather than all of it going either place. Additionally, carryover from washing may also cause significant particulate emissions or duct buildup. However, the estimates do show that the velocity at which a MES operates affects the magnitude of the value at which carryover becomes significant.

RESULTS OF MES SIMULATIONS

This section presents the carryover results for the MES simulations in the airwater pilot facility. Results for vertical-flow ME systems are presented first, followed by results for the horizontal-flow MES. General results from the wash tests of the various MES designs are also discussed.

Carryover Results

Each MES design was tested for carryover over a range of velocities at several different mist loadings. For the eight vertical-flow ME systems, carryover results for a mist loading of 1.5 gpm/ft² are presented since this is the mid-point of the range tested. Each of the vertical-flow ME systems was tested at other mist loadings. The relative performances of the ME systems at these conditions generally followed the carryover results for the mist loading tests at 1.5 gpm/ft². The horizontal-flow MES design that was simulated performed very well. Carryover did not occur until very high mist loadings and gas velocities were tested. Therefore, carryover results are presented at loadings of roughly 3.1 and 5.2 gpm/ft² for the horizontal-flow MES simulation.

It should be noted that the carryover results are plotted on semi-log scales (for Figures 6 and 7). This is important since a change in the gas velocity of 1 to 2 ft/sec can result in an order of magnitude change in the carryover rate. It is also important to note that the results presented in this paper are based on the actual velocity through the mist eliminator in the pilot facility. To equate the results presented here to gas velocities in full-scale systems, the superficial velocity in the full-scale system must be adjusted for blockage of the MES support structure.

<u>Vertical-Flow ME Systems</u>. Figure 6 shows the carryover rates of the two singlestage vertical-flow ME systems over a range of velocities from about 8.5 ft/s to roughly 16.5 ft/s when loaded with mist at 1.5 gpm/ft². With all the vertical-flow ME systems simulated, 0.0001 gpm/ft² was considered to be the lower measurement limit for the pilot unit due to the small liquid volumes collected and the amount of condensation occurring in the test facility. Points shown on the 0.0001 gpm/ft² axis are considered to signify conditions that were tested for which there was no measurable carryover. The Koch single-stage MES appeared to have less carryover than the Munters single-stage MES for velocities below approximately 14.5 ft/s for a mist loading of 1.5 gpm/ft². Above 14.5 ft/s, the Munters single-stage system performed better.

Figure 7 gives the carryover results for the multiple-stage vertical-flow ME systems with a mist loading of 1.5 gpm/ft². The Munters two-stage MES had no measurable carryover over the range of conditions tested, even at higher mist loadings. The ABB three-stage MES appeared to have the next highest performance with no measurable carryover below roughly 15 ft/s; however, the ABB three-stage MES results may be low for reasons discussed below. The Koch two-stage MES also had little carryover below approximately 15.7 ft/s, but the carryover rate increased much more rapidly than for the ABB three-stage MES at velocities higher than 15 ft/s. The ABB two-stage MES with the second stage in the horizontal position had no measurable carryover at velocities below approximately 12.8 ft/s, and slightly higher carryover than the Koch two-stage MES above that. The ABB two-stage MES had essentially the same performance when the second stage was tilted at 2.5° as when flat. The B&W MES design had measurable carryover at all conditions tested which was significantly above that for the other MES designs tested. Velocity traverses above the ME stages indicated that some maldistribution of gas occurred during the tests with the B&W MES. This may have been due to the lack of a gas-straightening section on the chevron bledes at the ME exit. This caused some of the carry-up exiting the first ME stage to impinge on one 3-ft side of the vertical test section. The impingement of droplets on the 3-ft side of the tower removed carry-up which would otherwise have reached the second ME and is not believed to have increased the overall carryover of the system.

For the ABB three-stage MES, the gas flow exiting the angled test section made a vertical turn into the disengagement zone due to the modular construction and size constraints of the pilot facility (see Figure 4). The turn caused some of the droplets to impinge on the vertical wall of the test facility. If the 45° angled test section had extended through the disengagement zone, some of the droplets impinging on the wall may have been collected and measured as carryover. It was not possible to quantitatively estimate the potential increase in the measured carryover values.

<u>Horizontal-Flow MES</u>. Table 2 shows the carryover rates measured for the Munters two-stage horizontal-flow MES. The good performance of the Munters horizontal-flow MES is suspected to be due to good drainage down the vertically oriented blades which prevented re-entrainment. Conditions with lower velocities and loadings than those shown in Table 2 produced no measurable carryover. The measurement limit when testing in the horizontal-flow configuration is 0.00001 gpm/ft²; this is loter than for the vertical-flow configuration due to the lack of ductwork prior to the carryover collection point which prevents condensation from becoming a significant factor.

It is important to remember that, in full-scale FGD systems, washing of the MES generally only occurs on an intermittent basis on a portion of one ME face. For example, a wash system may wash 15% to 30% of one ME face for 1 to 5 minutes every 1 to 4 hours. Instantaneous carryover due to washing could be high for the MES section being washed. However, the instantaneous carryover based on the entire MES cross-sectional area could be 15% to 30% of the carryover rate of the section being washed, and the time-averaged carryover due to washing could be 10 to 100 times less due to the intermittent nature of the wash.

The MES designs were tested over a range of wash loadings and gas velocities; the ME faces that were washed were intended to simulate operation of the particular designs in full-scale FGD systems (combinations of first-, second-, and third-stage wash tests on the upstream and downstream faces were conducted, depending on industry practice). Because of the complexity of the wash test results and the limited space available in this paper, only general results and conclusions are presented. In general, MES designs which had lower carryover rates during the carryover tests (no washing) also had less additional carryover during washing.

Single-stage MES designs (both vertical and horizontal gas flow) are particularly sensitive to the wash rate used on the upstream side of the ME. When there is only one stage, this stage has to prevent carryover from washing in addition to all of the mist loading to the MES. During washing of single-stage systems, carryover was observed to increase by a factor of 10 or more, particularly at gas velocities in excess of 13 ft/sec.

Washing the downstream side of a single-stage MES design or the downstream side of the last stage in a multiple-stage MES design can result in high carryover rates. With this type of wash, carryover rates were observed to increase by 2 to 3 orders of magnitude, even at gas velocities below what would be typically found during full-load operation. During one set of tests, about 10% of the wash water was entrained in the gas and ended up as carryover; this can amount to a significant amount of liquid even at relatively low wash rates and with intermittent washing. Wash water generally does not have a significant suspended solids content which could lead to duct buildup. However, carryover of relatively large volumes of water can lead to other problems such as stack rainout of an acidic liquid, deterioration of stack linings not designed for wet operation, and a significant increase in reheat costs among others. These are just a few examples of the problems that could occur depending on the specific equipment and operating conditions at each site.

Carryover due to ME washing of two- and three-stage MES designs was found to be affected most by the wash rate on the upstream side of the last ME stage. Carryover from washing the top or bottom of the first stage was generally an order of magnitude less or below detection limits. Most of the multiple-stage designs could be washed on the upstream side of the last stage at a rate of about 1.7 gpm/ft² at velocities up to about 12 ft/sec without a significant increase in carryover. This is a fairly high wash rate for the last stage in a multiple-stage design. Most of the vertical gas flow MES designs had problems preventing carryover when the gas velocity exceeded about 13 ft/sec; above this velocity, carryover rapidly increased by an order of magnitude or more. This points out the need for good gas distribution in absorber towers.

SUMMARY AND CONCLUSIONS

Nine commercial ME systems were tested in the air-water pilot facility, including two single-stage and six multiple-stage (two and three stages) MES designs for vertical gas flow, and one two-stage, horizontal-flow MES design. To put the test results into perspective, the typical operating conditions of commercial FGD systems need to be considered. The most important conditions include gas velocity through the mist eliminator and the carryover limit. Typical superficial gas velocities in the mist eliminator area are generally about 10 ft/sec for vertical gas flow and 20 ft/sec for horizontal gas flow. However, the results presented here are for actual velocity through the mist eliminator in the air-water pilot facility. To equate the results presented to gas velocities in full-scale systems, the superficial velocity in the full-scale system has to be adjusted for the MES support structure. After an average support structure blockage area is taken into account, the typical average mist eliminator operating velocities are about 12.5 ft/sec and 25 ft/sec for vertical and horizontal gas flow, respectively.

Carryover is the main concern in evaluating mist eliminator performance since the carryover limit is important in preventing problems with particulate emissions or the buildup of slurry or solids in downstream ductwork. As discussed earlier, this is a site-specific value which will depend on a number of factors. For this discussion, assume that carryover limits are represented by the values that were calculated earlier to cause particulate emissions problems-0.0004 gpm/ft² and 0.0009 gpm/ft² for vertical and horizontal gas flow, respectively.

All but the two B&W MES designs that were simulated met these limits at typical mist eliminator design operating velocities, assuming a mist loading of 1.5 gpm/ft^2 . It should again be noted that B&W no longer offers this design; they produce competitive bids based on customer specifications.

Gas velocities have been observed to deviate by well over 50% in full-scale FGD systems as a result of poor distribution of the flue gas between multiple towers in an FGD system and/or maldistribution of flue gas within an individual tower. Considering that carryover increases dramatically with increasing gas velocity (up to an order of magnitude with 1-2 ft/sec velocity increases), it is important to evaluate the potential effect of higher gas velocities.

Gas maldistribution of up to about 20% would not be an unreasonable expectation in full-scale FGD systems. This would increase the highest gas velocity treated by a mist eliminator to around 15 ft/sec (about 30 ft/sec for horizontal gas flow). If the high gas velocity occurred over about 20% of the mist eliminator area, a carry-over rate exceeding 0.002 gpm/ft² (0.0045 gpm/ft² for horizontal gas flow) for the high gas flow area would cause problems even if the remainder of the mist eliminator did not have any carryover. The MES test results indicate that the single-stage MES designs as well as the B&W MES designs would clearly have problems meeting the carryover limit specified earlier, and the performance of the ABB two-stage design would be marginal.

Similar considerations also need to be taken into account with respect to carryover caused by washing the mist eliminators. However, it is important to remember that mist eliminators are generally only washed a small percentage of the time. There-fore, the time-averaged carryover rate needs to be calculated and evaluated, assuming that the instantaneous carryover rates which occur intermittently will not pose any problems. It is also important to consider which ME face(s) is being washed and the wash intensity.

Future work planned as part of the EPRI MES program includes testing a "dirty" MES, testing optimized MES designs, updating the "FGD Mist Eliminator System Troubleshooting Manual," and developing a mist eliminator design handbook. The "dirty" MES that will be tested will only have a light coating of scale, not excessive scaling and pluggage. All of the testing to date has been with clean ME's, and the effect of cleanliness needs to be evaluated. Based on the MES simulations already performed, future work will also involve trying to identify and test the optimum MES design (e.g., number of stages, blade and stage spacing, peaked or flat stage orientation, etc.) in the pilot facility and in a full-scale FGD system. Based on all of these results, the existing MES troubleshooting manual will be updated, and a handbook to assist utilities in designing ME systems will be developed.

ACKNOWLEDGEMENTS

The pilot test facility was designed by NELS Consulting (St. Catharines, Ontario, Canada) with input from Radian and EPRI. NELS provided the materials and labor for the initial construction of the test facility free of charge. Special thanks are extended to NELS for the time, effort, and ingenuity put into the design, construction, and operation of the test facility.

We would also like to thank the members of the Mist Eliminator Advisory Committee for their comments and suggestions on the design of the test facility and on the test plan for the program. The chairman of the committee is N. N. Dharmarajan (Central and South West Services), and the committee members are: Rui Afonso (New England Public Service Company), Bill Horrocks (Penn Power Company), Jeff Jernberg (Hoosier Energy), George Munson (Tennessee Valley Authority), Jim Russell (Houston Lighting and Power), John Smigelski (New York State Electric and Gas), Steve Wolsiffer (Indianapolis Power and Light), Bob Wright (Associated Electric Cooperative, Inc.), and Kent Zammit (Los Angeles Department of Water and Power).

Table 1

PILOT FACILITY TEST CAPABILITIES

Operating Conditions	Vertical <u>Test Section</u>	Horizontal <u>Test Section</u>
Superficial Gas Velocity, ft/sec	4 to 20 ¹	4 to 30 ¹
Mist Loading, gpm/ft ²	0 to 5	0 to 6
Mist Eliminator Wash Intensity, gpm/ft ²	0 to 5	0 to 6
Mist Eliminator Stages	1 to 3	1 to 2
Disengagement Zone, ft	0 to 4	NA ²

¹The actual velocity achievable depends on the ME pressure drop. ²NA = not applicable

Table 2

HORIZONTAL-FLOW MES CARRYOVER RESULTS FOR MUNTERS TWO-STAGE MES

Loading gpm/ft ²) 5.2 3.0	Velocity <u>(ft/s)</u>	Carryover <u>(qpm/ft²)</u>		
5.2	28.4	0.00020		
3.0	28.3	0.00002		
3.1	27.8	0.00003		



Figure 1. Layout of Air-Water Pilot Mist Eliminator Test Facility



Figure 2. Blade and Stage Spacings for Vertical Gas Flow MES Configurations Tested



Figure 3. Detailed View of the Peaked MES Designs Tested (Munters Two-Stage MES and ABB Three-Stage MES)



Figure 4. Pilot Facility Design Used to Test the ABB Three-Stage MES



Figure 5. Munters Two-Stage Horizontal-Flow MES

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Figure 6. Carryover Results at 1.5 gpm/ft^2 Mist Loading for the Single-Stage, Vertical-Flow ME Systems



Figure 7. Carryover Results at 1.5 gpm/ft^2 Mist Loading for the Multiple-Stage, Vertical-Flow ME Systems

CEMS VENDOR AND UTILITY SURVEY DATABASES

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ABSTRACT

Regulations require most fossil fuel-fired power plants to monitor stack gases continuously for SO_2 , NO_X , and opacity. Electric utilities have installed and are operating a broad range of Continuous Emission Monitoring Systems (CEMS). The Clean Air Act Amendments of 1990 have placed even greater emphasis on electric utility industry's need to select accurate and dependable CEMS to meet the requirements of environmental regulations.

One of EPRI's current research programs is designed to aid members in obtaining up-to-date information concerning CEMS. Two separate databases are being developed. The utility database contains historical data obtained from coalfired electric utilities and will reflect the experience of the industry with specific CEMS. The vendor database contains CEMS specifications and costs from selected vendors and will summarize the monitoring equipment commercially_ available. Approximately 372 coal-fired plants were selected for the study. The CEMS vendor survey included fifteen pollutant and opacity equipment vendors and seven velocity measurement equipment vendors.

This paper will discuss each database's organization and will present summaries of utility and vendor experience, availability, failure ranked by frequency, maintenance requirements, etc. of the various CEMS. •

CEMS VENDOR AND UTILITY SURVEY DATABASES

BACKGROUND

Regulations require most fossil fuel-fired power plants to monitor stack gases continuously for SO_2 , NO_x , and opacity. To meet this need, electric utilities have installed and are operating a broad range of Continuous Emissions Monitoring systems (CEMS). The Clean Air Act Amendments of 1990 have placed an even greater emphasis on the electric utility industry's need to select accurate and dependable CEMS to meet regulatory requirements.

One of EPRI's current research programs is designed to aid members in obtaining up-to-date information concerning CEMS. Surveys were conducted to construct two databases to assist member utilities in the selection of CEMS. The utility database contains historical data obtained from coal-fired electric utilities and will reflect the experience of the industry with specific CEMS. The vendor database contains CEMS equipment descriptions and costs from selected CEMS vendors and will summarize the monitoring equipment commercially available.

EPRI has contracted Engineering-Science (ES) to assist in the preparation of the survey questionnaires, to conduct the survey, and to compile the survey data into databases. EPRI selected 372 coal-fired utility plants from across the continental United States for the study. EPRI member and non-member utilities with at least 100 MW generating capacity were included in the initial utility survey. A total of 254 EPRI member and 118 non-member plants were sent survey questionnaires and instructions. By September 17, 1991, 158 EPRI member and 40 non-member plants had responded to the survey.

The CEMS vendor survey included 15 pollutant and opacity equipment vendors and 7 velocity equipment vendors. The pollutant and opacity equipment vendors were selected based on their reputation in the industry and EPRI's familiarity with each vendor. The velocity vendor survey was sent to those who offered velocity equipment. A total of 12 pollutant and opacity and 5 velocity equipment vendors responded to the survey by September 17, 1991. Two additional equipment vendors

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returned questionnaires; however, they were completed in a manner not compatible with the questionnaire.

Project progress is shown in Table 1, and future plans for the project include those items noted in Table 2. The updates to the initial utility database will be conducted to keep current with the CEMS purchased during the two years following the initial survey. This will allow member utilities to have timely information on the quality of the new CEMS on the market from users in their industry. A one-time database summary will be provided to all EPRI non-member utilities participating in the survey. EPRI members will continue to receive database updates as they become available.

RESULTS

The initial utility survey data required a great deal of manipulation to allow for the construction of a uniform database. Because of this, the first update to the survey is being used to quality control the initial utility survey. Quality control is currently being performed on the utility data received from the October update surveys and will not be completed until after December 5, 1991. The vendor database, however, is available to EPRI members in dBase dbf file format on IBM compatible floppy disks and in ASCII semicolon delineated format on EPRINET. The utility database should be available for EPRI members by January, 1992, utilizing the same formats. Contact EPRI for the latest information on availability of the databases.

Vendor Results

The vendor survey results, based on 70 entries, are summarized in Tables 3 through 5. An example summary report for SO_2 is displayed in Table 6. A description of the vendor database is available for review in Table 7. Since survey responses were not uniform, considerable editing was necessary to correct this problem, and to present a more understandable database. Many manufacturers used different terms to express the monitor analytical technique or method of sampling. Cost estimates are inconsistent because some vendors included different items in the cost categories, but did not specify cost for those different items. Quality control procedures were followed in compiling the database including error-indicating data entry screens, database editing using dBase sort and browse commands, and a successful quality control review of 2.5% of the records.

Utility Results

Preliminary results from the utility survey based on 778 entries are summarized in Tables 8, 9, 10 and 11. An example SO₂ summary report is found in Table 12. The database description for the utility data is available for review in Table 13. A wide variety of answers were found for most survey questions. Many hours of survey questionnaire editing prior to data entry were necessary. Survey results were not uniform for the same analyzer and were at times confusing. Estimates of staff-hour requirements for preventive and non-preventive maintenance, accuracy assessment, and zero and span checks were incomplete. References to error and accuracy assessments were not understood by many of the respondents. After data entry was completed many more hours of database editing and quality control work were necessary to provide a database with uniform responses. Quality control work included performing a successful quality control review of 2.5 percent of the records.

CONCLUSIONS

Once the databases are available in dBase format the three standard reports, the dBase query and quick summary reports, and the dBase command line functions will be available for generating dBase reports. Tables 6 and 12 are examples of two of the standard dBase reports. The third standard dBase report is a printout of each record formatted to look like the utility survey questionnaire. Quick reports allow the user to use any of the record fields in a formal formatted dBase report.

The command line functions of dBase are more informal and two examples of the several available commands may serve to show how simple and helpful these commands can be. For example, the database can be searched to find all the utilities that use Lear Siegler CEMS equipment or the number of records which show CEMS maintenance performed by a contractor. If data desired in this first example included the utility contact person's name and telephone number, the model number and parameters sampled by the Lear Siegler equipment, the following command could be entered into the dBase command line at the dot prompt while using the utility database:

List First_Name. Last_Name. Telephone, Mon_Model, Parameters for Monitor_MF = "LEAR SIEGLER" to print

The results of such a command line query is shown in Table 14. The number of records which show CEMS maintenance performed by a contractor can be performed by executing the following command while using the utility database:

Count for Maint_Who = "CONTRACTOR"

The dBase response will be a number, 45 in this case, shown after the dot prompt.

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Similar commands can be used for any data field of interest plus the entire database can be sorted based on the contents of one or more data fields. It is important when using these types of commands that the field titles from the record are copied exactly as they appear in the database and the quote enclosed variable be identical to the entries in the database for that specified field or the command will not work. The "record number" listed on the printout can be used to locate the complete record in the database. The data field "Cntrl_No" is also useful for this purpose on the standard reports or if the database has been moved to a spreadsheet.

REFERENCE

1. Managers and Plants databases, Utility Data Institute, Inc., Washington, D.C.

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SIGNIFICANT PROJECT MILESTONES

Description	Date Completed	
Completed questionnaire data entry	8/28/91	
Completed questionnaire quality assurance work	8/30/91	
Submitted draft utility and vendor databases to EPRI for review	8/30/91	
Submitted final vendor database to EPRI for distribution	9/30/91	
Mail first update of utility surveys to utilities	10/1/91	

TABLE 2

FUTURE MILESTONES OF INTEREST

Description	Date Completed
End quality assurance work on utility database	12/5/91
Submit copy of utility database to EPRI for distribution	12/31/91
Mail second update of utility surveys to utilities	10/1/92
End quality assurance work on utility database	1 2/5/92
Mail third update of utility surveys to utilities	10/1/93
End quality assurance work on utility database	12/5/93
Submit final copy of utility database to EPRI for distribution	12/15/93
Complete final report	12/30/93

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TABLE	3
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Number of
MonitorsC012C0215Dust5NH32N04N021N0x19Opacity80211PM1S0225THC3Temperature1Velocity6

VENDOR DATABASE POLLUTANTS SAMPLED

*There is one CEMS that purports to monitor $\rm SO_2, \ NO_X, \ CO, \ CO_2, \ and \ NH_3$

TABLE 4

VENDOR DATABASE TYPES OF SAMPLING

Туре	Number of Monitors		
 Dilution	1		
Dilution Extraction	15		
Extractive	9		
Extractive-Heated	1		
Extractive-Gas Cooler	ī		
Extractive-Probe	26		
In-situ	1		
In-situ (path)	10		
In-situ (point)	4		
In-situ (point, optical)	i		

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VENDOR DATABASE MONITORING TECHNIQUES

Technique	Number of Monitors	
Second Derivative UV	1	
Acoustic	1	
Chemiluminescence	11	
Continuous Gas Purge	1	
Flame Ionization	3	
Fluorescence	2	
Gas Filter Correlation	1	
IR	2	
IR, GFC	1	
NDÍR	13	
NDIR, GFC	3	
NDIR, Paramagnetic	1	
Non-pulsed UV Fluorescence	1	
Paramagnetic	1	
Sonic and Ultrasonic	3	
Thermal Dispersion	1	
UV	4	
UV Fluorescence	2	
UV Visible and Electrochemical	3	
UV. Visible	4	
Visible-Side Scatter	1 '	
Visible Light	4	
Zr0 ₂	6	

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EPRI CEM VENDOR AND UTILITY DATABASES EXAMPLE VENDOR SO2 SUMMARY

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Company	Contact	Telephone	Control	Туре	Monitor	Parameters	Monitor	Manufacturer	Preventive M	aintenance
Name	Name	No.	No.	Sample	Principle	Sampled	Manufacturer	Model No.	(Staff I	Hours)
						· · · · ·			Annual	Daily
Company A	John Doo	(808) 637-5352	V004	Dilution Extraction	UV	SO2,CO2,CO	Company E	150	96	0
Company B	May Jane	(808) 953 1013	V042	Dilution	NDIR	SO2,NOx	Company B	7000	48	0
Company C	Sam Doe	(808) 552-8997	V041	Extractive With Gascooler	NDIR	SO2,NOx	Company C	100	48	1
Company D	Tim Smlth	(808) 204–1064	V040	Extractive Heated	NDIR	SO2,NOx,NH3	Company D	8100	48	0

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STRUCTURE FOR VENDOR DATABASE

Field	Field Name	Туре	Width	Company Name
1	COMPANY	Character	40	Company Name of Firm Supplying CEMS
2	STREET1	Character	30	Street Address
3	STREET2	Character	28	2° Street Address
4	CITY	Character	15	City
5	STATE	Character	2	State
6	ZIPCODE	Character	10	Zipcode
7	PREFIX	Character	2	Mr or Ms Designation of Contact Person
8	FIRST_NAME	Character	10	First Name of Contact Person
9	MI	Character	3	Middle Initial of Contact Person
10	LAST_NAME	Character	15	Last Name of Contact Person
11	TITLE	Character	15	Title of Contact Person
12	TELEPHONE	Character	14	Telephone Number of Contact Person
13	EXT	Character	4	Telephone Extension of Contact Person
14	FAX_NUMBER	Character	14	Fax Number of Contact Person
15	CNTRL_NO	Character	4	Control Number of Record (unique for each record)
16	MONITOR_MF	Character	30	Analyzer Manufacturer Name
17	MON_MODEL	Character	15	Analyzer Model Number
18	SYS_SUPPLY	Character	26	CEM System Supplier Name
19	COND_MANF	Character	26	Gas Conditing System Manufacturer Name
20	COND_MODEL	Character	15	Gas Conditioning System Model Number
21	PARAMETERS	Character	20	Parameter Sampled and Analyzed by CEMS
22	TYPE_SAMPL	Character	25	Location and Technique Used to Obtain Sample
23	MONTR_PRIN	Character	20	Detection Principle Used by Analyzer
24	MON_RANGE	Character	35	Upper and Lower Concentration Range of Analyzer
25	CAL_STD	Character	27	Standard Against Which Analyzer Readings are Compared
26	MAX TEMP F	Character	4	Maximum Temperature Sample Probe Sees in *F.
27	MX DUST LD	Character	6	Minimum Temperature Sample Probe Sees in *F.
28	ANNUAL_PM	Character	4	Annual Preventive Maintenance Requirement in Staff Hours
29	DAILY_PM	Character	• 4	Daily Preventive Maintenance Requirement in Staff Hours
30	Z_SPAN_TCH	Character	30	Technique and Location of Zero-Span Checks
31	Z_SPAN_LMT	Character	20	Control Limits for Zero-Span Checks
32	Z_SPAN_FRQ	Character	10	Frequency of Zero-Span Checks
33	Z_SPAN_HOW	Character	15	Automation Status of Zero-Span Checks
34	C_PROBE_SA	Character	8	Cost of Probe and Sampling System
35	C_COND_SYS	Character	8	Cost of Conditioning System

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STRUCTURE FOR VENDOR DATABASE (Continued)

Field	Field Name	Туре	Width	Company Name
36	C_ENCLOSUR	Character	8	Cost of Enclosure Requirements
37	C_MONITOR	Character	8	Cost of Analyzer
38	C_CNTL_RPT	Character	8	Cost of CEMS Control and Data Reporting System
39	PART_CNTRL	Character	30	Particulate Control Device (type and location)
40	MOIST_REMV	Character	30	Moisture Removal Device Type
41	SLINE_SPEC	Character	30	Sample Line Specifications
42	PUMP_SPEC	Character	30	Pump Specifications
43	MOIST_INDR	Character	20	Method of Reporting Moisture in Conditioning System
44	ENCLOS_REQ	Character	30	Enclosure Requirement
45	WARRANTY	Character	40	Summary of Warranty
46	CUST_SERVE	Character	10	Committment to Customer Service (normally in hours)

TABLE 8

UTILITY DATABASE POLLUTANTS SAMPLED

Pollutants	Number of Monitors		
S02	223		
CO	27		
CO2	53		
02	106		
NÕx	123		
Opacity	385		
Velocity	6		
Temperature	3		

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UTILITY DATABASE TYPES OF SAMPLING

Туре	Number of Monitors	
Dilution extraction	27	
Extractive	86	
Extractive with probe	40	
Gas extractive	6	
In-situ	60	
In-situ (electrolyte)	5	
In-situ (point)	80	
In-situ (path)	449	
In-sity (probé)	2	
Sonic transducer	1	

TABLE 10

UTILITY DATABASE MONITORING TECHNIQUES

Technique	Number of Monitors	
Second derivative spectroscopy	1	
Second derivative UV	1	
Chemical reactivity	1	
Chemiluminescence	26	
Double pass optical	1	
Electro-chemical cell	4	
Electrolyte sensor	5	
Emf electrode	3	
Emf electrode, UV	1	
Flourescence	3	
FTIR	1	
IR	33	
IR, GFC	2	
K ₂ SO ₄ cell	1	
Mīcrófuel cell	1	
NDIR	20	
NDUV	7	
Paramagnetic	5	
Pitot tube	2	
Pulse light	2	
Pulsed fluorescence	2	
Transmissometry	369	
UV	157	
UV, second derivative spectroscopy	7	
UV, Electro-chemical cell	2	
UV, IR	12	
UV, NDIR	3	
White light, IR	5	
Zr0 ₂	65	

UTILITY DATABASE MONITOR BRANDS

Monitor Manufacturer	Monitor Model	Number of Monitors	
ACS Fuji	3300	11	
Ametek/Thermox	FCA	2	
Ametek/Thermox	III	8	
Ametek/Thermox	WDG	3	
Ametek/Thermox	WDG III	5	
Ametek/Thermox	WDG INS	1	
Beckman	951 E	1	
Beckman/Rosemount	951 A	1	
Columbia Scientific	1600	2	
Columbia Scientific	SA700	3	
Combustion Engineering	501	1	
Contraves Goerz	100	5	
Contraves Goerz	100 GEM	2	
Contraves Goerz	400	20	
Contraves Goerz	400-0010	1	
Contraves Goerz	400-0013	2	
Contraves Goerz	500	4	
Contraves Goerz	701,700	1	
Contraves Goerz	GEM 1	3	
Contraves Goerz	GEM 100	1	
Contraves Goerz	GEM 400	1	
Contraves Goerz	TR 4034	1	
Datatest Corp.	90 A	1	
Datatest Corp.	900 A	2	
Datatest Corp.	900 RM	4	
Dupont	400	2	
Dupont	460	11	
Dupont	460/1	1	
Dupont	463	10	
Durag	280, 281	1	
Durag	281	2	
Durag	DR 280 AV	2	
Durag	DR 281 AV	1	
EDC	1000 A	1	
EDC	2841	24	
EDC	DIGA 1100	2	
EDC	DIGA 1200	2	
EDC	DIGA 1400	3	
EDC	DIGA Series	2	
EDC	NA	1	
TABLE 11 (Continued)

UTILITY DATABASE MONITOR BRANDS

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Monitor Manufacturer	Monitor Model	Number of Monitors	
Erwin Sic Company	RM 41	2	
Hartmann-Braun	URAS-2T	2	
Horbia	PIR 2000	4	
KVB	531	2	
KVB	NA	6	
Land Combustion, Inc.	7000	3	
Land Combustion, Inc.	9000	2	
Lear Siegler	4200	4	
Lear Siegler	8100	2	
Lear Siegler	CM 50	37	
Lear Siegler	CM 60	8	
Lear Siegler	CM 70	6	
Lear Siegler	EX 4700	2	
Lear Siegler	RM 41	204	
Lear Siegler	RM 4200	11	
Lear Siegler	SM 800	5	
Lear Siegler	SM 810	72	
Lear Siegler	SM 8100	16	
Lear Siegler	SM 812	1	
Lear Siegler/Dynatron	1100	3	
Lear Siegler/Dynatron	1100 M	42	
Lear Siegler/Dynatron	301	1	
Lear Siegler/Dynatron	401	2	
Meloy Labs	SA700	5	
Monitor Labs	0X 01 0	1	
Monitor Labs	8830	1	
Monitor Labs	8840	2	
Monitor Labs	8850	1	
Monitor Labs	8850 S	1	
Rosemount	260	1	
Rosemount	5100	6	
Sampling Technology, Inc.	NA	1	
Siemens	Oxymat 5E	5	
Thermo Electron	10 A/R	22	
Thermo Electron	100	2	
Thermo Electron	14 B/E	1	
Thermo Electron	200	10	
Thermo Electron	40	5	

TABLE 11 (Continued)

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UTILITY DATABASE MONITOR BRANDS

Monitor Manufacturer	Monitor Model	Number of Monitors
Thermo Electron	400	14
Thermo Electron	400/23205-209	1
Thermo Electron	43	1 .
Thermo Electron	500	2
Thermo Electron	701	1
Thermo Electron	703 D	1
Thermo Electron	DIGA 1400	1
Thermo Environmental	14 B/E	1
Thermo Environmental	200	2
Thermo Environmental	400	15
Thermo Environmental	400, 500	5
Thermo Environmental	400, 700	1
Thermo Environmental	500	2
Thermo Environmental	DIGA 1300	5
Thermo Environmental	EDC 1400	2
Thermox	NA	1
United Sciences, Inc.	500 C	4
United Sciences, Inc.	Digital 100	3
United Sciences, Inc.	Ultra Flow 100	1
Western Research	720 AT	1
Western Research	721 A	15
Western Research	72'1 AT	9
Western Research	721 ATZ	4
Western Research	722 A	2
Westinghouse/Rosemount	1500	1
Westinghouse/Rosemount	260	2
Westinghouse/Rosemount	EC960	7
Westinghouse/Rosemount	Hagen #218	1
Yokogawa	Land O ₂ Analyzer	2

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EPRI CEM VENDOR AND UTILITY DATABASES EXAMPLE UTILITY SO2 SUMMARY

Company	Contact	Telephone	Control	Туре	Monitor	Parameters	Monitor	Manufacturer	Start Up	CEM	Vendor
Name	Name	No.	No.	Sample	Principle	Sampled	Manufacturer	Model No.	Rating	Rating	Rating
									(10 =)	Good, 1	= Poor)
Company A	Mary Smith	(808) 534-2363	U747	In Situ	NDIR	SO2,CO2,CO	Company X	210	5	7	7
Company B	John Doe	(808) 262-8020	U328	In Situ	NDIR	SO2,NOx	Company Y	160	7	3	5
Company C	John Smith	(808) 563-1711	U301	In Situ(Path)	IR	SO2,NOx	Company W	100	4	7	8
Company D	Sam Doe	(808) 459-6181	U489	In Situ(Path)	IR	SO2,NOx,NH3	Company Z	600	8	6	5

STRUCTURE FOR UTILITY DATABASE

Field	Field Name	Туре	Width	Company Name			
1	COMPANY	Character	40	Company Name			
2	PLANT	Character	40	Plant Name			
3	STREET1	Character	35	Street Address of Contact Person			
4	STREET2	Character	35	2° Street Address of Contact Person			
5	CITY	Character	30	City of Contact Person			
6	STATE	Character	2	State of Contact Person			
7	ZIPCODE	Character	10	Zipcode of Contact Person			
8	PREFIX	Character	2	Mr or Ms Designation of Contact Person			
9	FIRST_NAME	Character	10	First Name of Contact Person			
10	MI	Character	3	Middle Initial of Contact Person			
11	LAST_NAME	Character	20	Last Name of Contact Person			
12	TITLE	Character	15	Title of Contact Person			
13	TELEPHONE	Character	14	Telephone Number of Contact Person			
14	EXT	Character	5	Telephone Extension of Contact Person			
15	FAX_NUMBER	Character	14	Fax Number of Contact Person			
16	CNTRL_NO	Character	5	Control Number of Record (unique for each record)			
17	UNIT_NO	Character	20	Plant Boiler Number			
18	MONITOR_MF	Character	30	Analyzer Manufacturer Name			
19	MON_MODEL	Character	15	Analyzer Model Number			
20	SYS_SUPPLY	Character	30	CEM System Supplier Name			
21	COND_MODEL	Character	30	Gas Condition System Supplier			
22	PARAMETERS	Character	20	Parameters Sampled and Analyzed by CEMS			
23	INSER_DATE	Character	8	CEMS In-Service Date			
24	TYPE_SAMPL	Character	25	Location and Technique Used to Obtain Sample			
25	MONTR_PRIN	Character	18	Detection Principle Used by Analyzer			
26	LOCATION	Character	27	Location of Sampling Probe			
27	MAX_TEMP_F	Character	4	Maximum Temperature Sampling Probe sees in *F.			
28	MIN_TEMP_F	Character	4	Minimum Temperature Sampling Probe sees in *F.			
29	SATURATION	Character	3	Sampling Location's Status on Saturation			
30	REHEAT USE	Character	3	Status of Reheat Use			
31	UP OR DOWN	Character	4	Status of Reheat Downstream of Probe			
32	BOILER HRS	Character	4	12-Month Total of Boiler Hours of Operation			
33	CEM HRS	Character	4	12-Month Total of CEM Hours of Availability			
34	ANNUAL_PM	Character	4	Annual Preventive Maintenance Requirement in Staff Hrs			

STRUCTURE FOR UTILITY DATABASE (Continued)

Field	Field Name	Туре	Width	Company Name
35	ANNUAL_NPM	Character	4	Annual Non-Preventive Maintenance
26	MATNT UUO	Character	15	Status of Supplion of CEMS Maintonanco
20	DATE C DDD	Character	12	Pating of Start Up Problems (1 many 10 four)
3/	RATE_S_PRO	Character	2	New Ausilability of CCM Due to Deily
38	DAT_CAL_HK	Unaracter	3	Calibration Needs in Hrs
39	QA_AUDT_YR	Character	4	Times/Year QA Audits are Performed
40	QA_HRS_PER	Character	2	Non-Availability of CEM Due to QA Audit Average Time in Hrs/Time
41	DRIFT_P_YR	Character	4	Times/Year Out-of-Control Due to Drift Specifictions
42	DRIFT_HR_P	Character		Non-Availability of CEM Due to Drift Specifications Average Time in Hrs/Time
43	HAND_SYS_P	Character	4	Times/Year Sample Handling System Caused Non-Availability
44	HAND_HRS_P	Character	3	Non-Availability of CEM Due to Sample Handling System Average Time in Hrs/Time
45	MON_PER_YR	Character	4	Times/Year Analyzer Caused Non-Availability
46	MON_HRS_P	Character	3	Non-Availability of CEM Due to Analyzer Average Time in Hrs/Time
47	CNTRL_P_YR	Character	4	Times/Year Control and Data Reporting System Caused Non-Availability
48	CNTRL_HR_P	Character	3	Non-Availability of CEM Due to Control and Data Reporting System in-House/Time Average Time
49	PST DATE	Character	8	Date of Most Recent PST Certification
50	CERTS P YR	Character	15	Times/Year of Performance Certifications
51	Z_SPAN_TCH	Character	30	Technique and Location of Zero-Span Check by Parameter Sampled
52	Z_SPAN_LMT	Character	20	Control Limits for Zero-Span Check by Parameter Sampled
53	Z_SPAN_FRQ	Character	10	Frequency of Zero-Span Check by Parameter Sampled
54	Z SPAN HOW	Character	15	Automation Status of Zero-Span Checks
55	WHY CEM IN	Character	20	Reason for CEMS Installation
56	ASSESS TYP	Character	20	Type of Gas Accuracy Assessment Used
57	WHY_ASSESS	Character	20	Reason Gas Accuracy Assessments Conducted

STRUCTURE FOR UTILITY DATABASE (Continued)

Field	Field Name	Туре	Width	Company Name			
58	WHO_ASSESS	Character	15	Who Accomplishes Gas Accuracy Assessments			
5 9	CAL_ERROR	Character	7	Calibration Error Percentage			
6 0	REL ACCURY	Character	7	Relative Accuracy Percentage			
61	G_ASSESS_D	Character	8	Last Date of Gas Accuracy Assessment			
62	O_ASSESS_D	Character	8	Last Date of Opacity Precision Assessment			
63	ASSESS_LOW	Character	7	Opacity Low Range Precision Assessment			
64	ASSESS_MID	Character	7	Opacity Mid Range Precision Assessment			
65	ASSESS_HI	Character	7	Opacity High Range Precision Assessment			
66	CEMS_CNTRL	Character	15	Control Equipment for CEMS			
67	REP_SYS_CN	Character	15	Control Equipment for Data Reporting System			
68	MT_FRE_PRB	Character	25	Most Frequent Problem with CEMS			
69	MO_FRE_PRB	Character	25	More Frequent Problem with CEMS			
70	FRE_PROBLM	Character	25	Frequent Problem with CEMS			
71	LT_FRE_PRB	Character	25	Less Frequent Problem with CEMS			
72	RATE_CEM	Character	2	Overall Rating of CEMS (1 poor, 10 recommend)			
73	RATE_VENDR	Character	2	Overall Rating of CEMS Vendor (1 poor, 10 recommend)			

TABLE 14

EXAMPLE dBASE LIST COMMAND

Record#	First_Name	Last_Name	Telephone	Mon_Model	Parameters	
20	David	Smith	(808) 462-9251	SM 810	NOx	
51	Ken	Jones	(808) 249-8377	EX 4700	CO ₂	
53	Linda	Doe	(808) 330-7633	EX 4700	C0 ₂ ,C0	
63	Scott	Smith	(808) 393-1408	CM 50	NOX	

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Determination of Continuous Emissions Monitoring Requirements at Electric Energy Inc.

6A-115

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> B. Parker Electric Energy, Inc. Joppa Steam Electric Station Box 165 Joppa, Illinois 62953

ABSTRACT

More stringent air pollution emissions monitoring requirements have resulted from enactment of the U.S. Clean Air Act Amendments of 1990. Utility companies will be required to retrofit Continuous Emissions Monitoring Systems (CEMS) to steam generating units that are affected units under Title IV of the Act. Draft regulations governing the requirements and operation of CEMS have been prepared by the EPA. Final CEMS regulations are due to be promulgated by May 1992.

This paper discusses these proposed regulations and a range of options with which the Electric Energy, Inc. Joppa Power Station may respond to the requirements. A general survey of CEMS instrumentation, system configurations, and related cost factors applicable to the Joppa Station are also presented.

INTRODUCTION

The U.S. government believes that the SO₂ allowance trading component of the Acid Rain Program (Clean Air Act Amendments of 1990 (CAAA) - Title IV) is an innovative, market-based approach to compliance with new SO₂ emission limitations set by the Act. In order to allow this system to work, the government further believes that complete and accurate emissions data are the keys to implementation of and confidence in the approach. Reliable Continuous Emissions Monitoring System (CEMS) data is a critical component to the smoothly operating market that is envisioned. To this end, EPA has proposed regulations to require that CEMS be installed to monitor SO₂ emission concentration, volumetric flow rate, NO_x emission concentration, diluent gas fraction, and opacity at each affected facility. In addition, Section 821 of the Act requires that all affected units in the Acid Rain Program monitor and report CO₂ emissions, although not necessarily by continuous gaseous instrumentation techniques.

The CAAA establishes the requirements for CEMS through section 412 of the Act, "Monitoring, Reporting, and Recordkeeping Requirements". The title defines a CEMS as "...the equipment as required...used to sample, analyze, measure, and provide on a continuous basis a permanent record of emissions and flow...as the Administrator may require." The applicability of this section extends to any source subject to Title IV (Acid Deposition control). Since all six steam generating units at the Electric Energy, Inc. (EEI) Joppa Station have been identified in Section 404 (Phase I) of the Act as affected units, CEMS must be installed, operated, and certified by November 15, 1993 (due to a requirement of the proposed regulations to conduct initial CEMS certification no later than 120 days prior to the above date, the actual installation, operation, and certification deadline is July 15, 1993).

This paper discusses the proposed CEMS requirements that must be met at the Joppa Station and presents a range of options that may be implemented to satisfy the requirements.

PROPOSED REGULATIONS

Regulations that detail specifications and requirements for CEMS are currently in force for new air pollution sources. In general, these existing regulations are not as stringent as those proposed for the Acid Rain Program, but they form the initial basis of the new requirements. Much of the data upon which the new Acid Rain Program CEMS requirements are based were provided through experience with the existing instrumentation and systems used for new source monitoring requirements. The proposed CEMS regulations discussed in this paper were developed for the Federal Office of Management and Budget (OMB) and the Acid Rain Advisory Committee (ARAC). These preliminary draft regulations will be reviewed, modified if necessary, and published by EPA for comment in the Federal Register in the fall of 1991 (perhaps prior to presentation of this paper). After close of the comment period, the proposed regulations will once again be modified, then finalized and promulgated by May of 1992. This process will allow opportunity for significant changes to occur to the currently proposed regulations.

<u>General CEMS_Requirements</u>

Under the proposed rule, the owner or operator of an affected unit (or units) would be required to install a CEMS on each affected unit unless otherwise specified in the regulation. The CEMS is defined as including the following components: (1) an SO₂ pollutant concentration monitor, (2) a NO_x pollutant concentration monitor, (3) a volumetric flow monitor, (4) an opacity monitor, (5) a diluent gas monitor, and (6) a data acquisition and handling system (usually computer-based) for recording and performing calculations with the data.

Measurements of SO₂ concentration must be combined with measurements of volumetric gas flow (exhausting from the unit) to obtain estimates of SO₂ mass emissions per unit time (in lbs/hr), as required by the Act. Flow monitors always measure gas flow rate on an actual or "wet" basis. Some SO₂ pollutant concentration monitors, however, measure SO₂ concentration on a "dry" basis. The measurements used to determine SO₂ emissions in lbs/hr must be on the same moisture basis. Accordingly, units that employ "dry" SO₂ pollutant concentration monitors must correct their gas flow rate measurements for moisture. Under the proposed rule, EPA would allow any moisture determination method, including standard saturation/temperature tables and continuous moisture monitors, provided the corrected flow rate measurements satisfy the performance standards for monitor certification (i.e. hourly averages, relative accuracy/bias requirements, etc.).

Similarly, measurements of NO_x concentration must be combined with the appropriate EPA F or F_c factor and measurements of a diluent gas, either oxygen (O₂) or carbon dioxide (CO₂), exhausting from the unit to obtain the estimates of the NO_x emission rate relative to the heat input of the fuel (in lbs/MMBtu). Accordingly, the proposed rule defines a NO_x CEMS as the combination of a NO_x pollutant concentration monitor and a diluent gas monitor.

Only an opacity monitor is needed for monitoring the obscuration caused by particulate matter in the gas; actual particulate loadings are not required by Title IV of the CAAA.

Units that monitor CO₂ continuously could use a flow monitor to estimate CO₂ emissions in lbs/hr, which are to be aggregated into daily totals for reporting. The proposed rule would require only some units (i.e., units that generate CO₂ emissions by means other than fuel combustion, for example, by wet limestone scrubbers during the flue gas desulfurization process) to continuously monitor CO₂ emissions discharged into the atmosphere. Most units would be allowed to calculate CO₂ mass emissions (in lbs/day) using specified methods and procedures based on the measured carbon content of the fuel and the amount of fuel combusted.

Under the proposed rule, each monitor in the CEMS and the system as a whole must be installed, and its performance verified and certified by the EPA, before it can be used in the Acid Rain Program.

Performance Certification Requirements

The following performance certification tests would be required for continuous emission monitoring systems: (1) calibration error tests for each pollutant concentration monitor and diluent gas monitor; (2) an electronic stability test for the flow monitor; (3) relative accuracy and bias tests for the SO₂ pollutant concentration monitor, the flow monitor, and the NO_x emission monitoring system; (4) a cycle response time test for the SO₂ pollutant concentration monitoring system; and (5) an orientation sensitivity test and an interference test for differential pressure flow monitors only.

No later than January 1, 2000, relative accuracy and bias tests would be added for the combined SO_2 emission monitoring system (pollutant concentration monitor and flow monitor). For continuous opacity monitoring systems, performance certification tests for calibration error, response time, zero drift, and calibration drift would be conducted according to the requirements in 40 CFR 60, Appendix B.

For each CEMS, the proposed rule also requires the development and implementation of a written quality assurance/quality control plan. Daily performance checks of the monitoring equipment, including gas calibration error tests and visual and electronic inspections, would be required by the proposed rule. In addition, test audits and bias tests would be required for the SO_2 pollutant concentration monitor, the flow monitor, and the NO_x emission monitoring system. A three-point calibration error test would also be required quarterly for all pollutant concentration and diluent monitors.

Alternative Monitoring Systems

No alternative monitoring system has been proposed as a preapproved system equivalent to a CEMS on the required criteria of precision, reliability, accessibility, and timeliness.

In order to receive approval to use an alternative monitoring system in lieu of a CEMS or a component of a CEMS (e.g., SO₂ pollutant concentration monitor or flow monitor), the affected unit would be required to submit long-term statistical evidence and other data that demonstrate the proposed alternative would provide information equivalent or superior to a CEMS. Under the proposed rule, EPA would use the performance of certified SO₂ pollutant concentration monitors, flow monitors, and NO₂ emission monitoring systems as benchmarks for approving or rejecting proposals for alternative monitoring systems. The proposed CEMS regulations specify procedures, analyses, and supporting documentation that would be required for demonstrating the equivalency of alternative monitoring systems to CEMS on the required criteria of precision, reliability, accessibility, and timeliness.

Phase I Qualifying Technology

Affected units which apply for and are granted approval to implement the optional compliance method using Phase I qualifying technology (e.g., achieves a 90-

percent reduction in SO₂ emissions) would have to employ additional monitoring. The proposed rule requires that each such unit be equipped with an SO₂ pollutant concentration monitor and a flow monitor for measuring SO₂ emission at the inlet to the control device in addition to the required monitors for measuring SO₂ emissions discharged to the atmosphere. Provisions are included in the proposed rule for demonstrating achievement of the required 90 percent reduction in SO₂ emissions through Phase I qualifying technology, on an annual basis, from 1995 through 1999.

Common Stack

The proposed rule would allow (or perhaps require) EEI to combine SO_2 allowances according to the procedures in 40 CFR Part 73 and install one monitoring system where two or more affected units utilize a common stack.

 NO_x emissions could be determined in the exhaust from a single unit or measured in a common stack. It is not currently clear, however, if NO_x emissions from discrete and separate stacks or flues may be averaged to represent multiple units or a plant wide "bubble".

<u>CEMS Availability</u>

All CEMS would be required to be in continuous operation and to be capable of sampling, analyzing, and recording at least every 15 minutes. All emissions and flow data would be reduced to one-hour averages. Four data points would comprise a valid hour. During calibration or other required quality assurance activity periods, however, two or more data points would be allowed to comprise a valid hour. Failure of the system to acquire the required data points would result in the loss of data for the entire hour. In this event, the utility would be required to use prescribed procedures for calculating emissions for the missing data periods.

The proposed rule contains procedures for compiling "information satisfactory to the Administrator" for substituting data where no valid data have been recorded for the SO_2 pollutant concentration monitor, the flow monitor, or the NO_x (consisting of the NO_x pollutant concentration monitor and the diluent gas monitor).

For the SO_2 and flow monitors, where valid data have not been recorded for either monitor, the missing data procedure would apply to each monitor individually. For the NO₂ CEMS, if either monitor (NO₂ monitor or diluent monitor) is without a valid hour of recorded data, the data for both monitors would be deemed invalid, and substitute data must be provided for both monitors using the prescribed missing data procedures. Such information establishes preapproved information satisfactory to the Administrator. The proposed approach establishes the methods that may be used to "fill in" missing data, following the general principle that the longer the gap in the recorded data and/or the lower the annual monitor availability, the more conservative the value to be substituted. Annual monitor "availability" refers to the number of total hours of valid data capture per year, expressed as a percentage of total unit operating hours. Table 1 summarizes the proposed missing data procedures. Three availability categories are identified by the EPA:

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- A>95%
- 2) 3) 90%<A<95%
- A<90%

For each category, substitution criteria for estimating values for missing data periods are identified on the table.

This information and approach clearly emphasize EPA's intent regarding the quality and reliability that will be required of continuous monitoring systems. Potentially severe economic penalties will result from operating systems that have low availability. As an example, the data presented in Table 2 has been prepared for the Joppa station with CEMS operation at less than 90% availability and with implementation of fuel switching and blending as an SO_2 control option. The six steam generating units at the station exhaust, two each, through a common stack for a total of three active stacks. A CEMS could be installed on the ducting from each unit or in the common stack for two units. The numbers in Table 2 were based on the difference between the SO, emissions that would be measured by an in-service CEMS (boilers firing on 100% low sulfur subbituminous coal) and the substitute SO₂ emission value that would be required if the CEMS were off-line or deemed "out of control" under the proposed regulations. A number of estimated SO_2 allowance values are assumed, as are two different past coal fuel scenarios. As can be observed by inspection of the table, once the CEMS is placed on-line (proposed deadline July 15, 1993) the highest measurement that it records would be used as a substitute value for an out-of-service CEMS (for any period of time) resulting in potentially thousands of dollars of lost value of SO, allowances.

Notification, Recordkeeping, and Reporting

The proposed rule includes requirements for notification, recordkeeping, and reporting for the Acid Rain Program. The requirements include:

- Monitoring plans to be submitted as part of the compliance plan and permit required by CFR 40, Part 72,
- Written notifications of monitor certification tests,
- Daily recording of hourly emissions and flow data and other information.
- Maintaining records of emissions and flow data, other measurements and system maintenance,
- Initial and quarterly reports of quality assurance and quality control tests for the continuous emission monitoring systems,
- Reports of recorded emissions, flow, unit operating status, and monitoring performance data.

The proposed rule would require the owner or operator to electronically report the required information on a quarterly basis as an ASCII flat file via either an IBM-compatible personal computer floppy diskette or a modem.

AVAILABLE CEMS EQUIPMENT

The need for the development of Continuous Emissions Monitoring technology was a direct result of the Clean Air Act and the Code of Federal Regulations.

When Congress passed the clean air act in 1970, there were few, if any, true continuous emissions monitoring systems available. There were a few instrument manufacturers that packaged some laboratory grade instruments, but there were no systems designed to operate on a continuous basis while being located in the utility plant environment. After the clean air act was passed, the EPA and some states began to require CEMS installations which created a market to which many analyzer manufacturers and system integrators responded. Unfortunately, due to a lack of uniform monitoring requirements, when CRF 40, Part 60, Subpart A, Section 60.13, (Monitoring Requirements) was promulgated in 1975, the majority of CEMS installed prior to this date could not comply with this performance standard.

Over the years since 1975, there have been attempts by various manufacturers to revolutionize CEMS technology, but as of this date, the most successful CEMS employ analyzer technology that was designed more than a decade ago. Many of these analyzers have been updated by adding some state-of-the-art electronics, but the basic designs have not changed.

In addition to providing a permanent record of emissions, most sources with a CEMS are also required to report their emissions on a periodic basis to the local and/or state and/or federal air quality organization. To automatically produce the required reports directly from the analyzer outputs, most CEM suppliers also provide (at extra cost) a Data Acquisition System (DAS). Some suppliers have attempted to supply DAS systems with canned software packages which, through menu driven options, allow an operator to make keyboard selections of the calculations to be made, the report format and the frequency of the reports. Unfortunately, there has been no uniformity of reporting requirements by the local districts, the states or even between EPA regions. Therefore, it is common that capital costs for a CEMS also include costing for the DAS computer and printer and substantial computer programmer time for development of the customized software. This will most likely still be the case in responding to the proposed CEMS requirements driven by Title IV of the CAAA.

Gaseous monitoring

Current CEMS technology exists which can accurately and reliably measure the normally permitted gases such as NO_x , SO_2 , O_2 , CO_2 , CO_2 , NH_3 , and Hydrocarbons. A variety of techniques are available for the measurement of these gaseous air pollutant emissions from combustion sources. Among these technologies are: Insitu, Conventional Extractive, and Dilution Extractive monitoring systems. Each of these techniques offers advantages and disadvantages, dependent upon the specific application requirement.

<u>In-Situ.</u> Under the in-situ category, there are two basic types of systems. The two types are single point (Figure 1) and cross stack (Figure 2) systems.

The single point in-situ system with sensing elements inserted into the gas stream produces an electrical output signal proportional to the concentration of the gas being measured. The cross stack system projects a light beam through the sample to be analyzed by a receiver located on the opposite side of the stack. The single point system has less sensitivity than the cross stack system because of the significantly shorter measurement path length. However, the single point system has the ability to be dynamically calibrated with calibration gas which is a definite requirement of the proposed CEMS regulations. There are two analytical methods used by the single point system. The first is an electrocatalytic type analyzer which uses a continuous flow of calibration gas as a reference across a sample cell. The second is a second derivative ultraviolet spectroscopy analyzer that inserts a protected mirror into the gas stream which provides a return path for the ultraviolet light source to measure the absorption caused by the component of interest.

The advantages of in-situ are:

- 1. Standard Design
- 2. Low Purchase Price
- 3. Low Installation Cost
- 4. Low Scheduled Maintenance

The disadvantages of in-situ are:

- 1. Cross stack version would be uncertifiable under proposed regulations
- Single point system would have difficulty passing new "bias" test requirements of the proposed regulations.
- 3. Limited gas measurement capability
- 4. Limited ability to measure low concentrations
- 5. System exposure to hostile environments
- 6. Limited operating temperature
- 7. Some types have high operating costs
- 8. Some are difficult to verify accuracy which makes quarterly audits very expensive
- 9. Single analytical technique, not best for all gases
- 10. At Joppa, equipment would have to be installed in a location that would make maintenance more difficult.

In-Situ gas monitors are not generally recommended for application at Joppa, primarily because of disadvantages 1 and 2.

<u>Conventional Extractive</u>. An extractive CEMS (Figure 3) withdraws an unaltered sample of the flue gas to be processed for analysis at some remote location. This flue gas is protected by maintaining, or, in some cases, increasing the flue gas temperature as it is being transported. It is also necessary to prohibit the flue gas sample from contacting any material that could alter the concentration of the sample until conditioning is complete. When conditioning is complete, only the particulate matter and moisture have been removed from the flue gas leaving all other components unaltered. After conditioning, the gases are provided to a gas manifold which distributes the flue gas to each analyzer.

Conventional extractive systems can be configured to accomplish gas analysis prior to removal of moisture in the "hot-wet" approach. This approach, while generally increasing system costs, would be more consistent with elements of the proposed CEMS regulations that require determination of SO₂ emissions on a wet flue gas basis. Alternatively, if the gas sample is analyzed "dry", a moisture correction factor will be required, complicating the measurement and reporting process.

The conventional extractive system allows the design to include many different analytical techniques within one system in order to offer the best analytical technique for each gas component being analyzed. The typical techniques employed by an extractive system are NDIR, NDUV, flame-ionization, chemiluminescence, paramagnetic, and electrochemical sensing cells.

Some conventional extractive systems elect to use a single analyzer to measure all gaseous components. This approach may reduce overall system costs.

The advantages of conventional extractive systems are:

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- 1. Flexible, usable in most applications
- 2. Accuracy
- 3. Verifiable
- 4. Moderate operating cost

The disadvantages of conventional extractive systems are:

- 1. High capital cost
- 2. High installation cost
- 3. Long runs of expensive, high temperature sample line
- 4. Sample conditioning system maintenance intensive
- 5. Negative pressure system creates leak potential

<u>Dilution Extractive.</u> Under the dilution extractive category, there are two types of systems; (1) a dilution probe system that dilutes the sample within the probe (Figure 4) and (2) a dilution box which dilutes the sample in a box just down stream of the sample probe. The dilution systems are designed to extract a small sample of flue gas and dilute that flue gas with large amounts of clean and dry air. The clean and dry air lowers the moisture dew point to an acceptable level for analysis by an analyzer which has been designed for ambient air monitoring. The dilution ratios can be as high as necessary to dilute the source concentration to ambient air levels. The dilution ratio is controlled by the dilution air pressure and a critical orifice. Dilution ratios as high as 350:1 are common.

The advantages of dilution type systems are:

- 1. No heat traced sample line required
- 2. No sample conditioning required downstream of dilution
- 3. Low maintenance requirements in proper application
- 4. Lower initial cost than conventional extractive
- 5. Positive pressure system minimizes leak potential
- 6. Uses well proven ambient monitoring instrumentation

The disadvantages of dilution type systems are:

- 1. Some parameters may be diluted below analyzer sensitivity range
- 2. Requires high purity air for operation
- 3. Potentially slower response time

Volumetric Flow Monitoring

There are three main types of flow monitors currently being used for the continuous monitoring of flue gas flow: ultrasonic, differential pressure, and

thermal. Although all flow monitors estimate the flue gas flow rate by multiplying the cross-sectional area inside the flue (stack) by the average gas velocity, each type employs a different principle to measure average gas velocity. Ultrasonic flow monitors determine average gas velocity directly by measuring the time it takes for sound bursts to travel between two transceivers, one located downstream of the other. Differential pressure flow monitors determine average gas velocity by measuring the pressure at one or more points in the flue gas stream, and using the established relationship between gas pressure, temperature, molecular weight, and velocity. Thermal flow monitors measure the difference in temperature between a heated and an unheated element in the flue gas stream.

While flow monitoring is a proven technology, the proposed CEMS regulations represent the first major air pollution control regulations to require flow monitors for the continuous monitoring of flue gas flow. Accordingly, utilities in the U.S. have had limited experience in the installation, operation, and maintenance of flow monitors for this particular application. This limited experience has led to some concern regarding the reliability and accuracy of flow monitors, particularly in wet stack environments.

EPA believes, however, that available knowledge is sufficient to support the proposed requirement for flow monitors in Phase I as well as Phase II of the CAAA.

In many cases, single point flow monitoring will not be allowed. For applications at the Joppa plant, ultrasonic flow monitoring would probably be the first choice for well behaved flow locations with relatively flat velocity profiles (e.g., the typical stack test level). For locations that could exhibit gas flow irregularities and maldistribution (e.g. induced draft fan outlet manifold flue), a pitot tube array may be preferable.

Opacity Monitoring

Opacity monitors have been in service for a number of years and, in general, have performed reliably during that time. The opacity monitoring technique acceptable to EPA is a measurement system based upon the principle of transmissometry. Light having specific spectral characteristics is projected from a lamp through the effluent in the stack or duct, and the intensity of the projected light is measured by a sensor. The projected light is attenuated because of absorption and scattered by the particulate matter in the effluent; the percentage of visible light attenuated is defined as the opacity of the emission. Transparent stack emissions that do not attenuate light will have a transmittance of 100 percent or an opacity of zero percent. Opaque stack emissions that attenuate all of the visible light will have a transmittance of zero percent or an opacity of 100 percent.

Several opacity monitors based on this principle are commercially available and would perform well in satisfying Joppa CEMS requirements. One limitation affecting these opacity monitoring systems is that they generally cannot be located downstream of a <u>wet</u> FGD system.

JOPPA SITE OPTIONS

There are a number of CEMS alternatives that are created as a result of the specific requirements and layout of the Joppa plant steam generating units.

These alternatives involve options derived from the general arrangement of plant equipment (e.g. determination of monitoring configurations that best satisfy proposed regulations) and from other factors that could significantly impact design choices (e.g. using the NO_x /diluent system to fine tune boiler operation in addition to providing compliance data).

To address this assortment of requirements and goals, the application scenarios presented in Table 3 have been developed. Additional scenarios exist, but may generally be considered a variation (or combination) of those presented.

Each of the configurations mentioned in the table are briefly discussed below.

<u>Configuration (1) - One CEMS each stack</u>

Configuration (1) represents the minimum CEMS installation. These three systems would be installed, one in each stack at the existing stack test level. New ports would be installed at this level to accommodate the opacity monitor, flow monitor, and gaseous sampling probe (for SO_2 , NO_x , and CO_2 or O_2 samples). Existing ports would still be usable to conduct particulate tests and newly required instrument certification tests (nominally EPA Test Methods 2, 3, 4, 6, and 7). Sample gas via the sample probe and line would be conveyed to instrumentation located at grade. Sample handling and conditioning equipment, gas analyzers, control modules, span gases, etc. would all be housed in a stand alone enclosure near the stack base, in a suitable environmentally acceptable existing structure (e.g. within the base of each stack), or contained in an enclosure placed within an existing structure (many choices are available but final location selection should be made after vendor recommendations). At this instrumentation location, gas samples would be further conditioned (if appropriate) and analyzed. Electronic output from opacity monitors and flow monitors would be transmitted to the same general location (Figure 5 shows a typical schematic of this arrangement).

Analyzer signal output would be stored in a data logger and input to the CEMS data handling and reporting system. The major components of the CEMS data handling and reporting system could be remotely located at the respective control room or at a central CEMS data processing center. At a minimum, it would be desirable to locate strip chart recorders in the appropriate control room to allow operator tracking of important CEMS data items.

Gaseous monitoring would be by the conventional extractive or dilution extractive technique. A stack mounted transmissometer would be used to determine opacity and an ultrasonic system would, most likely, be used to monitor flow. These general approaches to specific monitoring tasks were described previously in this paper, as was the rationale for preferring one system to be used at the Joppa station over another potential system.

Configuration (2) - SO_/flow/opacity in stack, time shared NO_ in ducts

Configuration (2) also contains three basic CEMS with some significant modifications from Configuration (1). For Configuration (2) opacity and flow would still be monitored in the stack at the stack test level (Figure 6). A gas sample would also still be withdrawn from this location to provide SO₂ emissions data for both units exhausting to the stack. NO₄ and diluent gas samples (CO₂ or O₂), however, would be withdrawn from the induced draft (ID) fan outlet manifold of each steam generation unit, just prior to commencement of the common

duct connecting to the stack. In this manner, a discrete sample from each unit may be analyzed for NO_x concentration. This data may then be used not only for compliance determination, but as an operational tool for adjusting and optimizing marginal NO_x emissions from each boiler. A composite sample taken from the stack would not be usable for this latter purpose.

In general, the same amount and description of instrumentation and auxiliary systems as in configuration (1) will be required.

To accomplish the dual purpose NO, monitoring objective with the same amount of instrumentation as that indicated for configuration (1), time sharing of the NO_/diluent monitoring system between the first and second steam generation units would be required. Although not expressly prohibited by the proposed regulations, various new requirements for instrument certification may essentially eliminate "time sharing". If this proves to be the case, Configuration (3) could be applied.

<u>Configuration (3) - S0,/flow/opacity in stack, dedicated N0, in ducts</u>

This configuration is the same as (2) except that an additional $NO_x/diluent$ system could be installed in each CEMS. This arrangement would avoid limitations presented by a time-share system as discussed above.

Configuration (4) - One CEMS each stack with one portable backup CEMS

Configuration (4) would be identical to Configuration (1) or Configuration (3) except with the addition of a backup CEMS. The purpose of this backup system is to increase overall CEMS reporting reliability and availability. Because of the high potential economic impacts of operating systems with low availability, redundant systems may be highly desirable.

One approach would be to operate a complete backup CEMS in hot stand-by mode. This system could be fully portable and designed for quick relocation and hookup (within 1 to 2 hours) to any of the three in-service systems that were experiencing operational difficulties or were deemed to be out of control under the proposed regulations.

It would be necessary to certify, maintain, and quality assure this system in the same manner as the three dedicated systems.

Configuration (5) - 6 CEMS in ducts or stacks

This configuration is presented to further increase system reliability and availability above that allowed by previous configurations. Six CEMS would be installed in the I.D. fan outlet ducting and designed so that SO₂ and NO_x emissions requirements would be met on an individual unit basis. Reliability would be improved by configuring the systems for time-sharing on sister units in case of a CEMS failure. Penalties for low availability would also be minimized due to the fact that an instrument system outage in this configuration would only require high substitute values to be recorded for one unit's emissions instead of two.

If time-sharing or other limitations discourage or prohibit duct installation of the 6 CEMS units, an alternative could be employed. This would be the

installation of two CEMS in each stack for a total of six CEMS for the plant. In this manner, each on-line stack CEMS would be continuously backed up by another complete system held in the hot standby mode.

CEMS Costs

Estimates have been made of relative cost factors associated with each of these CEMS configurations. These factors are presented to allow relative economic, technical, and regulatory impact comparisons. Costs related to chimney and/or test platform modifications to accommodate CEMS and related activities are <u>not</u> included.

Relative cost factors include the following CEMS specific cost elements:

- Equipment costs
- Installation costs
- CEMS Certification
- Training
- Quality Assurance Plan
- A&E Services

Table 4 presents the data.

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- 4. <u>Continuous Emissions Monitoring</u>. R-C EST Report, December 1989.

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5. U.S. Environmental Protection Agency. 1979. <u>Continuous Air Pollution</u> <u>Source Monitoring Systems Handbook</u>. EPA 625/6-79-005. Cincinnati, OH



Figure 1. Single Point In-Situ System



Figure 2. Cross Stack In-Situ System

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Figure 3. Conventional Extractive System



Figure 4. Dilution Extractive System

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Figure 5. Configuration (1) - Three Dedicated CEMS Installed One in Each Stack



Figure 6. Configuration (2) - CEMS Compliance Monitoring With Unit Specific NO_x Emissions Data Option

			TABL	.E 1		
SUMMARY	0F	CEMS	SUBST	ITUTION	CRITE	RIA FOR
ESTIMATI	NG	VALUE	S FOR	MISSING	DATA	PERIODS

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Annual availability (%) of monitor or system	Number of hours missing (N)	Value substituted for each missing hour		
Greater than or equal to 95%	N ≤ 24 hours	Average of N hours recorded before missing data period and N hours recorded after missing data period		
	N > 24 hours	Maximum hourly value recorded in previous 30 days of service		
Less than 95% but greater than or equal to 90%	N ≤ 3 hours	Average of the hour recorded before missing data period and the hour recorded after missing data period		
	$N > 3$ and ≤ 24 hours	Maximum hourly value recorded in previous 30 days of service		
	N > 24 hours	Maximum hourly value recorded from previous 365 days of service		
Less than 90%	N > 0 hours	Maximum recorded hourly value for the monitor since initial service		

TABLE 2 LOST VALUE OF SO2 ALLOWANCES FOR <u>1-HOUR</u> OF CEMS DOWNTIME

(for CEMS with <90% reliability and full load boiler operation with 100% Black Thunder Coal)

	Estimated Worth of SO ₂ Allowance (\$)
	200 400 600 800
FUEL AND CEMS SCENARIO	Lost Value of Allowances (\$)
50% bituminous/50% subbituminous burned at any time since 7/15/93	
Shared CEMS Between two_units	420 840 1,260 1,680
100% bituminous burned at any time since 7/15/93	
Shared CEMS between two units	780 1,560 2,340 3,120

Configuration Description	No. of CEMS	Comments			
(1) One CEMS for each stack, sample probes and sensors located at the stack test level	3	Combine units' allowances acceptable under proposed regulations			
(2) SO_2 /flow/opacity probes and sensors located in each stack at the stack test level. NO_x /Diluent probes located at each steam generation unit outlet	3	NO _x /Diluent time shared and used for diagnostics and to fine tune boiler operation			
(3) Same as (2) above except with a NO _x /Diluent system dedicated to each steam generation unit	3 (+ 3 extra NO _x /Diluent systems)	Time sharing of compliance monitors may seriously challenge proposed EPA requirements demanding dedicated monitors. Dedicated monitors may be required.			
(4) Same as (1) except with portable backup CEMS	4	Increased reliability			
(5) Six CEMS - one per unit, Opacity Monitors located in stacks at the stack test level, all other probes and sensors located at each steam generation unit outlet	6	Systems configure to allow time sharing in case of CEMS failure if allowed by EPA. Increased reliability			

TABLE 3 JOPPA STATION CEMS CONFIGURATIONS

TABLE 4							
COST	FACTORS	FOR	JOPPA	STATION	CEMS	CONFIGURATIONS	

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Configuration Description	Relative Cost Factor
<u>Configuration (1)</u> -1 CEMS installed in each of 3 stacks	1.00
<u>Configuration (2)</u> -Same as Configuration (1) except NO _x /CO ₂ measured (time-shared) at each unit outlet	1.03
<u>Configuration (3)</u> -Same as Configuration (2) except with NO _x /CO ₂ monitors dedicated to each unit	1.12
<u>Configuration (4)</u> -Same as Configuration (1) except with a backup CEMS	1.32
<u>Configuration (5)</u> ~1 CEMS installed in each of 6 units except with opacity monitors located in 3 stacks	1.81

Improving Performance of Flushless Mechanical Seals in Wet FGD Plants through Field and Laboratory Testing

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ABSTRACT

With the need to control water-balance and process efficiency, mechanical seals requiring no flush water are acknowledged as an important component of the Flue Gas Desulfurization (FGD) process.

For mechanical seals to be applicable in FGD systems, the seals must handle a variety of process conditions and upsets, including situations where high percentages of abrasive solids such as flyash enter the process stream.

To improve reliability and performance of flushless mechanical seals in centrifugal slurry pumps in FGD applications, comprehensive laboratory and field testing was undertaken.

This paper reports the results of the laboratory and field testing, explores modes of failure in these applications, defines ways to improve Mean Time Between Failures and demonstrates that flushless mechanical seals can operate successfully in highly-abrasive applications.

INTRODUCTION

With the need to control water-balance and process control, mechanical seals requiring no flush water (flushless) are an important component of the Flue Gas Desulfurization (FGD) process. Most current FGD scrubber projects specify flushless mechanical slurry seals in place of packing. In recent literature exploring design and operation of FGD systems for cycling service, flushless mechanical seals were recommended to reduce waste water generation (1). Although waste water production varied for the different types of FGD scrubbers evaluated, production of waste water was thought to be significant in all cases during load changes and low output. Since flushless mechanical slurry seals use no flush water, a significant reduction in water consumption is realized. For example, flushless slurry seals can be used on recycle pumps to reduce water consumption, to eliminate dilution of lime reactant slurry and reduce water content in waste slurry transferred to settling ponds. Eliminating flush water usage provides the opportunity to introduce fresh water into the scrubber process at locations where dilution is beneficial.

The wet FGD process creates a variety of operating conditions for the flushless slurry seal. In absorber recycle pumps, solids range from 10-15% by weight. In contrast, a thickener underflow pump may reach 40% solids by weight. FGD slurries consisting of lime or limestone and gypsum also contain varying amounts of flyash. Flyash is very abrasive because it is largely composed of aluminum oxide and silicon dioxide. Flyash content will normally increase during load changes and can reach high levels in the event of a precipitator or prescrubber failure. The slurry seal is also subjected to pH levels ranging from 2-10 and Chloride levels that may approach 100,000 ppm. To provide long service life, the flushless slurry seal must provide dependable performance in the above operating conditions.

Important consideration must be given to the slurry pump when adapting the flushless slurry seal. Slurry pumps are heavy and rugged by design and do not typically have the concentricity and precision fits associated with process pumps. Axial and radial clearances found in certain bearing arrangements allow significant shaft movement. The mechanical slurry seal must accept normal misalignment and shaft deflection found in slurry pumps.

This paper provides practical guidelines to improve the performance and life of flushless mechanical slurry seals in FGD and related applications. Information presented in this paper is based on years of Field Experience and results of extensive Laboratory Testing. The recommendations given in this paper are consistent with designs currently supplied by many slurry pump manufacturers.

MECHANICAL SEAL DESIGN CONSIDERATIONS

Slurry is a mixture of solids suspended in a liquid. Certain criteria must be met for successful operation of a flushless mechanical seal operating in a slurry. By design, slurry seals must be different than conventional mechanical seals used in the petrochemical industry.

Conventional seals normally use a single coil or multiple pocket springs to provide uniform load on the dynamic seal ring (Fig. #1). These springs normally are exposed to the product and will pack or scale when used in slurry applications. This prevents movement of the spring and can lead to seal failure. In addition, conventional seals have a secondary sliding gasket which seals between the shaft or flange and the rotating or stationary face. The close clearances between these sliding components is susceptible to packing with solids. If these close fits become packed with solids, flexibility of the seal face is limited and can lead to seal failure. Welded diaphragm rotating bellows seals are considered self cleaning and are used in some slurry services. These bellows designs are susceptible to abrasive wear, solids buildup, stress corrosion and fatigue, which can limit effectiveness in high concentration slurries.

Figures #2-4 show three examples of flushless mechanical slurry seal arrangements. All three slurry seal designs utilize a spring system that is protected from the slurry. This is done by encapsulating the spring in rubber or using rubber as the spring (rubber in shear) or placing the springs outside of the slurry. The encapsulated cone spring and the rubber in shear spring designs are inherently non-clogging designs and have no sliding fits. In the spring pusher slurry seal (Fig. #4), a specially designed o-ring groove is utilized to prevent packing of solids and allow movement of the dynamic seal ring.

PUMP SHAFT TO HOUSING ALIGNMENT AND SHAFT DEFLECTION

A good slurry seal design must include self aligning features. Many slurry pumps do not provide adequate alignment of shaft to stuffing box mounting surfaces for good

mechanical seal performance. Figures #5-8 demonstrate the various alignment concerns that may be encountered in a typical slurry pump.

Figure #5 shows the shaft to stuffing box bore concentricity. Worn fits found on older pumps will aggravate this type of misalignment. This problem can be overcome by mounting a floating flange or adapter that allows centering the seal to the pump shaft.

Figure #6 shows perpendicularity of pump shaft to stuffing box mounting surface. This relationship is built into the pump and difficult to overcome. Excessive run-out in this area causes several problems. If the slurry seal is of the rotating spring design, misalignment will cause the springs to flex with every revolution. This may cause leakage and lead to seal failure. In the case of the stationary spring design, face load will be uneven. It is possible to eliminate these problems by attaching the stationary seal member to a flexibly mounted flange or to the bearing frame (Fig. #2).

Figure #7 shows axial travel of the shaft. This motion is the result of bearing clearances in most cases, but can be caused by clearances in the impeller adjusting mechanism. Before installing any mechanical seal, bearing condition should be checked and axial travel should be limited to the bearing manufacturers recommendations.

Figure #8 shows shaft sag and hydraulic offset. This is a function of shaft overhang, bearing radial clearances and hydraulic loading of the impeller during operation. Slurry seals are designed to tolerate normal deflections of this type by incorporating wider seal faces with matching wearing surfaces.

MATERIALS OF CONSTRUCTION

In FGD services, the primary concerns are chemical resistance to slurries with low pH and high chloride levels and abrasion. The choice of materials for metal components must be based on a knowledge of the operating conditions of the FGD system. To provide good seal life in these conditions, materials ranging from 316SS, CD4MCu, Hastelloy and High Chrome Iron are available.

With the abrasive and chemical nature of FGD slurries, seal face material selection is critical. Results from field installations and laboratory testing confirm that Silicon carbide vs Silicon carbide gives the best seal performance. The performance of Silicon Carbide can be attributed to its high hardness, thermal conductivity, chemical resistance and excellent sliding properties. Ethylene propylene rubber (EPR) is normally used for gaskets and rubber components and has provided excellent performance in water based slurries.

SEAL CHAMBER DESIGN CONSIDERATIONS

Seal chamber design is important for successful seal operation. Studies have been conducted to evaluate how seal chamber design effects mechanical seal performance in process pumps (2)(3). In these studies, radial clearance between the mechanical seal and stuffing box bore were evaluated to determine their influence on liquid behavior around the seal faces. Mechanical seal faces rely on the product or flush media for lubrication and cooling. Results of these studies concluded that close clearances between rotating seal components and the stuffing box bore create heat buildup and limit product circulation around the seal faces. For flushless or dead-ended seals, large stuffing box bores and open throat areas provide the best environment by promoting product circulation in the seal chamber.

Similar studies have been conducted on slurry services (4). Results of these studies report that a large radial clearance is needed to promote circulation and that a tapered seal chamber will provide additional benefits. The natural swirling flow of slurry in a tapered seal chamber centrifuges heavy abrasives from the seal rotating parts and provides better heat removal. In addition, the tapered seal chamber design is self venting during startup and operation and retains no slurry when the pump is drained. A self venting tapered or open seal chamber provides the best environment for flushless mechanical slurry seals. Figures #9 & 10 show tapered and open seal chamber designs, with back vanes removed from the impeller.

DISCONTINUITIES IN THE SEAL CHAMBER

Discontinuities in a self venting seal chamber upset the uniform flow and create localized pockets of turbulence. These discontinuities can be in the form of strakes or drilled vent or drain ports. The effects of this turbulence can produce accelerated wear of pump and seal components. In cases where a high percentage of solids or large particle abrasives are found, wear can be heavy. Impeller back vanes that extend into the seal chamber cause high flow rates and produce excessive turbulence, which accelerate abrasive wear. A properly configured self venting seal chamber eliminates the need for a vent or flush port.

IMPELLER BACK VANES

Impeller back vanes are designed to reduce pressure in the stuffing box. Efficient back vanes can produce a vacuum in the seal chamber under conditions of low suction and low discharge pressure and high flow (Fig. #11). This condition robs the mechanical seal of lubrication and cooling and can cause seal failure. This condition is typical at start-up where little or no pressure is in the discharge pipe. Maintaining static head on the discharge or throttling the discharge on start-up greatly reduce the
potential of this problem. In cases where pump discharge pressure is high, back vanes reduce seal chamber pressure, which may be beneficial to the slurry seal.

LABORATORY TESTING

Most testing of slurry seal designs has been conducted using water for the test medium. Although this testing yields some measure of seal performance, it does not address the concern of abrasive wear to seal faces and adaptive components. To determine effects of slurry solids on seal performance, requires a test rig capable of circulating slurry.

A unique test rig was constructed with the express purpose of testing mechanical seals in abrasive slurry(5). Refer to Figures #12 and 13. The design utilizes two slurry pumps in series. The first stage pump is used to circulate the slurry and provide increased suction pressure to the second test pump. The second stage pump, the main test pump, is coupled to a variable speed drive which provides a range of shaft speeds and corresponding seal chamber pressures. A 700 gallon cone bottom tank fitted with a heat exchanger provides a source of controlled temperature slurry. The large volume tank slows the process of slurry breakdown, increasing the effective life of the slurry. Variable orifice flow control valves are used to regulate flow and pressure in both pumps. A flow control valve placed in the suction pipe of the second test pump allows simulation of starved suction operation. The system is designed to provide adequate flow rates to maintain slurry solids in suspension, yet slow enough to prevent excessive wear to piping. Test Rig specifications:

- 1. Accommodate Seal Sizes From 1.875 to 4.5" Diameter
- 2. Controlled Temperature Range of 100 to 160 F
- 3. Controlled Seal Chamber Pressure Range of 50-110 PSI
- 4. Accommodate Most Water Based Slurries
- 5. Vary Test Pump Suction Pressure
- 6. Real Time Data Acquisition System
- 7. Capable of Unmanned Operation

The choice of a slurry is very important, since the key goal of testing is to obtain meaningful results in a short time. A long test duration would be required, if a soft slurry was used for the test media (limestone or gypsum, Mohs 3-4). Table #1 lists the Mohs scale and selected mechanical seal face materials. Softer slurry would also require frequent replacement, since the softer particles would breakdown quickly. Flyash slurry was chosen because it contains a large percentage of abrasive particles Mohs 7 and harder. This material was readily available from a power plant in which flushless slurry seals were being evaluated. This flyash was primarily composed of 50 micron and smaller particles which provide the most aggressive environment for evaluating seal performance. Refer to Table #2 for flyash slurry description. It is important to consider the effects of flyash on seal performance since this material is present in most FGD slurries.

TEST RESULTS

Flyash slurry has proven to be a very effective media for evaluating flushless mechanical slurry seal design. To date, nearly three years of testing have been conducted. Test programs have included development of seals for large particle abrasive applications, increasing slurry seal life and performance, seal face material evaluation, evaluation of adaptive hardware and seal chamber design.

SEAL DESIGN.

Results of testing confirmed that even small amounts of flyash leakage would lead to abrasive wear and eventual washout of the seal faces. A close look at failed seal faces, revealed a pitted or sandblasted appearance. This is caused by micro-spalling or chipping of the seal face when hard slurry particles enter the sealing gap. Slurry particles entering the sealing gap, move across the seal faces from stuffing box to atmospheric pressure. While traveling across the seal faces, particles slide and tumble. They produce a high localized load when a high spot on the particle is forced between the seal faces. At this point, one of two things happen, the slurry particle is crushed or the seal face fractures (micro-fracture producing a very small chip). In the case of high leakage, this chipping will occur quickly and cause seal face washout. The above mechanism is referred to as three body abrasion (6). Figure #14 contains additional information on abrasive wear.

An improved design which reduced seal face leakage to "near zero" (no visible leakage) was developed using analytical tools and results from early testing. This improved design has undergone extensive testing under a wide range of operating conditions and consistently provided excellent seal performance. Using the new design in hard abrasive slurries eliminated seal face washout, in fact after a 1500 hour test, seal faces were in excellent condition.

Utilizing the improved design, extensive seal face material testing was conducted. Results confirmed that Silicon carbide vs Silicon carbide provides the best performance in abrasive applications. In field applications Silicon carbide has given excellent performance in FGD, mineral and ore processing, and tailings services.

ADAPTIVE HARDWARE,

To evaluate the effects of seal chamber design on circulation and heat transfer, testing was conducted with a quartz based slurry, 25-30% solids by weight. The slurry test pump used had no back vanes and had an enlarged seal chamber opening to adapt to various seal chamber configurations.

In tests evaluating a seal chamber with close clearances over the seal, the seal failed from poor circulation and packing of solids in the chamber. Using a tapered seal chamber design, no packing of solids was found and the seal performed well.

To monitor seal chamber pressure and temperature, a vent port was drilled into the tapered seal chamber. Over a period of 400 hours testing in sand slurry, localized abrasive wear was pronounced in the vent port area. This same type of localized wear was also seen in the seal chamber used during the flyash testing, although it took several thousand hours for the wear to occur. This confirmed the need for uniform uninterrupted contours in the seal chamber area.

FIELD TEST RESULTS

Although much was learned from laboratory testing, the ultimate test is always success in the field. Over the past several years slurry seal performance has improved significantly. The knowledge gained in laboratory testing has provided new opportunities for the flushless mechanical slurry seal. Slurry seals are now providing extended life not only in FGD applications, but also in flyash scrubber applications, mine tailings, iron ore processing, alumina and chemical applications.

Four slurry applications are reviewed in this paper, two typical FGD applications and two field test applications. Each application covers a different facet of the guidelines presented in this paper. Results of each application with operating conditions are presented in Tables #3-6.

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FIGURE *1 CONVENTIONAL MULTIPLE SPRING PUSHER MECHANICAL SEAL

CHARACTERISTICS:

- * MULTIPLE COIL SPRINGS EXPOSED TO PRODUCT
- * SPRING POCKETS EXPOSED TO PRODUCT
- * DYNAMIC GASKET EXPOSED TO PRODUCT
- * ROTATING SPRING DESIGN
- + CARTRIDGE DESIGN



FIGURE *2 FLUSHLESS RUBBER IN SHEAR MECHANICAL SLURRY SEAL

CHARACTERISTICS:

- * NO DYNAMIC GASKETS OR SLIDING FITS
- * RUBBER IN SHEAR SPRING ELEMENT
- * STATIONARY SPRING DESIGN
- * STATIONARY MEMBER MOUNTED TO BEARING FRAME



FIGURE •3 FLUSHLESS ENCAPSULATED CONE SPRING MECHANICAL SLURRY SEAL

CHARACTERISTICS:

- * NO DYNAMIC GASKETS OR SLIDING FITS
- * RUBBER ENCAPSULATED CONE SPRING ELEMENT
- ROTATING SPRING DESIGN
- CARTRIDGE DESIGN



FIGURE •4 FLUSHLESS PROTECTED MULTIPLE SPRING MECHANICAL SLURRY SEAL

CHARACTERISTICS:

- * SPECIALLY DESIGNED DYNAMIC GASKET EXPOSED TO PRODUCT
- * MULTIPLE COIL SPRINGS PROTECTED FROM PRODUCT
- STATIONARY SPRING DESIGN
- ***** CARTRIDGE DESIGN





FIGURE * 9 SLURRY PUMP WITH FLUSHLESS SLURRY SEAL IN A SELF VENTING TAPERED SEAL CHAMBER



FIGURE • 10 SLURRY PUMP WITH FLUSHLESS SLURRY SEAL IN A SELF VENTING OPEN SEAL CHAMBER



Figure #11. At higher flow rates the pressure developed by the impeller drops off quicker than the pressure developed by the backvanes. If suction pressure is low, the seal chamber will be exposed to a vacuum. This condition may be experienced during startup or under high flow rates with low suction pressure. It is important to provide adequate suction pressure to prevent this mode of operation, as it will shorten seal life.



Figure #12 The Slurry Test Rig



Figure #13 Slurry Test Rig Flow Schematic



Figure #14. The effect of abrasive hardness / material hardness ratio on abrasive wear rate and wear mechanism. Abrasive wear can be caused from two-body abrasion or three-body abrasion. Key parameters that affect wear are hardness, load and rotational velocity (6).

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FLYASH SLURRY PROPERTIES AND CONCENTRATION AS TESTED

-Al ₂ O ₃ (Mohs 9 Hardness) -SiO ₂ (Mohs 7 Hardness) -misc. soft compounds		27% 43 30%
-Particle size Distribution (%)		
particle size	new	400 hrs*
3-5 micron	54%	54%
5-15	32%	29%
15-25	8%	16%
25-50	5%	1%
50-larger	1%	>1%
-Slurry Solids by Weight (%)		11-15%
-Water by Weight (%)		85-89%
-Slurry Specific Gravity		1.2-1.3

MOHS HARDNESS SCALE WITH SELECTED SEAL FACE MATERIALS

Moh	s Hardness Scale	Knoop Scale*
10	Diamond Boron Carbide Silicon Carbide, Alpha Sintered Titanium Diboride Silicon Carbide, Direct Sintered	3000 2800 2700 2500
9	Corundum (Al ₂ O ₃) Silicon Nitride Tungsten Carbide	2000 1300-2000 1500-1800
8	Topaz	
7	Quartz (SiO ₂) Taconite	
6	Orthoclase	
5	Apatite	
4	Fluorite	
3	Calcite Limestone	
2	Gypsum	
1	Talc	
	*Knoop Scale included for reference	

FGD APPLICATION #1 - Louisville Gas & Electric Co.

-Plant Name: -Plant Location:	Louisville Gas & Electric Co. Cane Run Station
-Process Description: -Pump Location:	Wet Lime Flue Gas Desulfurization Absorber Recycle, Unit #4 - 2 pumps Unit #5 - 2 pumps
-Slurry Description:	Recycle Slurry
-Solids: -% Solids: -% Flyash: -Temperature: -Seal Chamber Press: Disch Bress:	Lime/Gypsum/traces flyash 5-15% 1-2% 120-135 F 25-35 psi
-DISCIL FIESS:	od psi

-System Operation: Absorber recycle pumps operate around the clock, with occasional shutdown for standby. Pump is drained for standby condition and filled and vented prior to startup.

-Pump Description: -Shurry Seal Size & Type: -Slurry Seal Construction:	Warman 550 TUL RIS-9500 316SS metal parts EPR Rubber in Shear Element & gaskets Reaction Bonded SiC Sta. & Rot. Faces
-Total Time in Service:	1987-1991, 3 years unit #4 pumps unit #5 pumps still in operation

-Approximate # of Hours: Unit #4 - about 18,000 operation Unit #5 - 20,000+ & still in operation

-Seal Performance Evaluation: Slurry seal performed flawlessly for 3 years in unit #4 with no visible leakage. Both pumps in unit #4 were removed from service to replace worn liners. One seal was removed for inspection at this time. A new seal was installed per standard maintenance practices. After 18,000 hours service this seal had no measurable wear and looked as new. The two seals in the unit #5 pumps continue to run and have not required any maintenance for nearly 5 years.

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FGD APPLICATION #2 -Texas Municipal Power Agency

-Plant Name: -Plant Location:	Texas Municipal Power Agency (TMPA) Gibbon Creek S.E.S.
-Process Description:	Wet Limestone Flue Gas Desulfurization
-Pump Location: -Slurry Description:	Absorber Recycle Limestone Reagent/Gypsum
-Solids: -% Solids By Weight -% Flyash in slurry solids: -Temperature -Seal Chamber Pressure: Discharge Brassure:	Limestone/Gypsum/traces Flyash 5-15% 2-5% 120-135 F 20-35 psi
-Discharge Pressure:	Vertical line, 60 ft.

-System Operation: The absorber recycle pumps operate continuously. They are shut down for normal inspection and scrubber maintenance. The pump is normally in operation for 9 1/2 months of the year.

-Pump Description:	Warman 450 STL
-Slurry Seal Size & Type:	RIS-7500
-Matl's. of construction:	316SS metal parts
	EPR Rubber in Shear Element & gaskets
	Reaction Bonded SiC Sta. & Rot. Faces

-Total Time in Service: 1989-1991, 1 years, 2 months

-Approximate # of Hours: 8,000 hours

-Seal Performance Evaluation: This was new pump with a factory installed slurry seal. Due to a clerical error, seal was supplied with incorrect seal faces, Tungsten vs. Silicon carbide. Shortly after startup, seal began to leal and failed from abrasive washout of seal faces. A replacement seal with Reaction Bonded Silicon Carbide faces and improved design was installed. This seal has given flawless performance since installation. Recently, the pump was removed from service for a routine warranty pump inspection. At this time, the seal was examined and found to be in excellent condition with no signs of wear. Prior to reassembling the pump, seal faces were reconditioned per standard maintenance practices.

TABLE #5

FIELD TEST #1 - Potomac Electric Power Company

-Plant Name:	Potomac Electric Power Company
-Plant Location:	Dickerson Station
-Process Description:	Flyash Particulate Scrubber
-Pump Location:	Absorber Recycle
-Slurry Description:	Flyash Slurry
-Solids:	Flyash, 26% Al ₂ O ₃ , 43% SiO ₂
-% Solids By Weight	2-5%
-pH	2-4 (Chlorides level is low)
-Temperature	110-120 F
-Seal Chamber Pressure:	45-55 psi
-Discharge Pressure:	65-75 psi

-System Operation: Two absorber recycle pumps are used on each unit, one on line, the other on standby. During normal operations, each pump is cycled, 8 hours on and 8 hours off. While on standby, the pumps remain filled.

-Pump Description:	ASH DG-9-5
-Mechanical Seal Details:	RIS-6500
-Matl's. of construction:	316SS metal parts
	EPR Rubber in Shear Element
	Reaction Bonded SiC Sta. & Rot. Faces

-Total Time in Service: 1989-1991, 2 years, 4 months

-Approximate # of Hours: Over 6,000 hours run time

-Seal Performance Evaluation: Initial seal installations provided inconsistent performance. This site was used to test improved seal designs. Results of testing confirmed that success depended on reducing leakage to zero visible leakage. Currently standard O-ring Retained seals with over 2 years service continue to operate successfully. Plant has converted 4 of the 6 recycle pumps to mechanical slurry seals and plans to convert all pumps. This plant is also successfully applying mechanical slurry seals in bottom ash transfer pumps.

TABLE #6

FIELD TEST #2 - USX MINTAC

-Plant Name:	USX Mintac/GPM
-Plant Location:	Mountain Iron, MN
-Process Description:	Taconite Concentrate
-Pump Location:	Hydro Sizer Underflow
-Slurry Description:	Taconite Slurry Concentrate
-Solids: -% Solids By Weight -Temperature -Seal Chamber Pressure: -Discharge Pressure:	Taconite/Quartz (Mohs 6.5-7) 18-25% Ambient 20-35 psi

-System Operation: This pump is operated on a continuous basis. The pump is coupled to a variable speed drive which is used to vary pump speed and maintain a constant concentration of 18-25% solids by weight. The plant operates on a 16 week cycle and then shuts the process down for 1 week of maintenance.

-Pump Description:	Denver Frame 4
-Mechanical Seal Details:	RIS-4500
-Matl's. of construction:	316SS & 416SS(Ht.Treated) metal parts EPR Rubber in Shear Element & gaskets Reaction Bonded SiC Sta. & Rot. Faces

-Total Time in Service: 11/90-9/91

-Approximate # of Hours: 6000 hours

-Seal Performance Evaluation: This seal gave excellent performance for nearly a year. On 9/11/91, the seal failed when the pump was started dry and left to run for several minutes before unblocking the suction valve. This installation utilizes a tapered seal chamber with a vent port (the pump has no backvanes). A new seal has been installed in this pump and is running at this time. It should be noted that localized abrasive wear was found in the area of the vent port after the year in service. The customer is planning to install seals into the three remaining pumps in this service (the cover will not have a vent port in these pumps). SULCIS FGD DEMONSTRATION PLANT LIMESTONE-GYPSUM PROCESS: PERFORMANCE, MATERIALS, WASTE WATER TREATMENT

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ABSTRACT

ENEL has installed 3 FGD demonstration plants, each of 40.000 Nmc/h, at the Sulgis power plant, Sardinia, to experiment limestone-gypsum, Wellman-Lord, Walther processes. ENEL chose the limestone-gypsum process for its FGD installations in the building stage on a first series of new multi-fuel power units (coal, oil, natural gas) and on inservice coal units. The other two processes are taken into consideration as perspectives, both in local socio-economic situations of a particular nature, and with a view to diversifying the resultant by-products.

The first phase of limestone-gypsum process experimenting, which lasted about 3200 hours, was completed in 1990 with the following results:

- plant performance is assured (with 1 % S coal and 3 % S fuel oil) to be well within the legally required limit of 400 mg/Nmc of SO₂ in emission.
 The validity of ENEL's plant choice for "Sulcis Project" was also confirmed (use of Sulcis-basin coal having 7-8 % S) which envisages 2 absorption towers in series;
- The on plant study of materials and equipment, conducted through periodical NDT inspections, along with the installation of a series of specimens of alternative materials, supplied a wide-ranging view of useful information; the behaviour of a wide range of metal materials, organic coatings and equipment was defined in the different environmental conditions typical of a wet FGD plant;
- The waste-water process treatment designed by ENEL for its commercial power plants was verified and optimized on a 200 l/h pilot plant. The treatment allows to meet the stringent italian laws on water effluents.

1. INTRODUCTION

The need to gradually reduce in Italy too the sulphur oxide emissions from the various industrial sources was recognized at the end of the seventies. Early in the eighties, the Board of ENEL decided that a demonstration scale experiment should have been set up in order to acquire direct experience with a new and complex technology and to investigate the problems connected with its application in the particular Italian context. A Working Group was organized by ENEL Construction Department who examined about ten processes which had already reached a sufficient degree of development, taking into account the cost, the complexity of the plant, the technological maturity and the marketabilility of the end products.

The final proposal approved by the Board relates to experiments with the following processes:

- limestone-gypsum process, capable of producing commercial quality gypsum;
- Wellman-Lord process, of the regenerative type with separation of pure SO₂ which can be converted to sulphur or sulphuric acid;
- Walther process, which uses ammonia to produce ammonium-sulphate usable as a fertiliser.

The construction of the three desulphurization systems was entrusted to Italian companies which had received licences (Idreco with a Bishoff licence for the limestonegypsum process, CIFA with a Davy-McKee licence for the Wellman-Lord process, and Termokimik with a Walther-Krupp Koppers licence for the ammonia/ammonium sulphate process), whilst Ansaldo was given the task of constructing the common works (civil engineering and interface systems with the power station).

The project for the construction of the experimental complex was the responsibility of the Milan office of ENEL Construction Department and the most suitable site for constructing this plant was identified in the Sardinia island at Sulcis power station in view of the proposed use of local coal which has a high sulphur content.

Following the Decree N° 105 of 10.3.87 of the Ministry of the Environment relating to thermal power station emissions that took up the commitment contained in the Helsinki protocol for the percentage reduction of SO_2 emissions, bringing it forward to 1990, ENEL made up the decision to install FGD systems for all the new multi-fuel power stations and for coal-fired existing power stations. The technology chosen for the first series of FGD plants to be installed (for a total of Z 8,000 MWe) was the limestonegypsum process. This decision, together with the new emission limit of 400 mg/Nmc set up by the Ministry of the Environment for individual power stations, made it all the more urgent to have some results from the experiments on the demonstration scale, in particular with regard to the limestone-gypsum process, but also for the other processes which are potentially valid alternatives either in particular local situations from the economic and social point of view, or from the point of view of diversifying the end-products. Desulphurization plants involve the use of specific liquid effluent treatment processes. It was therefore considered desirable to also validate the design of this treatment by means of tests on an ``ad hoc'' pilot plant in order to guarantee a discharge in accordance with Italian regulation.

2. OBJECTS OF EXPERIMENTATION

The object of the experimentation is to verify:

- plant performance for all the three processes with imported coal (S about 1%), Sulcis coal (S up to 8%), fuel oil (S about 3%);
- end products characteristics (gypsum and ammonium sulphate);
- emissions characteristics;
- waste water treatment performance;
- construction materials and linings behaviour;
- emissions monitoring instrumentation operation.

It is also planned to train operating personnel for future commercial FGD plants.

The entire experimentation is divided into four steps:

- 1. limestone-gypsum tests 1st phase
- 2. Wellman-Lord tests
- 3. Walther tests
- 4. limestone-gypsum tests 2nd phase.

So far only step 1 has been accomplished and it is foreseen to end up with the other three by the end of 1992.

3. DESCRIPTION OF EXPERIMENTAL PLANT

3.1 <u>Desulphurization systems</u>

3.1.1 Limestone-gypsum system. The schematics of the plant for the limestone-gypsum system is illustrated in Fig 1.

The plant contains a bypassable prescrubber, which is useful to obtain a high purity gypsum, particularly in case of high levels of impurities (especially hydrochloric and hydrofluoric acid and ash) in the flue gases.

Absorption and oxidation take place in a counter-flow tower (scrubber). The injection of sorbent is provided by 9 spray nozzles on 9 different levels connected three by three to a recirculation pump. In the lower part (oxidation zone), the gypsum suspension is extracted and is sent to the filtration system.

The limestone is supplied in coarse particle size and is stored in this form; it is then grounded and suspended in water.

The make-up water maybe industrial water or sea water; the latter possibility is of great advantage for the installation of desulphurization plants at coastal sites where there is little fresh water available.

3.1.2 <u>Wellman-Lord system</u>. In the Wellman-Lord system, illustrated in Fig 2, a highefficiency prescrubber is used in which hydrochloric and hydrofluoric acid and ash, which would create problems in the absorption circuit, are removed.

The absorption is carried out in a tower with trays and packs, in which a solution of sodium salts sprayed in counterflow to the flue gas absorbs the SO_2 . The exhausted solution is regenerated thermally in an evaporator and is then re-used. The circuit is only theoretically closed, since purging takes place to limit the accumulation of non-regenerable by-products such as sodium sulphate; the make-up consists of sodium carbonate supplied in powder form and stored in solution.

The SO₂ released by the evaporator in commercial plants is converted to sulphur or H_2SO_4 ; in the Sulcis plant, the conversion system was not constructed. The SO₂ is therefore sent, together with the desulphurized gas, to the gas duct of the thermal unit.

The plant is equipped with tanks for storing the fresh and exhausted absorbent solutions so as to make independent the absorption and regeneration systems, in order to be able to operate the former system for about 24 hours with the second system out of operation.

3.1.3 <u>Walther system</u>. The Walther system, illustrated in Fig. 3, uses ammonia in an aqueous solution as an absorber of SO_2 , producing a dilute ammonium sulphite solution which is then oxydized to sulphate with air.

The plant contains a prescrubber for the partial removal of aerosols.

The absorption occurs in two spray towers in series, followed by two types of filters for the removal of solid and liquid particles. The first type is a coalescent filter, whilst the second is a wet E.P.

The ammonium hydrate is supplied in liquid form and is stored in tanks. The ammonium sulphate solution is treated in a production unit consisting of a crystallizer and a granulator. The plant is fitted with tanks for accumulating the ammonium sulphate solution in order to make the operation of the absorption and oxidation system independent of that of the production unit.

3.1.4 <u>Design Criteria</u>. The design criteria for the entire demonstration plant are as follows:

٠	gas flow rate	40,000 Nmc/h (10
		MWe)
•	SO ₂ conc. in gas	0.22% (equivalent to the
	-	combustion of coal with 3.5% S)

•	reagent storage	
	$(CaCO_3, NH_4OH, Na_2CO_3)$	1 month
	(sulphur)	2 months
•	intermediate storage of products in silo	
	(gypsum and ammonium sulphate)	3 days
	starse of products in base	

storage of products in bags
 (under cover) 3 months-1 year

The demonstration plant can operate, even though on reduced load, when supplied wi gases having characteristics deriving from the combustion of Sulcis coal (7-8% S

The design gas flow rate can be taken from Sulcis power station units 1 or 2 and distributed to the plants as shown in the schematics of Fig. 4.

It is possible to supply two plants simultaneously, with the total gas flow rate lin of 40,000 Nmc/h remaining the same.

The gases can receive additions of SO_2 or HCl from suitable systems in order to simula the desired chloride and sulphur content.

Before entering the plant, the raw gases pass through a Ljungstroem type regenerati heat exchanger (GAVO) in which the desulphurized gases are heated in counterflow The gas is circulated through the plant by means of two fans (one in reserve) situat between the desulphurization systems and the GAVO, so that inside the latter t desulphurized gas has a higher pressure

than that of the raw gas, thus avoiding the ingress of the latter into the desulphuri: gas which would result in a reduction in the desulphurization efficiency. The ammoni sulphate and gypsum produced are placed in silos and then packed in bags through bagging system.

3.1.5 <u>Operating auxiliaries</u>. The auxiliary fluids required for the operation of t plant are:

- steam obtained from the auxiliary header on Sulcis units 1-2
- demineralized, potable, industrial water taken from the power station main headers
- compressed air produced from an independent system
- sea water taken in by means of dedicated pumps installed in the intake works of the Sulcis power station

The electrical supply is provided by a main 6 kV switchboard which supplies the 1 blowers directly and, via two transformers (6 kV/380 V), two power switchboards. (switchboard supplies the control panels of the Walther and the Wellman-Lord plant the common plant and the flue gas additive system; the second switchboard is entired dedicated to the electricity requirements of the limestone-gypsum plant.

The control and instrumentation equipment is located in the control room inside (General Services Building of the demonstration plant with the exception of the ammon: sulphate production unit which has its own control room located near the product: unit itself.

In addition to being indicated and recorded on control and monitoring panels in a control room, the process data flow to a data acquisition and processing systeminstalled inside the General Services Building for data storage, real time calculat: of performance and material balances.

A chemical laboratory has been constructed inside the General Services Building in order to carry out the analyses relating to the process control.

3.2 Waste water treatment

The fluid waste to be treated consists of gas wash water, coming from limestone-gypsum and Wellman-Lord processes.

Fig. 5 shows the schematics of the three stage process.

The design flow rate of the pilot plant is 200 1/h. The first stage of treatment involves an initial addition of lime to neutralise the acidity, followed by a second addition to increase the pH to 8.7:9, which allows the precipitation of a large proportion of metals as hydroxides. It is also planned to add sulphide in order to remove Hg and Cd, FeCl₂ to precipitate the excess sulphide, and polyelectrolyte which has a flocculating effect. This stage includes a circular clarifier.

The 2nd stage is designed to remove the residual Se by coprecipitation with ferric hydroxide to pH 6:7 and subsequent sedimentation by means of lamellar packing. Dosing with ferric chloride and acid and/or soda is provided to regulate the pH.

Finally, the purpose of the 3rd stage is to oxidise, by the use of oxygenated water, the residual sulphites and sulphides, the nitrites and, more generally, all oxidizable substances (COD).

4. RESULTS OF THE EXPERIMENTS ON THE LIMESTONE-GYPSUM PROCESS (1st phase)

4.1 Process

The tests performed up to now were carried out in the period January-March 1990 in order to verify the design assumptions adopted by ENEL during the procurement specification phase for the flue gas desulphurisation systems for 660 and 320 MW multifuel units and for the 240 MW units at the Sulcis power station. In this station, where local high sulphur content coal (7:8% by weight) will be used, two absorption towers in series are foreseen.

In particular, a determination was made of the overall desulphurisation efficiency and of the SO_2 concentration in the emissions when the liquid/gas ratio of the absorber was varied over a range of SO_2 concentration at the plant inlet from 2,000 to 16,000 mg/Nmc (equivalent to a coal sulphur content between 1% and 8%).

In all, 20 tests were carried out with various plant configurations.

The emission values have been measured downstream of the regenerative heat exchanger.

With reference to the standard design of desulphurization plants for 320 and 660 MW units the global plant performance is confirmed. The full compliance with the SO_2 regulatory limit of 400 mg/Nmc in emission with an inlet concentration range varying from 2,000 to 4,000 mg/Nmc and a L/G ratio equal to 15 and 20 respectively, has been ascertained.

The max. inlet SO_2 concentration compatible with the 400 mg/Nmc emission limit at a L/G ratio = 20 is about 7,000 mg/Nmc (3.5% sulphur in coal).

Also when simulating the Sulcis coal, the hypotheses concerning the performance of the first absorption tower of the Sulcis FGD plants (expected outlet about 4,500 mg/Nmc, with 16,000 mg/Nmc at the inlet and a L/G ratio = 14) are confirmed. As a consequence and according to the above data, the second absorption tower will reduce the SO₂ below the regulatory limits (tab 1).

The above considerations are better visualized in figs. 6a and 6b. The first one shows the SO_2 concentration in the emissions as a function of the L/G ratio for two significant values of SO_2 concentration at the inlet (2,000 mg/Nmc and 4,000 mg/Nmc, corresponding to 1% S imported coal concentration and to 3% S fuel oil concentration, respectively). It can be seen that, in order not to exceed the 400 mg/Nmc legal limit at the outlet, the ``critical'' L/G ratios are around 8 and between 13 and 14 with a SO_2 inlet concentration of 2,000 mg/Nmc and 4,000 mg/Nmc respectively.

Fig. 6b is in a certain way the reverse of fig. 6a, since it shows in the ordinates again the SO_2 concentration in the emissions but as a function of the inlet SO_2 concentration for three L/G ratios (10,15,20). From this figure it is particularly interesting to note that with a L/G ratio equal to 20 one must go to an inlet SO_2 concentration as high as 6,000 mg/Nmc in order to exceed the 400 mg/Nmc legal limit; but also that even with a relatively low L/G ratio of 10 it is still possible to operate the plant with an inlet SO_2 concentration of around 3,000 mg/Nmc.

The characteristics of the gypsum produced during the tests comply with the specifications (tab 2) and, according to its composition, for the Italian regulation can be classified as a non hazardous waste and therefore can be utilized in industrial and civil activities.

To be more precise, the soluble chlorides concentration exceeds the specification limit but that was very well expected due to the high level of chrorides in the water used to wash gypsum (from 700 to 1,000 mg/l): this type of water was actually the only one available at the site for the experimentation.

High quality limestone has been used for the tests (fig 7).

The particulate emissions were about 10 mgNmc (legal limit: 50 mg/Nmc) with about 20 mg/Nmc at the plant inlet.

The chloride emissions were about 1 mg/Nmc with 50 mg/Nmc at the inlet (legal limit: 100 mg/Nmc).

The fluorides emissions were 1 mg/Nmc with about 4 mg/Nmc at the inlet (legal limit: 5 mg/Nmc).

Measurements of SO_3 were taken at GAVO inlet, at the prescrubber inlet and outlet as well as in reheated desulphurized gases (GAVO outlet).

The first indications show a total SO3 reduction in the plant by at least 50%.

4.2 <u>Waste Water Treatment</u>

The tests carried out concerned the treatment of the prescrubber blow-down using coal as a fuel.

The results of the tests were positive since the legal limits are already met in the lst stage of treatment (fig. 8).

It is worth while mentioning that the Italian regulation sets a double limitation: the first one on the concentration of individual microelements; the second one requires that the sum of the ratios of the actual concentration of each microelement to its limit legal concentration be less than one.

Going back to the obtained results, the first stage of treatment is able to drastically reduce the concentration even for the most difficult elements to separate (such as Cd and Hg); for the Se too the efficiency (60:80%) is still sufficient to permit to remain within the legal limit at the second stage exit.

The final oxidative treatment has not been defined yet, but it seems to give no problems. In order to improve the fluorides removal, lab tests are being run.

The process sludges are easy dewatered due to their high content in gypsum; they belong to ``non hazardous'' waste class.

4.3 Plant materials and test specimens

In the design phase, materials were chosen on the basis of technical solutions already adopted abroad for such type of plant, also taking economic aspects into account. Due to the experimental nature of the plant, different alternative materials and linings have been installed and tested.

The evaluation has then been based on the following two criteria:

- Checking of the behaviour of plant materials, linings and components;
- Checking of the behaviour of test specimens installed in positions of particular interest and on specially prepared secondary loops.

As for specimens, lined and unlined metallic materials have been tested (tab. 3). For the unlined specimens, the following metallic classes have been considered: carbon steel, stainless steel type 18-8, high Cr-Mo stainless steels, nickel alloys, titanium. As for the lined specimens, carbon steel with glass flake vinylesters, fluoroelastomers, GFRP (composite materials) have been employed.

The location of the specimens in the plant (prescrubber, scrubber, GAVO) are shown in fig. 9.

Visual, telecamera and photographic documentation was acquired during the base line inspection before the start-up of the plant.

Periodical inspections were made afterwards.

After about 3000 hours of operation the main observations obtained are as follows:

- the rubber applied to the prescrubber and scrubber towers gave satisfactory esults with the exception of some little damage on pipes edges which project inside the two towers. The rubber applied to the pipes proved not able to stand high turbolence, such as that occurring near the throttled valves;
- the glass flake vynilester in the flue gas ducts and dampers turned out to behave satisfactoryly in the cold raw flue gas section. On the contrary, in the cold desulphurized flue gas duct the upper layer of this liner showed exfoliation, whereas in the hot desulphurized flue gas duct it showed cracks and poor resistance to the environment;
- a fluoroelastomer in the cold raw flue gas duct showed small blistering phenomena;
- as for metals, the following were observed: active pit corrosion signs on the pipes in superaustenitic alloy used for air distribution in the scrubber; slight pitting corrosion on the fans in austenitic steel; pitting corrosion on the dampers in 316 L steel placed on hot and cold desulphurized flue gas ducts;
- generally no serious problems were observed on the pumps, specially for those in continous operation; some pitting and crevice corrosion was viceversa observed in those pumps which were out of operation for long periods;
- the GAVO showed the detachment of plastic elements from the cold layers. The enamelled plates of the hot layer were still in good conditions and only a few points of rust were present.

As far as the specimens installed on the plant are concerned, it is worth while to underline that they enabled to identify the problems connected with the typical environments of a desulphurization plant and to evaluate the behaviour of a large number of metals and linings.

The prescrubber environment is extremely corrosive for all metallic materials: even titanium suffered very severe corrosion, while nickel alloys gave better results. The linings gave satisfactory results.

In the scrubber, mainly pit and crevice corrosion were found: the classes of metallic materials that gave good results include some nickel alloys, while the behaviour of some superaustenitic and austeno-ferritic steels with a high molybdenum content were not always been satisfactory also related to the long outage periods of the plant. The glass flake vynilesters showed erosion problems only near the spray nozzles.

Fluoroelastomers and GFRP (composite materials) were still in good conditions.

Pit and crevice phenomena were also found both in the hot and cold raw flue gas ducts and in the cold desulphurized ducts: the less resistant materials is the 316L stainless steel.

Particularly interesting is the environment of the hot desulphurized flue gas duct: it caused mainly generalized corrosion and it turned out to be more aggressive than expected even to high-quality alloys due to the relatively high temperature (in any case below the dew point).

The corrosion rates of the different metallic materials classes fall within a rather limited range. However, the best materials are nickel alloys, titanium and superaustenitic alloys as shown in table 4.

The test specimens of organic liners installed in the ducts gave results in accordance with those observed for the liners applied on the ducts except for the glass flake vynilester in contact with the cold desulphurized flue gas: the specimens gave good results showing no surface exfoliation.

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

Preliminary conclusions can be drawn on the basis of limestone-gypsum process startup, operation and first phase experimentation.

The evaluation of the performance of the process has made it possible to verify the correctness of the design assumptions adopted by ENEL when drawing up the specifications for the procurement of the flue gas desulphurisation systems for multifuel 660 and 320 MW units and for the 240 MW units of the Sulcis power station, in which it is intended to burn local coal with a high sulphur content (7:8% by weight).

Particularly, it is confirmed that the guaranteed 400 mg/Nmc SO_2 outlet concentration for multifuel plants (burning 1% S imported coal and 3% S fuel oil) is met with a wide margin. As far as Sulcis power station FGD system design is concerned, it is also confirmed that the design choice of two absorbing towers in series is a valid one. The characteristics of the gypsum produced during the test comply with the specification required for its use in industrial and civil activities.

The results of the test of the waste water treatment system were also positive.

The test considered only the treatment of the prescrubber blowdown, with coal as a fuel, which represents the most critical fluid for the presence of major concentrations of metallic contaminants.

The microelement concentrations lie within the legal limits even in the 1st stage of the waste water treatment.

The behaviour of a wide range of metal materials, organic coatings and equipment was defined in the different environmental conditions typical of a wet FGD plant. Metallic materials, even the most resistent ones, showed signs of active pitting corrosion and their choice must be carefully made.

Rubber linings gave satisfactory results but it is necessary in the detailed design phase to pay special attention to the suspension transportation pipes in order to prevent the occurrence of the contrary problems of erosion and fouling at local points, due to high or low velocities.

Flake glass vinilesters and fluoroelastomers gave different results depending on the ambient conditions and the geometry of the surfaces to be protected.

As far as future developments are concerned, activities similar to those accomplished in the limestone-gypsum first phase experimentation will be run on both Wellman-Lord and Walther processes. Actually the first ammonium sulphate production has been accomplished and presently quality analysis are being done.

Besides, it is foreseen to run a second phase for the limestone-gypsum process in which the following aspects will be more deeply examined:

- material balances (water and solids);
- validation and determination of the parameters which affect the sulphate and sulphite saturation index;
- evaluation of the hydrocyclone separation system as a function of the particle size of the separated solid phases;
- characterisation of the gypsum with variations in the residence times, the solids content in the recirculation suspension and the pH;
- evaluation by means of dedicated measurement campaigns of the performance of the prescrubber with regard to the removal of dust, Cl⁻ and F⁻
- chemico-physical characterisation of the emitted dust;
- evaluation of the instrumentation in the field for the measurement of emissions;
- construction materials and linings behaviour, particularly in the hot desulphurized duct were a section lined with three nickel alloys and titanium (through wall papering technique), boro-silicate bricks and fluoroelastomers have been installed.

ACKNOWLEDGMENTS

The authors wish to thank Mrs I. Binecchio for her very valuable contribution to the content of the present paper.



Figure 1. Schematics of limestone-gypsum plant

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Figure 2. Schematics of Wellman-Lord plant



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Figure 3. Schematics of Walther plant

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Figure 4. Schematics of desulphurization demonstration plant



Figure 5. Schematics of waste water treatment pilot plant



Figure 6a. SO_2 emissions as a function of L/G ratio for two inlet SO_2 concentrations



Figure 6b. SO_2 emissions as a function of the inlet SO_2 concentration

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		MACROCO	MPONENTS		
Date	CaCO3	MgO	Inert	SiO2	Moisture
	(%)	(⁹ .)	(%)	(%)	(%)
25/01/90	98.9	<0.05	0.44	0.20	0.17
29/01/90	98.9	<0.05	0.50	0.21	0.21
05/02/90	99.1	<0.05	0.30	0.15	0.43
13/02/90	99.3	<0.05	0.40	0.85	0.26
19/02/90	99.1	<0.05	0.61	0.16	0.16
26/02/90	99.1	<0.05	-	0.16	0.16
13/03/90	98.9	<0.05	0.32	0.17	0.28
19/03/90	99.0	<0.05	-	0.14	0.15
28/03/90	98.9	<0.05	0.45	0.18	0.16
	м	ICROCOMPON	IENTS		
	Parameter	Uni	ts Va	lue	
	As	ua	/a <1	.0	
	Se	ug	/ g 0	.3	
	Cu	uq	/ 9 2	.6	
	Pb	uq	/a 0	.9	
	Cr	ug	/g 2	.0	
	Ni	ug	/g 8	.0	
	Tl	ug	/g <1	.0	
	Те	ug	/g <1	.0	
	Cd	ug	/g 0	.1	
	Be	ug	/g <0	.1	
	Hg	ug	/g <0	.2	
	Sb	ug	/g <0	.5	
	Mn	ug	/g 13	.0	
	Zn	ug	/g 97	.0	
L	IMESTONE REACT	TUITY	PART	ICLE SIZE D	ISTRIBUTION
Reactivity (~		Percentage 1	y volume C/	b
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Figure 7. Limestone characteristics

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Figure 8a. Waste water treatment 1ST stage reduction efficiencies



Figure 8b. Waste water treatment reduction efficiency for specific microelements (inlet concentration increased by dosing)



Figure 9. Schematics of the materials position in the demonstration plant

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Table 1

DESULPHURIZATION EFFICIENCY (comparison between design data and experimental results)

Design data for 320 and 660 MWe power stations

1% S coal L/G = 15 SO₂ emissions: 400 mg/Nmc

3% S fuel oil L/G = 19 SO, emissions: 400 mg/Nmc

8% S Sulcis coal L/G = 141st tower SO₂ outlet: 4500 mg/Nmc L/G = 192nd tower SO₂ outlet: 400 mg/Nmc Experimental results

SO, inlet c.a 2000 mg/Nmc L/G = 15 SO₂ emission: <400 mg/Nmc

SO, inlet c.a 4000 mg/Nmc L/G = 19 SO₂ emission: <400 mg/Nmc

SO, inlet c.a 16000 mg/Nmc L/G = 151st tower SO₂ outlet: c.a 5000 mg/Nm L/G = 192nd tower SO₂ outlet: <400 mg/Nmc

Table 2

GYPSUM CHARACTERISTICS

Parameter	Unit of mesaurement	Typical value	Technical specification	l value
CaSO x 2H O	%	98.9	95	min
$C_{3}SO \times 1/2HO$	%	0.03	0.25	max
CaCO	%	0.84	1.5	max
CI Sol ³	%	0.005	0.01	max
Mg Sol	w w	0.002	0.01	max
Na Sol	9%	0.01	0.006	max
Na Sul.	<i>n</i>	83	10	max
Terrorsture	70 07	0.5	10	matr
Impunity		· 0.25		
рн	pH Unit	7.4		
S1	%	0.05		
Al	%	0.03		
Ti	%	<0.01		
Р.	%	-		
Ba	%	< 0.01		
ĸ	%	< 0.01		
Mn	%	< 0.01		
V	92	< 0.01		
70	70 97	< 0.01		
	70 07	0.07		
re	70	< 0.07		
N1	70	< 0.01		

Table 3

SPECIMENS INSTALLED ON THE PLANT - MATERIALS USED

Materials	Cr (%)	Ni (%)	Fe (%)	Mn (%)	Жо (%)	Ti (%)	с (%)	Si (%)	N (%)	P (%)
Aisi 316 L	17.45	11.45	67	1.08	2.2	-	.026	.53	-	.025
904 L. Avesta	19.9	24.8	48.85	1.43	4.3	-	.019	.46	-	.02
31803 Austenoferr.	22.01	5.77	66.82	1.66	2.9	-	.02	.59	.15	.025
31254 6Mo Austenit.	19.84	17.5	55	.8	6	-	.013	.4	.19	.016
Hastelloy C 276	16	61.9	· 5	1	16	-	.02	.01	-	-
Hastelloy C22 (2C224)	22	54	5	5	13	-	.015	.8	-	-
Hastelloy H9M (3H1)	22	47	19	1	9	-	.03	1	-	-
Cronifer 1925 LCN	20.55	24.85	48	1.29	4.7	-	.011	.3	.18	.018
Cronifer 1925 hMo	20.75	25.1	46.57	.82	6.2	-	.004	.33	.21	.019
Nicrofer 4823 hMo	23.0	47	19	.52	6.9	-	.008	.1	-	.017
Nicrofer 6020 hMo	22	63.45	1.76	.06	8.78	.19	.013	.08	-	.003
Nicrofer 5716 hMoW	15.30	59.1	5.69	.25	15.7	-	.005	.04	-	.009
Nicrofer 5621 hMoW	21.45	57.1	3.89	.16	13.7	-	.008	.07	-	.002
Nicrofer 6616 hMo	16.0	67.28	.23	.05	15.9	.28	.005	.03	-	.004
Nicrofer 5923 hMo	24.0	57.3	1.5	.5	16.5	-	.010	.1	-	.015
Uranus 52	24.82	6.37	61.43	1.02	3	-	.018	.45	-	.018
Titanium grade 7	-	-	.3	-	-	98.8	.10	-	.03	-
Titanium grade 2	-	-	.3	-	-	99	.10	-	.03	-
Flakeline 282	Lining	- Flack g	lass Vini	lester						
Fuji Flake	Lining	- Flack g	lass Vini	lester						
Keraflake 6H	Lining - Flack glass Vinilester									

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Keraflake 6R Lining - Flack glass Vinilester

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Table 4

CORROSION RATE IN HOT DESULPHURIZED GAS OUTLET REFERRED TO THE FIRST 500 AND THE FOLLOWING 2500 OPERATING HOURS

Material	500 h mm/year	2500 h mm/year
Carbon steell	0.241	0.459
Aisi 316 L	0.022	0.136
904 L Avesta	0.009	0.049
31803 (austeno ferritic)	0.068	0.161
Hastellov C 276	0.054	0.073
Hastelloy C 22		0.056
Titanium grade 2		0.050

Session 6B

CLEAN COAL DEMONSTRATIONS

RECOVERY SCRUBBER - CEMENT APPLICATION OPERATING RESULTS

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ABSTRACT

The first full scale installation of the Recovery Scrubber, a cost effective flue gas scrubbing process and a DOE ICCT Program project, began operation at the Dragon Cement plant in Thomaston, Maine on December 20, 1990. Waste cement kiln dust containing limestone, alkali, and calcium sulfate was utilized as flue gas scrubbing reagen and high efficiency sulfur dioxide removal was achieved. Processed waste cement kiln dust was chemically altered by the process to make it totally acceptable as raw material feed for the cement kiln, allowing use of the waste and elimination of the need for landfill disposal. Chemical modification of the waste included conversion of gypsum to limestone, carbonation of CaO to CaCO,, and dissolution of alkali salts. By-product potassium sulfate was recovered from solutio by use of waste exhaust gas heat energy for evaporation and concentration of dissolved salts to form crystalline solids as high valued, marketable by-product. System description, operating experience, flue gas scrubbing data, and input/output material analyses, and other potential applications are discussed.

INTRODUCTION

The system, demonstrated as part of the U.S. Department of Energy Innovative Clean Coal Technology Program, at the Dragon Products Company Inc. cement plant in Thomaston, Maine has been described here in previous meetings. A brief overview of the process will provide introduction to the technology. Emphasis in this discussion will be on operating experience and results achieved.

This application of the Recovery Scrubber" addresses flue gas and solid waste pollution problems at New England's only Portland Cement producing plant (not a concrete or "Ready Mix" batch plant). The process, through use of fly ash, biomass ash, cement kiln dust, and other alkali rich materials is applicable to utility boilers, pulp and paper mills, waste incinerators, waste to energy plants, and a variety of industrial boilers and furnaces.

PROCESS DESCRIPTION

The Recovery Scrubber uses alkaline potassium and/or sodium containing wastes as reagent for sulfur dioxide removal from flue gas. These wastes allow production of marketable by-product and generate a tipping fee by their use. There have been questions raised whether sufficient alkali waste is generally available for widespread use of this process. Drawing on the mass of fly ash, biomass ash, and waste cement kiln dust produced annually in the U.S. it is estimated that in excess of 75,000 MW of installed generating capacity, or its equivalent in industrial boiler output, can be efficiently scrubbed.

Sulfur dioxide is hydrated, oxidized, and removed from the flue gas as the dissolved potassium and/or sodium sulfate salt. It is then separated from the remainder of the waste constituents which are insoluble. It is important to note that sulfur is not removed as calcium sulfate or sulfite. Recovery of the dissolved solids is accomplished by evaporation of water from the solution using waste heat extracted from the flue gas. Insoluble waste solids are returned to the cement making process as raw material feed to the cement kiln.

All water and process solids are recycled or used. No waste discharge of any solid or liquid is required.

Calcium sulfate present in the initial waste is dissolved (Ca" and SO, ions in solution) and converted to calcium carbonate precipitate and sulfate in solution (potassium sulfate). Calcium oxide or calcium hydroxide present in the initial waste is also converted to calcium

carbonate.

Figure 1 shows the essential process flows. The flows of: flue gas; solids in slurry; heat; and crystalline precipitate are discussed separately as follows.

<u>Flue_Gas</u>

Flue gas flows through the RECOUPERATOR (A) where heat is extracted, to the REACTION TANK (b) where it is scrubbed, and exits the stack.

Solids in Slurry

Waste cement kiln dust is added to the STORAGE TANK (D) through vortex mixer (C). Slurry is recirculated through the REACTION TANK (B) where it reacts with flue gas. Reacted material is then settled from solution in the FIRST SETTLING TANK (E), rinsed with distilled water, settled from solution again in the SECOND SETTLING TANK (F), and delivered to the cement plant raw material preparation system.

<u>Heat</u>

Heat is recovered from the flue gas stream in the RECOUPERATOR (A), conveyed to HEAT EXCHANGER (G) and to CRYSTALLIZER (H) where it is the energy source for evaporation of water from the potassium sulfate solution.

Crystalline Precipitate

The supernatant liquid (potassium sulfate solution) from the FIRST SETTLING TANK (E) is conveyed to the CRYSTALLIZER (H) and evaporated using heat recovered from the flue gas. Crystalline potassium sulfate is recovered by centrifugation.

INITIAL OPERATION

Weather

Operation began in December 1990, a time which should be avoided for start-up of anything in Maine. All fluid piping, whether for process flows, cooling water, or seal water in slurry pumps, must be heat traced or otherwise protected from freezing. All inadequately heated pumps and pipes were quickly identified.

Seal Water

Construction continued during start-up operation in order to complete detail work. The work force became a valuable asset for correcting problems that were quickly apparent. The first malfunction was loss of seal water flow to a slurry pump. Because of the extremely abrasive nature of the slurry produced from cement kiln dust, a momentary interruption of seal water flow caused immediate failure of the shaft seal and shut down of the pump. Two seals were lost before constancy of seal water pressure was established.

<u>Motor Bearings</u>

A forced draft fan moving flue gas from the cement plant through the scrubbing system is the largest power consumer in the process. During the second week of operation a motor bearing failed causing failure also in one fan bearing. The project owner had instructed the contractor to provide the lowest cost (used) motor available. The unit supplied did not meet design specifications but was installed by the contractor as a cost saving measure. The ultimate cost of the failure, in equipment, lost time, and manpower could have covered the cost of a new motor. Replacement required four weeks.

General Piping and Pumping

Other minor problems were encountered in piping and pumping equipment and solved with little difficulty. Operation continued and adjustments to the process flows were made to optimize conditions. In June 1991 corrosion of a heat exchanger shell required replacement of the shell material with a more resistant alloy. Steel pipes leading to and from the shell were changed to high density polyethylene at the same time.

Cooling Water

Cooling water is required to condense water vapor generated in the evaporator, thereby maintaining vacuum. During June and July it became apparent that the cooling pond was not adequate. It was replaced with a gravity flow spray cooling system which has performed well since that time.

Slurry Preparation

Although the process converts gypsum to calcite (limestone), the conversion does not take place until the waste, which contains gypsum, or more accurately calcium sulfate, comes in contact with the flue gas.

When the waste cement kiln dust is first mixed with water the hydration of calcium sulfate already present in the waste forms gypsum crystals. Material precipitates onto pipe interior surfaces, gradually reducing flow until the pipe must be cleaned to allow continued operation.

The initial slurry mixing and transport system consisted of a mix tank where dust and wate. were introduced and agitation was provided. Slurry was then pumped to the reaction tank for use in scrubbing. Build-up of gypsum in the pipes necessitated a change.

The new system is called a vortex mixer. A cylindrical tank with a conical bottom is used. Slurry, which has been previously reacted, and therefore has no calcium sulfate left to be precipitated, is pumped into the top of the tank tangential to the tank walls. It flows around the tank circumference and spirals down toward the conical bottom, accelerating as it flows out. The reacted slurry serves to coat the tank with a layer of fluid that effectively prevents fresh dust, which is added at the center of the tank top, from coming in contact with the walls of the mixer. Mixing is thorough because of the high flow and turbulence in the tank. The

mixture exits the vortex mixer into the reaction tank where it joins a 9,000 GPM flow passing into a 72,000 gallon reservoir of reacted slurry. There have been no slurry handling problems since the change to this system.

Gas Distribution

A major problem in gas handling has existed throughout much of the operating period. Operation of the reaction tank, which is the system providing contact between gas and scrubbing fluid, depends on there being even distribution of gas throughout the plenum under the bubbling tray reactor. Any zones or pockets of low gas pressure under the tray, caused by inadequate gas distribution, result in downward flow of scrubbing liquid through the tray and eventual plugging of the tray holes. This causes a rise in operating pressure and, therefore, operating cost and is not acceptable for long term use.

Specifications in the process design called for appropriate duct and plenum design to assure gas distribution to within a set tolerance, measured in inches of water pressure, at any point on the under side of the tray. It is presumed that the initial design, which was provided by the design engineers engaged for the overall design work, would have achieved that distribution. Unfortunately, we will never The initial design was changed, as a cost saving measure, by know. the construction contractor. The change was not requested or approved by, or reported to either the owner, who acted as project manager, or to Passamaquoddy Technology, the process technology provider. As a consequence, the components of the 24 foot by 48 foot reaction tank were shop fabricated, shop coated with \$15 per square foot corrosion protection lining, and delivered to the construction site for erection before the changes were discovered. It was decided at that time to proceed with erection and to correct the inadequacies by retrofit changes within the ducting and plenum, rather than undergo the high cost to redesign, fabricate, and coat all new components.

Operation of the system has continued through testing and measurement of the gas flow characteristics and its interaction with the slurry flow on top of the tray. Plugging of the tray has been a continuing problem, causing repeated stoppages for cleaning. Continued operation has provided the necessary data for design of the retrofit fix, and has also allowed assessment of the performance of the rest of the scrubbing system, that is, scrubbing efficiency, adequacy of waste kiln dust renovation, heat recovery and evaporator function, and by-product potassium sulfate quality.

Gas flow distribution was corrected by addition of turning vanes (part of the original design) in the duct leading to the plenum. These turning vanes have distributed the gas over the entire six foot height of the entry duct and reduced inlet velocity by a factor of twelve. Also inserted into the duct were straightening vanes downstream of the turning vanes. These conduct gas toward two additional vane sets which complete the gas redistribution. Operation is now not complicated by flow through the tray and hole plugging.

Tray Flatness

Proper performance of the bubbling tray is not only dependant on proper gas distribution. It is also necessary to have equal slurry depth over the entire tray surface. The tray must be flat. Initial specification of flatness to within 1/8 inch was not met by the construction contractor. Mapping of tray topography resulted in corrective work that produced an even worse condition. The tray was made flat on the fourth try and problems resulting from unequal fluid depth have been eliminated.

<u>Heat Recovery</u>

Waste heat is recovered from flue gas for use in evaporation of water in the potassium sulfate recovery system. There have been no problems with the heat recovery and reuse system other than the previously referenced change in heat exchanger shell material.

K,SO, Evaporation

Production of potassium sulfate crystals from the alkali sulfate extracted from the waste cement kiln dust depends on evaporation of solution by use of recovered waste heat. Recovery and use of waste heat has worked well. The energy supply is more than sufficient for the evaporation needs.

K,SO, Crystal-Liquid Separation

Crystals of potassium sulfate form in the evaporation system as the potassium sulfate solution becomes saturated by evaporation of water. Crystals of any other dissolved solids present will also form. One constituent present in low concentration is calcium sulfate. Because potassium sulfate concentration in the liquid during the early operation was low, large volumes of water had to be evaporated to bring the solution to saturation. The crystals formed, therefore, included an accumulation of calcium sulfate.

Product crystals are removed by centrifugation of the liquid/crystal slurry. A moisture content of 12 percent in the product is desirable. The calcium sulfate crystals included in the suspended solids, however, are very fine and do not dewater well. Fifteen percent moisture in the centrifuge output was the lowest achieved. Therefore, pelletization of the final product was not performed. During later operation the initial concentration of potassium sulfate solution was increased, thereby increasing the relative concentration of potassium sulfate crystals that will be produced.

CONTINUED OPERATION

Operation has continued, with interruptions, since December 1990. Operation was interrupted during equipment changes as noted above. Operation was also interrupted by several extended periods of down-time on the cement kiln for required maintenance. Total operating time from January 1991 to October 1991 was 6,100 hours. The kiln will not operate during much of November, 1991 and, therefore, total operating time for 1991 is expected to be 6,800 hours. Operating time in 1992 is expected to be 6,000 to 7,000 hours.

OPERATING RESULTS

Flue Gas Scrubbing-Sulfur Dioxide

Average scrubbing efficiency is 92 percent. There have been periods during which the scrubbing efficiency has been 95 to 98 percent. The reason for the difference is the magnitude of the SO, input concentration. If the SO, concentration in the output scrubbed gas is 5 parts per million when the unscrubbed input gas contains 250 parts per million the removal efficiency is 98 percent. For the same emission, if the input SO, concentration is 25 parts per million the removal efficiency is only 80 percent. In either case, however, removal of all but 5 parts per million, when burning 11 tons per hour of 2.6 percent sulphur coal, is effective control. A coal fired cement kiln exhibits significant variation in flue gas composition because of process related variables. Normal unscrubbed SO, output concentrations may range from 10 parts per million to as high as 800 or 1,000 parts per million. The concentration in the scrubbed output stream from the Recovery Scrubber is frequently in the range of 1 part per million to 10 parts per million.

Figure 2, <u>Typical Scrubber Performance</u>, compares the records from continuous NO, and SO, monitors for the "before" scrubbing and "after" scrubbing emissions data taken during October 1991. Note the system purge and self calibration that occurs daily at midnight.

Flue Gas Scrubbing-Nitrogen Oxides

Removal efficiency for nitrogen oxides (NO₁) has been 5 to 25 percent (see Figure 2 for comparison of NO₁ emissions before and after scrubbing. Variability in NO₁ removal is probably due to changes in burning conditions within the kiln and the resulting proportions of NO₁ vs. NO in the flue gas stream.

Flue Gas Scrubbing-Carbon Dioxide

Use of carbon dioxide from the flue gas for recarbonating calcined lime and for carbonating calcium in solution which has been derived from dissolved gypsum results in scrubbing of carbon dioxide. In this, cement kiln application the exit carbon dioxide concentration has been reduced by 3 percent. In boiler applications the Recovery Scrubber" may remove up to 15 percent of the available carbon dioxide depending on the chemical nature of the waste used as scrubbing reagent.

Solid Waste Recycling-Cement Industry

One of the major economic and environmental benefits provided by the process is the opportunity to recycle solid waste. In most boiler applications use of waste as reagent will provide a significant source of income from tipping fees. In the cement application the process uses waste from the cement making operation, and so no tipping fee is generated. Use of waste from cement making as scrubbing reagent in this process, however, provides significant other savings to the cement plant.

Waste cement kiln dust (CKD) is produced at the Dragon cement plant

at the rate of 250 tons per day. The cost in raw material, landfilling expense, quarry lifetime, environmental controls, and handling is very large. CKD is wasted because it contains excess potassium and sulfate. Removal of those materials from the waste leaves calcium, silica, iron oxide, and alumina, the normal constituents of cement kiln raw material input. Table 1, <u>Raw Material</u> and <u>Waste Analyses</u>, shows analyses for a.) normal kiln feed, b.) CKD (waste cement kiln oust) as produced from the kiln, c.) reacted CKD after use and chemical modification in the scrubber, and d.) combined kiln feed produced by adding reacted waste CKD to normal raw feed in the proportions they are routinely produced.

The essential requirements for renovation and reuse of CKD are that potassium be reduced to near normal kiln feed levels, and that sulfate be significantly reduced. Table 1 shows that return of reacted waste CKD to kiln feed provides excellent raw material.

Solid Waste Recycling-Other Industries

Ash from combustion of biomass, fly ash from combustion of coal, and other caustic wastes may also be used as scrubbing reagent. In each of these, soluble alkali will be extracted as the sulfate salt while calcium compounds, for example gypsum, will be dissolved and reprecipitated as the calcium carbonate plus sulfate in solution. Use of these wastes as reagent, therefore, provides a spent reagent which at best will be used as raw material feed to a cement plant, and at worst will be landfilled as material free of soluble alkalis and leachable compounds.

<u>By-Product Production-Potassium Sulfate</u>

Cement kiln dust at the Dragon cement plant contains 3 to 5 percent K₂O as potassium oxide or potassium sulfate. During the scrubbing process the potassium is combined with sulfate scrubbed from the flue gas stream. Because the sulfate salt has high solubility it is easily separated from the various insoluble solids in the CKD. Use of heat recovered from the flue gas for evaporation of water allows economical recovery of solid crystalline potassium sulfate.

Table 2, <u>Potassium Sulfate Analysis</u>, gives the composition of the recovered solid. The sample represented here was taken early in the crystallizer operating history and includes material added to the crystallizer system as seed crystals needed to provide nucleation sites and promote growth of a large number of crystals. The added seed crystals were calcium sulfate. Therefore, both the calcium and the sulfate content of the recovered precipitated solids are higher than would be expected during normal production. Potassium sulfate comprises approximately 61 percent of the total sample. Material produced at a later time, after initial seed crystal material has been processed out of the system, is expected to be 78 to 80 percent potassium sulfate.

<u>By-Product Production-Distilled Water</u>

Evaporation of potassium sulfate solution for recovery of potassium sulfate crystals also yields distilled water. In the Dragon cement plant application the distilled water is returned to the process as part of the make-up water supply. In the future it will be sold and replaced in the process with other liquid effluent needing treatment. For other applications the distilled water may be sold or used as boiler make-up supply.

APPLICATIONS IN OTHER INDUSTRIES

References have been made to the applicability of the process to other industries throughout this paper. Examples of some specific applications which are currently under discussion may be helpful.

Pulp and Paper Industry

Many pulp mills now burn their waste biomass in order to avoid its landfill disposal and create instead an ash disposal problem. Use of biomass ash, which typically has significant potassium content, in the same manner as CKD in the scrubbing system can provide the scrubbing of flue gas from oil or coal fired boilers and income from the potassium sulfate produced.

The case for one mill currently being evaluated is instructive. They will scrub sulfur dioxide from flue gas allowing their continued use of 2.5 percent sulfur oil; consume ash which now costs \$1 million per year to landfill;

transport all spent ash to a cement plant for use there as kiln feed; and produce both potassium sulfate and distilled water as by-products. The process would generate no waste and provide in excess of \$6 million per year in combined savings and income while eliminating the mill's need to landfill ash.

Waste To Energy Industry

Generally the ash from municipal trash incinerators is deficient in alkaline material and will not be sufficient for complete reaction with the acid gas constituents. If biomass ash is added in some proportion the process works as in either pulp and paper or cement applications. The recovered soluble salts will be sodium chloride with some amount of potassium sulfate and potassium chloride rather than just potassium sulfate. The value of those recovered materials will, therefore, be lower.

Spent ash from the process will be useful in the manufacture of cement. It may contain small quantities of various heavy metals, but will consist primarily of silica, alumina, calcium carbonate, and iron oxide which are the principal required ingredients for cement kiln raw material input. If a cement kiln is not available to receive spent ash the material may be landfilled at relatively low cost. Low cost disposal is possible because the ash will no longer contain soluble materials. The leaching of toxic metals into the ground water table will no longer be a concern.

Utility Industry

A waste to energy plant now being evaluated will use ash from the waste incinerator, mixed with an equal mass of biomass ash, as scrubbing reagent. Alkali metal sulfate and chloride salts will be produced. Spent ash will be used as raw material input to a cement kiln.

Table 1

	d	þ	c Reacted	d Combined Waste
Oxide	Kiln Feed	Waste CKD	Waste CKD	and Kiln Feed
SiO ₂	21.3	18.7	19.9	21.2
A]_0_	4.8	3.7	6.0	4.9
Fe ₂ O ₃	2.1	1.8	2.7	2.1
CaO	65.6	54.5	62.4	65.3
MgO	4.2	2.8	4.3	4.2
SO₃	0.46	9.7	2.5	0.56
к <u>-</u> 0	1.07	8.6	1.6	1.1
Nago	0.2	0.7	0.2	0.2

RAW MATERIAL AND WASTE ANALYSES

Note: The balance of material in each analysis is carbon dioxide as present in calcium carbonate.

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Table 2

POTASSIUM SULFATE ANALYSIS

Chemical Species	Concentration (Percent)
K ₂ O	33.40
Na ₂ 0	0.12
CaO	12.12
SiO ₂	1.16
Al ₂ O ₃	0.26
MgO	1.63
CO3	8.07
SO₄	44.6

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Figure 2



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The NOXSO Clean Coal Technology Demonstration Project

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ABSTRACT

The NOXSO Clean Coal Technology Project is a 115 MW demonstration unit to be located at Ohio Edison's Niles Station. The project is co-funded by the U.S. Department of Energy (DOE) and a consortium of companies assembled by NOXSO including NOXSO Corporation, W.R. Grace & Co., MK-Ferguson Company, Ohio Edison, the Ohio Coal Development Office (OCDO), the Electric Power Research Institute (EPRI), the Gas Research Institute (GRI), and the East Ohio Gas Company. The DOE manages the project through the Pittsburgh Energy Technology Center (PETC). Both the NOXSO Process and its application to the Niles Plant are described in this paper. The status of the NOXSO Proof-of-Concept Pilot Plant is updated, and its impact on the Niles Demonstration Plant design is described. Finally, the NO_x recycle test program that is being performed concurrently with the pilot plant operations is discussed.

INTRODUCTION

The NOXSO Process is a post-combustion flue gas treatment technology that removes both sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from the flue gas of a coal-fired utility. Under development since 1979, the process is in the final three stages of commercialization. The first stage is a 5 MW Proof-of-Concept (POC) pilot plant that was built at Ohio Edison's Toronto Station in Toronto, Ohio (construction was completed in July of 1991). The second stage is a 500 lb/hr (coal feed rate) test of the NO_x recycle concept using a Babcock & Wilcox (B&W) cyclone combustor that will be conducted concurrently with the POC pilot tests. The third and final stage is a 115 MW full-scale demonstration plant to be built at Ohio Edison's Niles Station in Niles, Ohio. The 115 MW Demonstration Project will be cost shared between the Department of Energy through the third round of the Clean Coal Technology program by

a cooperative agreement between DOE and MK-Ferguson. DOE will provide 50% of the funds necessary to build and operate the plant while the remaining 50% will be covered by NOXSO, Grace, MK-Ferguson, Ohio Edison, OCDO, EPRI, and GRI. DOE will manage the demonstration project through the Pittsburgh Energy Technology Center (PETC). In this paper we describe the NOXSO Process as it will be implemented at Ohio Edison's Files Station and the current schedule for design, construction and operation of the 115 MW facility. We also describe the test programs planned for the POC pilot plant that will provide the final design and scale-up data necessary for the Niles Plant. Also, NO_x recycle data obtained previously during the 3/4 MW test program is described and the test program planned for the B&W NO_x recycle tests is described.

HOST SITE DESCRIPTION

The Niles Station is located on the Mahoning River in northeastern Ohio and is shown in Figure 1. It has a net demonstrated power production capability of 246 MW. Two coal-fired units produce 108 MW net each (115 MW gross each) and 30 net MW is obtained from a combustion turbine which is used for peaking purposes. At full load, the plant fires 97 tons of bituminous coal per hour. The average annual coal quality analyses for 1987 and 1988 are shown in Table 1. Of all the coal received at the Niles Plant, 60 percent is typically Ohio coal and 40 percent is non-Ohio (western Pennsylvania).

Both process and cooling water are withdrawn from the Mahoning River at a rate of 140,550,000 gallons per day. Ample water supply is available for the NOXSO Process requirements which amount to less than 200,000 gallons per day. NOXSO electricity requirements will be provided by the Niles plant and are estimated to be about 4% (or 4.6 MW) of the gross power output of Unit #1.

NOXSO PROCESS DESCRIPTION

The NOXSO demonstration plant will be retrofitted to Niles unit #1, a pulverized coalfired cyclone boiler with a rating of 115 MW (gross) and 108 MW (net). The tie-in point will be the flue gas ductwork between the existing electrostatic precipitator (ESP) and the plant stack. The NOXSO Process can operate either upstream or downstream of the particulate collection device; however, the current tie-in point was chosen to minimize the effect on ESP performance. The demonstration plant will occupy an area 120 feet by 150 feet. A description of the process technology is given below and a process flow diagram is shown in Figure 2. Flue gas from unit #1 will be combined with the Claus Plant tail gas stream and ducted to the NOXSO flue gas booster fan. Downstream of the flue gas fan, the flue gas is cooled by vaporizing a stream of water sprayed directly into the ductwork. After being cooled, the flue gas is passed through two parallel fluidized bed adsorbers where SO₂ and NO₄ are simultaneously removed using a high surface area γ -alumina sorbent impregnated with an alkali material. The cleaned flue gas is returned to the plant ductwork and exits through the stack.

The sorbent is removed from the adsorbers by an overflow pipe, and is then transported by one of two dense-phase pneumatic conveyors to the sorbent heater. Fresh make-up sorbent is added downstream of the adsorbers so that it may be calcined in the sorbent heater before making its first pass through the adsorbers. The sorbent heater is a three-stage fluidized bed where a hot air stream is used to raise the sorbent temperature to $1120^{\circ}F$. During the heating process, NO_x and loosely bound SO₂ are desorbed and transported away in the heating gas stream. This hot air stream is recycled back to the cyclone burners and replaces approximately 38% of the required combustion air. A portion of the recycled NO_x is converted to nitrogen (N₂) and either carbon dioxide (CO₂) or water (H₂O) by reaction with free radicals in the reducing atmosphere of the combustion chamber. NO_x recycle studies were performed during a previous NOXSO test program (a 3/4 MW pre-pilot scale test) and additional NO_x recycle studies are currently under way. These tests are discussed in more detail below.

Once the sorbent reaches a regeneration temperature of 1120° F, it is transported by means of a J-valve to a moving bed regenerator. In the regenerator, sorbent is contacted with reformed natural gas in a countercurrent manner. The reformed natural gas reduces sulfur compounds on the sorbent (mainly sodium sulfate) to primarily SO₂ and hydrogen sulfide (H₂S) with some carbonyl sulfide (COS) also formed. Approximately 20% of the sodium sulfate (Na₂SO₄) is reduced to sodium sulfide (Na₂S) which must subsequently be hydrolyzed in the steam treatment vessel. A moving bed steam treatment reactor follows the regenerator, and a concentrated stream of H₂S is obtained from the reaction of steam with Na₂S. The off-gases from the regenerator and steam treater are combined and sent to a Claus Plant. Elemental sulfur is the end product from the Claus Plant. The tail gas stream from the Claus Plant is passed

through an incinerator to convert all remaining sulfur compounds to SO_2 , cooled to about $350^{\circ}F$, and recycled to the flue gas stream prior to entering the adsorbers.

From the steam treatment vessel, the sorbent is transported by means of another Jvalve to the sorbent cooler. The cooler is a three-stage fluidized bed using ambient air to cool the sorbent. The warm air exiting the cooler is further heated by a natural gas fired in-duct heater before being used to heat the sorbent in the fluidized bed sorbent heater. The sorbent temperature is reduced in the cooler to the adsorber temperature of 250°F. Sorbent from the sorbent cooler overflows into a surge tank. The surge tank is used as a source and sink for sorbent to maintain constant bed levels in the other process vessels. From the surge tank, sorbent is transported to the adsorbers again by means of a J-valve thus completing one full cycle.

NILES DEMONSTRATION PLANT SCHEDULE

Much of the information required to design the full-scale demonstration plant is already available through earlier NOXSO test programs. The POC pilot plant will supply additional design data and scale-up information. Design of the Niles demonstration plant will begin during the operation period of the pilot plant. Thus, pilot plant data will be used to refine the Niles design. Preliminary design work on the Niles plant is scheduled to begin in September of 1991. Detailed design will be completed in October of 1992, at which time the POC test program will be complete. Plant construction will then begin in November of 1992 and run through March of 1994. The operations period will last for a period of 24 months through March of 1996. At the completion of the operation period, Ohio Edison will have the option to purchase the unit for continued operation. The schedule is summarized below in Figure 3.

Data for the Niles plant detailed design will come from three sources. The first source is previous NOXSO test programs. NOXSO Corporation has conducted laboratoryscale tests, pre-pilot scale tests (3/4-MW), and a life cycle test of the NOXSO Process. Each of these test programs have provided data useful in process design, and the results of each test program have been reported previously (1,2,3). The second source of design information is the POC pilot plant which will provide additional design and scale-up data as well as materials selection data through implementation of a corrosion test program. The third source of design information

will be from a NO_x recycle test program to be conducted at the Babcock & Wilcox (B&W) Research Center in Alliance, Ohio. The POC test program and NO_x recycle tests are discussed below.

POC PILOT PLANT TEST PROGRAMS

The POC pilot plant began cold start-up in July of 1991. Cold start-up was the first of three test series. The second test series is a hot start-up with inert gases and is currently in progress. The third test program is a set of parametric tests with the system fully operational, i.e., using flue gas in the adsorber and reactive (rather than inert) gases in the regenerator. There are thirty parametric tests planned and the process parameters being varied are sorbent circulation rate, adsorber settled bed height, regenerator solids residence time and adsorber gas flow rate. The parametric tests will be followed by a duration test at optimum process conditions as defined by the parametric tests. The results from these tests will be included in the detailed design of the Niles facility.

The first test program, cold start-up, was designed to verify the proper operation of each piece of equipment in the plant. After initial shakedown tests, sorbent was circulated through the system continuously for 43 hours. This test revealed the need to modify vessel internals in the staged fluid beds to achieve the maximum required sorbent circulation rates. After the modifications were completed, a hot sorbent circulation test was performed for 38 continuous hours. The hot circulation test showed that the fluid bed residence time needed to be increased to achieve adequate heat transfer in the sorbent heater and sorbent cooler. After these additional modifications were completed, a second hot sorbent circulation test was initiated. This current test program includes gas tracer studies and operator testing of the distributed control system trip matrix. Following this final hot inert test, flue gas will be treated in the NOXSO adsorber and the entire system will be run with reactive gases.

A corrosion test program is also planned during POC plant operation. Corrosion test spools containing metal test samples will be installed in seven different locations to assess corrosion rates in different gas and sorbent environments. Coupon weights and dimensions are measured before and after exposure, and these values are used to calculate corrosion rates of each material. Table 2 lists corrosion spool locations

at the POC and the process components that will experience the same environment. Figure 4 is a photograph showing a corrosion test spool prior to installation at the pilot plant. The materials to be tested on each corrosion spool of coupons are listed below in Table 3.

The expected duration of the entire POC test program is about 10 months. In this relatively short period of time, it may be difficult to distinguish corrosion rates between some of the materials tested. Therefore, concurrently with the POC test program, there will be an accelerated corrosion test program will be conducted by an independent laboratory. The accelerated corrosion tests will consist of exposing corrosion coupon spools to simulated regenerator environments. A total of six tests will be conducted. The tests will be at three different temperatures and two different gas compositions. The reactor tube containing the corrosion test spool will also be packed with sulfated NOXSO sorbent to simulate the regenerator vessel environment. The test matrix is listed in Table 4. Each test condition will last for three weeks of continuous exposure. The results of these two corrosion test programs will be used to select materials of construction for the Niles demonstration plant.

The NO_x recycle concept will not be tested at the pilot plant because the POC only uses a slipstream (12,000 SCFM) of flue gas. However, simulated NO_x recycle tests were conducted during the pre-pilot scale tests conducted at the DOE's Pittsburgh Energy Technology Center. These tests showed that from 65% to 75% of the recycled NO_x was destroyed in the combustion chamber (2). Additional NO_x recycle tests are planned at the B&W Research Center. B&W has a small boiler simulator (SBS) that mimics the operation of the Niles cyclone burners. A schematic of the B&W SBS is shown in Figure 5, and a comparison of operating parameters with a typical cyclone fired boiler is shown in Table 5.

The NO_x recycle tests are conducted by injecting bottled NO_x compounds into the coal combustion air in concentrations that reproduce the NO_x concentration in the sorbent heater off-gas.

The test program at B&W will consist of shakedown, baseline, simulated NO recycle, simulated NO₂ recycle, and novel concept tests. The shakedown tests are designed to

optimize furnace operation including cyclone burner settings, injection system equipment, and sampling instrumentation. Following the shakedown tests, baseline tests will be conducted to establish NO_x emission levels at three loads and three excess air levels without NO_x reinjection. Once the baseline NO_x emissions have been quantified, NO_x recycle tests will begin. First, NO will be injected in multiples of 0.5, 1.0, 1.5, and 2.0 times the baseline NO_x production rate. The first injection point will be in the primary combustion air and tests will be run at the four NO_x recycle rates, with three furnace loads, and three excess air levels for a total of 36 tests. NO will then be injected in the secondary air stream using the same four NO recycle rates, with two furnace loads and two excess air levels for a total of 16 additional tests. The same set of tests will be repeated (two injection points, four NO_x recycle rates, two loads, and two excess air levels) using NO_x injection in place of NO. An allowance for 15 additional tests has been included in the test plan. These tests could be used to examine novel ideas for the enhancement of NO_x destruction such as the addition of methane to the NO_x recycle stream.

SUMMARY

NOXSO Corporation's Clean Coal technology project is a 115 MW demonstration of the NOXSO flue gas treatment process. The host site for the project is Ohio Edison's Niles station located on the Mahoning River in Niles, Ohio. Preliminary design for the demonstration unit is scheduled to begin in late 1991 with detailed design being completed in late 1992. Plant construction should then be completed in early 1994 when operation will begin. Much of the necessary design data has been acquired through previous experimental test programs. The final design data required will be obtained from NOXSO's POC pilot plant, and the NO_x recycle studies will get under way at B&W's Research Center using their small boiler simulator.

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Figure 1. Ohio Edison's Niles Station, Niles, Ohio.



Figure 2. NOXSO Process Flow Diagram.

	1991	1992	1993	1994	1995	1996
Design						
Construction		-				
Operation & Test						

Figure 3. Clean Coal III Project Schedule.



Figure 4. Photograph of Corrosion Spool.



Figure 5. Babcock & Wilcox's Small Boiler Simulator (SBS) Schematic

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Table 1 Annual Coal Quality Analysis for the Niles Plant (1987 and 1988)								
	1987	1988						
Moisture (%)	7.82	7.51						
Ash (%)	11.72	11.98						
Sulfur	3.17	3.24						
Heating Value (Btu/lb)	11,694	11,735						

Table 2 Location of POC Corrosion Test Spools and Process and Components Affected						
Spool Location	Components					
# 1, Adsorber Inlet	Ductwork between spray cooler and adsorber, base of adsorber, and adsorber gas distributor.					
<pre>#2, Adsorber Outlet (top of adsorber)</pre>	Adsorber (above distributor), adsorber cyclone, and ductwork between adsorber and stack.					
# 3, Air Heater Outlet	Air heater, duct between air heater and sorbent heater, bottom gas distributor in sorbent heater, and sorbent heater.					
#4, Regenerator (gas space)	Regenerator, piping between regenerator and incinerator, and control valves on piping.					
#5, Regenerator (sorbent bed)	Regenerator, sorbent transfer line from sorbent heater to regenerator, and transfer line from regenerator to steam treater.					
# 6, Steam Treater (gas space)	Steam treater, piping between steam treater and incinerator, and control valves on piping.					
#7, Steam Treater (sorbent bed)	Steam treater, vessel surface in contact with sorbent.					

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Table 3 Materials to be Tested During The POC Corrosion Test Program								
	Spool No.						Accel-	
Materials	1	2	3	4	5	6	7	erated Tests
STAINLESS STEEL								
304 SS	x	x	x	x	x	x	x	x
304H SS			x	x	x	x	x	x
316 SS	x	x	x	x	x	x	x	x
446 SS	x	x	x	x	x	x	x	x
1010 CS	x	x	x	x	x	x	x	x
HASTELLOYS								
C-276	x	x						
C-22	x	х						
C-4	x	x						
304 SS (Alonized)			x	x	x	x	x	x
304H SS (Alonized)			x	x	x	x	x	x
316 SS (Alonized)			x	x	x	x	x_	x
1010 CS (Alonized)			x	x	x	x	x	x
304 SS (Chromized)			x	x	x	x	x	x
1010 CS (Chromized)			x	x	x	x	x	x
OVERLAYS								
304 SS with 556 SS			x	x	x	x	x	x
304 HS with HR-160			x	x	x	x	x	x
304 SS with 446 SS			x	x	x	x	x	x
304H SS with 446 SS			x	x	x	x	x	x
SPRAYCOAT, AFTER WELDS								
Alonized 304 SS with 446 SS		-	x	x	x	x	x	x
Alonized 304H SS with 446 SS			x	x	x	x	x	x
304 SS with 446 SS			x	x	x	x	x	x
304H SS with 446 SS			x	x	x	x	x	x
Haynes 556	x	x		[
Haynes HR-160	x	x	ſ					
Carpenter 20Cb3	x	x	[1	
Јевеор ЈS276	x	x		Ī				
Inco C-276	x	x	<u> </u>	1	<u> </u>			
Inco 625	x	x	1				<u> </u>	
Teflon	x	x						

Table 4 Accelerated Corrosion Test Conditions						
Test No.	Temp. (°F)	Gas Environment				
1	1200	40%CO, 40%SO ₂ , 10%H ₂ O, 10%CH ₄				
2	1400	40%CO, 40%SO2, 10%H2O, 10%CH4				
3	1600	40%CO, 40%SO ₂ , 10%H ₂ O, 10%CH ₄				
4	1200	50%H2S, 50%H2O				
5	1400	50%H ₂ S, 50%H ₂ O				
6	1600	50%H25, 50%H20				

Table 5 Comparison of Operating Parameters for the B&W SBS and a Typical Full-Scale Cyclone Burner							
Parameter	SBS	Typical Cyclone Burner					
Cyclone Temperature	>3000°F	>3000°F					
Residence Time at Full Load	1.4 sec	0.7-2 вес					
Furnace Exit Gas Temperature	2265°F	2200-2350°F					
NO, Level	900-1200 ppm	600-1400 ppm					
Ash Retention	80-85%	60-80%					
Unburned Carbon	1% in ash	1-20%					
Ash Particle Size	6-8 microns	6-11 microns					

Economic Comparison of Coolside Sorbent Injection and Wet Limestone FGD Processes

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ECONOMIC COMPARISON OF COOLSIDE SORBENT INJECTION AND WET LIMESTONE FGD PROCESSES

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ABSTRACT

The Coolside process is a duct sorbent injection process developed for retrofit SO_2 control on a coal-fired boiler. The process is attractive for retrofit applications because of low capital cost, low space requirements, and short procurement-through-installation time in comparison to wet flue gas scrubbers. The Coolside demonstration was conducted from July 1989 to February 1990, on the 104 MW Unit No. 4 Boiler 13 at the Ohio Edison Edgewater Station, Lorain, Ohio, under the partial sponsorship of the U.S. Department of Energy Clean Coal Technology Program. The Edgewater demonstration achieved 70 percent SO_2 removal while burning 3 percent sulfur coal. Short-term process operability was demonstrated during continuous process operations under steady state conditions for up to eleven days. The demonstration provided information on desirable process equipment design improvements which would be required for commercial operation. This paper analyzes the factors which influence Coolside process economics, i.e., sorbent price, utility plant capacity factor, book life, and waste disposal cost. The optimized Coolside process and wet limestone FGD capital and total levelized annual costs are compared as functions of boiler capacity and coal sulfur content.

INTRODUCTION

In 1987, Babcock & Wilcox (B&W) was awarded a Cooperative Agreement under the DOE Clean Coal Technology Program to demonstrate the Coolside and LIMB sorbent injection processes at the Ohio Edison Edgewater Station. In addition to DOE, project financial participants included B&W, Consolidation Coal Company, Ohio Edison Company (host utility), and the State of Ohio Coal Development Office. This paper describes the Coolside process results. The Coolside process demonstration was conducted from late July 1989 to mid February 1990. During that period, Edgewater Unit 4, Boiler 13 was burning compliance (1.2 to 1.6 percent sulfur) and non-compliance (2.8-3.2 percent sulfur) coals. The objectives of the full-scale test program were to verify short-term process operability and SO_2 removal, to determine factors which could affect long-term process operability, and to develop a Coolside process design and performance data base to establish process economics. The demonstration program included sorbent once-through and simulated recycle operations. Key process variables (Ca/S mole ratio, approach to adiabatic saturation temperayure (ΔT_{a}) , Na/Ca mole ratio) were evaluated in short-term (6-8 hr) parametric tests and longerterm (1-11 day) process operability tests. Two different commercially available hydrated limes were tested. Prior to the demonstration, pilot-scale tests were conducted to select hydrated limes to be tested and to develop Edgewater site-specific process performance data. The pilot data were used to develop the demonstration test program and aided in interpreting the full-scale results. This paper discusses a commercial Coolside process design, the factors which influence Coolside process economics, and the potential Coolside process market (boiler capacity and coal sulfur content).

General Process Description

The Coolside desulfurization technology involves pneumatic injection of dry hydrated lime (sorbent) into the flue gas downstream of the air preheater, followed closely in distance by flue gas humidification using water sprays. Flue gas SO₂ is captured by reaction with the entrained sorbent particles in the humidifier and with the sorbent collected in the particulate removal system. The humidification water serves two purposes. First, it activates the sorbent to enhance SO₂ removal and, second, it conditions the particulate matter to maintain efficient electrostatic precipitator (ESP) performance. Spent sorbent is removed from the gas along with fly ash in the existing particulate collector (ESP or baghouse). The sorbent activity can be significantly enhanced by dissolving sodium containing additives such as sodium hydroxide (NaOH) or sodium carbonate (Na₂CO₃) in the humidification water.^{1,2} Because of the relatively short demonstration period, NaOH was used as the additive in the Edgewater demonstration. Sorbent recycling can be used to improve the sorbent utilization if the particulate collector can handle the resulting increased solids loading.
Edgewater Coolside Performance

The Edgewater Coolside program demonstrated that the Coolside process can routinely achieve 70 percent SO₂ removal at the design conditions of 2.0 Ca/S mole ratio, 0.2 Na/Ca mole ratio of additive, and 20°F approach to adiabatic saturation temperature using commercially-available hydrated lime. Coolside SO₂ removal is dependent on Ca/S mole ratio, Na/Ca mole ratio, approach to adiabatic saturation (ΔT_s), and physical properties of the hydrated lime. A detailed discussion of the effects of these variables is presented elsewhere.^{3,4}

Although the data are limited, sorbent recycle showed significant potential to improve sorbent utilization. The observed SO₂ removal with recycle sorbent alone was 22 percent at 0.5 available Ca/S and $\Delta T_s = 18^{\circ}F$ approach. The observed SO₂ removal with simultaneous recycle and fresh sorbent feed was 40 percent at 0.8 fresh Ca/S, 0.2 Na/Ca (fresh), 0.5 available recycle Ca/S (about 7,000 lb/hr recycle feed rate), and $\Delta T_s = 18^{\circ}F$.

COOLSIDE AND WET LIMESTONE FGD PROCESS DESCRIPTIONS

Commercial Coolside Process Description

The Coolside process design described here is based on current FGD industry practice and the results of the Edgewater Coolside process evaluation. The design is based on mature Coolside technology. The Coolside process consists of four major process areas: sorbent and additive receiving/storage/preparation/feed; flue gas humidification; particulate removal and solids recycle; and waste disposal.

<u>Sorbent and Additive Receiving/Storage/Preparation/Feed</u>. There are two calcium sorbent preparation options. The first is purchase of quicklime (CaO) which is hydrated on-site. The second is purchase of hydrated lime (Ca[OH]₂). As presented in Figure 1, for 1.5 percent sulfur coal, the purchase of hydrated lime has a lower life cycle cost. For other coal sulfur contents, the purchase of hydrated lime is favored for all cases in which the Coolside process is economically attractive . compared to the wet limestone, forced oxidation process. In all cases, bulk delivery of hydrated lime is by rail. As shown in Figure 2, the hydrated lime is pneumatically transferred from the rail unloading area to bulk storage. From bulk storage, the sorbent is conveyed pneumatically to a day bin, and then volumetrically metered by a powder pump through a distribution bottle to the humidifier duct injection nozzles.

Because of its lower cost, soda ash (Na_2CO_3) is used as an additive to increase SO_2 removal and hydrated lime utilization. Dry soda ash is unloaded pneumatically from trucks into a 30-day, wet soda ash storage and supply system (shown in Figure 3). The soda ash feed system is a package unit which maintains a saturated solution of sodium carbonate. The saturated soda ash solution is metered, dependent upon the hydrated lime feed rate and the Na/Ca mole ratio setpoint, to an in-line mixer in the humidification water supply line.

<u>Flue Gas Humidification</u>. As shown in Figure 4, the boiler flue gas is conveyed to a single vertical downflow humidifier. In the humidifier, water containing the sodium additive is fed to an atomizer lance array of dual-fluid atomizing nozzles. Each nozzle is designed to operate at a 0.8-1 gpm throughput at an atomizing air-tohumidification water ratio of 0.5 lb of 120 psig air/lb of water. The dual-fluid nozzles produce very fine water droplets (~35 micron Sauter Mean Diameter) with less than 1 weight percent of the droplets greater than 100 microns. The humidifier is sized to provide three seconds residence time at full boiler load. The humidification water feed rate is controlled to maintain an outlet setpoint temperature which is typically 140 to 145°F.

The hydrated lime and recycle solids are conveyed to distribution bottles where the feed streams are split into several equal, smaller streams. The hydrated lime and recycle solids are blown into the flue gas through an array of injector pipes located in the plane of the humidification nozzles.

<u>Particulate Removal and Solids Recycle</u>. As shown in Figure 4, the humidified flue gas is conveyed to an ESP. All of the reference plants used in the economic evaluation are assumed to have ESPs with a specific collection area (SCA) of 400 $ft^2/1000$ acfm, ESP particulate collection efficiencies of 99.6+ percent and a particulate emission limit of 0.1 $lb/10^6$ Btu.

The fly ash, Coolside reaction products, and unreacted hydrated lime are collected and removed in the ESP. The collected solids are pneumatically conveyed from the ESP hoppers to a fly ash/spent sorbent silo for intermediate storage. The cleaned flue gas exits the ESP and passes through the induced draft fan to be discharged through the plant stack.

Recycle of the solids collected in the ESP is used to increase sorbent utilization. The solids in the fly ash/spent sorbent silo are metered through a volumetric feeder and pneumatically conveyed to the recycle solids distribution bottle. The distribution bottle uniformly splits the solids flow into several smaller streams prior to injection into the flue gas.

<u>Waste Disposal</u>. The waste material is a fine powder. To prevent dust emissions during silo unloading, the wastes are fed through a dustless unloader where water is added to moisten the solids before discharge into dump trucks. The waste is trucked to a landfill for disposal. Coolside waste was evaluated using the EP test procedure⁵ and was found to be non-hazardous.

Wet Limestone FGD Process Description

The wet limestone forced oxidation (LSF0) FGD process was selected for economic comparison with the Coolside process. The process is shown in Figure 5. Limestone is delivered by rail to the site and then transferred to a 30-day covered storage pile. The limestone is then fed to a day bin and, as required, to the grinding equipment for pulverization to 90 percent minus 325 mesh in a wet ball mill. The limestone slurry produced is metered to the SO₂ absorber. The absorber is a single module, rubber-lined, carbon steel, open spray tower which treats the flue gas from the boiler. Boiler flue gas passes through a booster fan and enters the absorber where the gas is contacted with limestone slurry. The SO₂ reacts with the slurry forming calcium sulfite, CaSO₃•1/2H₂O, and calcium sulfate (gypsum), CaSO₄•2H₂O. The reacted slurry collects in the absorber sump. Air is blown into the absorber sump at a stoichiometric ratio of 1.5 mole O₂/mole SO₂ absorbed to convert all the sulfite to sulfate. Large slurry pumps take suction from the absorber sump and recycle the slurry back through nozzle-equipped spray headers in the absorber. Slurry from the absorber sump is sent to a thickener for partial dewatering. The thickener overflow returns to the absorber while the underflow is pumped to rotary drum vacuum filters. Gypsum is dewatered to 80 percent solids and disposed of in a landfill. The clean flue gas is exhausted through a new wet stack.

Economic Premises

<u>Power Plant Parameters</u>. The reference plant performance assumptions are listed in Table 1. The site plan is assumed to be similar to those in DOE PON DE-PSO1-89FE61825. For the purpose of Coolside and wet FGD process layouts, all plant sizes (100, 150, 250, and 500 MW_e) are assumed to be equipped with two parallel air preheaters, ID fans, and ESPs. The designs are based on eastern bituminous coals containing 1.5 (2.2), 2.5 (3.7), and 3.5 (5.2) weight percent sulfur (lbs SO₂/10⁶ Btu). The fuel specifications are listed in Table 2. The nominal flue gas composition, rate, and temperature are listed in Table 3.

<u>Economic Assumptions</u>. The Consol Coolside and wet FGD models use a combination of capital equipment cost algorithms and look-up tables to estimate specific plant costs for individual equipment items or equipment packages. Specific equipment cost information was developed from internally funded FGD design reports, vendor quotes, and public literature sources. Installed plant costs (IPC) are determined by:

IPC =
$$\Sigma(EC, \times BF, \times RF) \times CI \times SF$$

where: EC_i = individual (denoted by ;) process equipment costs, BF_i = bulk factor (1.0 to 3.0), RF_i = retrofit factor, CI = process plant cost index adjustment, and SF = site factor. The retrofit factors were individually assigned. The average plant retrofit factors for the Coolside and LSFO processes were between 1.28 to 1.30. The southern Ohio site factor was 1.06.

The total capital requirement (TCR) is determined by:

$$TCR = IPC + IFC + HOC + BIC + PC + IDC + PSC + IC$$

where: IFC = indirect field costs (0.138 x IPC); HOC = home office costs (0.224 x IPC); BIC = bond and insurance costs (0.011 x IPC); PC = project contingency (0.18 x [IPC + IFC + HOC + BIC]); IDC = interest during contstruction; PSC = preproduction start-up costs; IC = inventory capital (working capital).

The calculations for IDC, PSC, and IC follow Electric Power Research Institute (EPRI) recommendations as outlined in the EPRI TAG^{m.⁶}

Variable costs are dependent on unit cost, process capacity, maintenance, and onstream factor. The unit costs for the economic evaluations are presented in Table 4. For the Coolside process, incremental operating labor (OL) is 1.33 men/shift (hydrated lime, purchased). For the LSFO FGD, the incremental operating manpower is 2.33 men/shift. The maintenance cost for labor and materials is calculated as follows:

$$AM = \Sigma(IEC_{1} \times MF_{1}/100)$$

where: AM = annual maintenance cost, IEC_i = installed equipment costs in process area (_i); and MF_i = maintenance cost percent in area (_j). MF_i is between 2.5 to 10 percent depending on service severity. Maintenance labor (ML) costs are 40 percent of annual maintenance cost. Administrative overhead cost is 30 percent of operating labor plus maintenance labor costs (0.3 x [OL + ML]).

The economic evaluations of process options are presented as capital cost, expressed at k/kW_{e} (net), and/or levelized revenue requirement, expressed as t of SO₂ removed. In some cases, the effect of short-term levelization (10 year) is considered. Short-term economic analysis is used by many utilities to determine if the long-term benefits of an option show economic advantage in the short-term when

unforeseen factors are less likely to occur. The economic factors needed for the financial calculations are presented in Table 5.

COOLSIDE PROCESS AND WET LIMESTONE FGD COST COMPARISON

Capital Cost Comparison

The published capital cost estimates for sorbent injection and wet limestone scrubbing vary over a wide range because of process and economic assumptions used in each study. This study used an internally consistent set of process and economic assumptions in developing the capital cost estimates. For this study, the relative cost comparisons of Coolside and wet FGD economics are valid. Site-specific factors will determine the absolute costs for "real world" applications.

Throughout this study, the LSFO FGD annual average SO₂ removal was assumed to be 95 percent and the Coolside annual average SO₂ removal was assumed to be 70 percent. The Clean Air Act Amendments of 1990 established a 1995 SO₂ emission limit of 2.5 lb $SO_2/10^6$ Btu which decreases in year 2000 to 1.2 lb $SO_2/10^6$ Btu. Assuming the utility will comply with the 1.2 lb $SO_2/10^6$ Btu limit at each site, the Coolside process can treat coal containing up to about 4 lb $SO_2/10^6$ Btu or about 2.7 percent sulfur coal (HHV = 13,400 Btu/lb).

The Coolside and LSFO FGD capital costs are compared in Figure 6 for the three design coals. In all cases, the LSFO FGD capital costs are higher than the Coolside process capital costs. The LSFO FGD capital costs are 2.2 to 2.5 times the Coolside capital costs. In cases where high SO_2 removal is not required, and remaining plant life is short, lower capital cost favors the installation of the Coolside process.

Total Levelized Annual Revenue Requirement

The total levelized annual revenue requirements in constant mid-1990 dollars for the Coolside and LSFO processes are presented in Figures 7, 8, and 9. The base case plant capacity factor and plant life are 65 percent and 20 years, respectively. For the 1.5 weight percent sulfur coal case (see Figure 7), the Coolside process is economically competitive with LSFO up to a crossover point plant size of about 350 MW_e. For the 2.5 weight percent case (see Figure 8), the Coolside process is economically competitive up to about a 130 MW_e plant size crossover point. For the 3.5 weight percent case (see Figure 9), the LSFO process is preferred over the entire reference plant size range. Clearly, coal sulfur content is a critical parameter in selecting the least-cost compliance technology.

A 65 percent plant capacity factor was assumed for the base case. The effect of plant capacity factor on the economic crossover point and the levelized annual revenue requirement at the crossover point between the Coolside and LSFO processes are presented in Figures 10, 11, and 12 for the design coals. For all reference coals, the economic crossover plant size increases as the capacity factor decreases. For the 1.5 percent coal sulfur case, the economic crossover plant size increased from 350 MW at 65 percent plant capacity factor to about 450 MW at 50 percent capacity factor. The total levelized annual revenue requirement, expressed as $\frac{1}{50}$ percent capacity factor, respectively. Similar results are observed with the 2.5 and 3.5 weight percent coal cases. The average capacity factor over the remaining plant life is an important process selection consideration.

Short-term economic analysis is used by many utilities to determine if the long range benefits of an option shows an economic advantage in the short-term when unforeseen factors such as changes in regulatory environment are less likely to occur. The results of short-term (10 year) cost analyses are presented in Figures 13, 14, and 15 for the 1.5, 2.5, and 3.5 percent coal cases, respectively. In the 1.5 and 2.5 percent sulfur coal cases, the economic crossover point is increased by 50 MW_e and 30 MW_e, respectively. For the high-sulfur coal case, LSFO is always favored over the Coolside process.

Variable Operating Costs

The effect of changing waste disposal unit cost on Coolside levelized annual revenue requirement is presented in Figure 17. The base case waste disposal cost is \$8.60/dry ton. If the waste disposal cost is \$7.00/dry ton, the levelized cost is lowered by about \$10/ton of SO₂ removed from the base case. If the waste disposal cost is increased to \$15/dry ton, the levelized cost is increased by \$40/ton of SO₂ removed for the 1.5 percent sulfur case.

Lowering the LSFO FGD SO₂ removal requirement from 95% to 70%, then to 50%, reduces the capital cost but the lower SO₂ removal increases the levelized SO₂ control cost from \$426/ton of SO₂ removed (95%), to \$512/ton of SO₂ removed (70%), and to \$630/ton of SO₂ removed (50%). Lowering the Coolside SO₂ removal from 70% to 50% reduces the levelized SO₂ removal cost from \$488/ton of SO₂ removed to \$481/ton of SO₂ removed. For non-compliance, low- to medium-sulfur coals, the Coolside process would tend to be economically favored.

CONCLUSIONS

The Coolside process is economically competitive with an LSFO FGD process for base load boiler operations (65% capacity factor) under the following conditions.

- 1. For 1.5% sulfur coal, up to 350 MW_ (net).
- 2. For 2.5% sulfur coal, up to 130 MW_e (net).

Process sensitivity analyses show that the following factors tend to favor the Coolside process for SO_2 control.

 Lower Boiler Capacity Factors--The Coolside process can be characterized as a low capital cost, high operating cost process. When compared to high capital cost, low operating cost processes like LSFO FGD, the economic attractiveness of the Coolside process increases with decreasing boiler capacity factor.

- 2. Lower Required SO₂ Percentage Reductions--The base case SO₂ removals are 70 percent and 95 percent for the Coolside and LSFO processes, respectively. As the SO₂ removal requirement decreases below 70 percent, the Coolside process becomes more economically attractive relative to the LSFO process.
- 3. Shorter Remaining Boiler Life.--A shorter remaining boiler life favors the low capital cost Coolside process.

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Figure 2. Hydrated lime sorbent receiving/storage/ feeding system.



Figure 3. Sodium additive (soda ash) storage and feed system.



Figure 4. Coolside process humidification and recycle solids feed system.



Figure 5. Wet limestone forced oxidation (LSFO) process.



Figure 6. Coolside LSFO capital cost comparison.



Figure 7. Levelized cost comparison Coolside versus LSFO (low-sulfur coal).



Figure 8. Levelized cost comparison Coolside versus LSFO (medium-sulfur coal).



Figure 9. Levelized cost comparison Coolside versus LSFO (high-sulfur coal).









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Figure 12. Effect of plant capacity factor on Coolside/LSFO economic plant size crossover point and levelized costs (high-sulfur coal).



Figure 13. Short-term (10 yr) cost comparison Coolside versus LSFO (low-sulfur coal).



Figure 14. Short-term (10 yr) cost comparison Coolside versus LSFO (medium-sulfur coal).



Figure 15. Short-term (10 yr) cost comparison Coolside versus LSFO (high-sulfur coal).



Figure 16. Effect of delivered hydrate cost on Coolside process levelized costs.



Figure 17. Effect of waste disposal charge on Coolside process levelized costs.

Table 1

REFERENCE PLANT PERFORMANCE ASSUMPTIONS

Plant Size		-		
MWe insti	100	150	250	500
MWe (gross)	105	158	282	530
Normanal Plant Haat Rate				
Without FGD, Bru/kWh (net)	9830	9770	9510	9480
ID Fane				
Cooleide		Ad		
Wat FGD	I	Add Bo	oster Fan	
ESP	1			
Regulated Envision Rate, 16/10" Btu	1		0,1	
Specific Collector Area, ft ² /1000 acfm			400	
SO, Emission Lanit				
2.5 to SO,/10" Btu. 1995		•	Yes	
1 2 lb SO,/10" Bru. 2000			Yes	
Plant Capacity Factor, %			65	
Plant Location	1	Near the	Ohio River	
Plant Retroit Factors	1			
Coolede (nominal)			1.3	
FGO (normal)			1.3	

Table 2

DESIGN FUEL SPECIFICATIONS

pel Sultur, WL % (AR)	1.50	2.50	3.50
igher Heating Value (HHV), Btu/B	1		
HHV (dry)	14180	14190	14190
HHV (AP)	13400	13400	13400
nel Composition, WL % (dry)			
c	79.69	78.65	77.60
н	4.93	5.12	5.19
•	4.03	4.03	4.04
N	1.52	1.51	1.43
5	1.59	2.65	3.70
Aan	8.04	8.04	8.04
	T00.00	100.00	100.00
Coal Moisture, Wt. %	5.50	5.50	5.50
Ash Content, Ib/10 ⁴ Btu	5.67	5.87	5.67
SO, Potential. 15/10" Btu	2.24	3.74	6.22
N S Aah Coal Moesture, Wt. % Aah Content. Ib/10 ⁴ Btu SO, Potentuel, Ib/10 ⁴ Btu	1.52 1.59 8.04 700.00 5.50 5.67 2.24	1.51 2.65 8.04 100.00 5.50 5.87 3.74	

Table 3

NOMINAL FLUE GAS COMPOSITION, RATE AND TEMPERATURE

Coal Suther, WL %	15	2.5	3.5
Flue Gee Competition, mai %			
н,0	6.16	0.35	8.43
co,*	12.11	11.96	11.86
ο,	5.89	5.86	5.85
SO, (ppm)	912	1523	2141
Boiler Size, MWe (net).	Fi	ue Gee Rate, MSCFM	7
100	237.3	236.8	235.7
150	353.7	352.9	351.3
250	574.0	573.4	570.7
500	1154.3	1151.8	1146 4
File Ges Temperature, *F		304	
" Less than 1 percent of coel carbo T At 60 'F & 1 Atmosphere.	on last to carbon in fly	ash and flue gas CO.	

Table 4

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UNIT COSTS: MATERIALS, UTILITIES, DISPOSAL AND LABOR

Item	Unit Cost
Water	\$0.65/1000 gallons
Lime	\$60.00/Ton
Hydrated Lime	\$60.00/Ton
Limestone	\$15.00/Ton
Soda Ash	\$155.00/Ton
Replacement Power	\$29.00/MW-hr
Fly Ash Disposal	\$7.00/Ton (dry)
Gypsum Disposal	\$7.00/Ton (dry)
Dry Sorbent Waste Disposal	\$8.60/Ton (dry)
Operating Labor	\$22.92/man-hr

Table 5

ECONOMIC FACTORS FOR COST ANALYSES

Base Year of Estimate	1990 Mi	d Year
Book Life, years	2	0
Tax life, years	1	5
Discount Rate	6.	1
Constant Dollar Levelizing Factors	<u>Life Cycle</u>	<u>Short-Term</u>
		<u>10 yr</u>
Expenses	1.000	1.000
Capital	0.118	0.134
Construction Period, years		
Coolside process	2	2
LSFO FGD	3	8

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OHIO EDISON CLEAN COAL PROJECTS

CIRCA: 1991

Rita E. Bolli Ohio Edison Company 76 South Main Street Akron, OH 44308

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3	CC Fuels Management	Flow Chart of Computer Model
4	LIMB	Flow Diagram of LIMB Process
5	NOXSO	Flow Diagram of NOXSO Process
6	SNRB	Flow Diagram of SNRB Process
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10	Battelle	Gypsum Recovery Process Schematic

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ABSTRACT

Ohio Edison is participating in 10 clean coal demonstrations which are in various stages of development. These projects include LIMB, E-SOx, NOXSO, SNRB, REBURN, SNOX and SORBTECH. This paper presents current design features and recent test results from these demonstrations. Content emphasizes specific technology advantages/problems from the utility's perspective. The presentation also focuses on the status of the technology and the important attributes to consider for a utility's specific compliance strategy. Additional R&D activities and progress summaries are presented to encompass Ohio Edison's current SO₂-related technology advancements including FGD waste utilization and regeneration. This paper is a review and status of each clean coal project involving Ohio Edison and has been divided into three major categories:

- COMPLETED PROJECTS
- PROJECTS IN PROGRESS
- PROJECTS ON THE HORIZON

A brief description, technical assessment and utility advantages have been identified for information applicable to current R&D developments. The real benefit from investing and participating in these demonstrations is the detailed examination of the technical and economical operating aspects of technology not commercially available.

A figure for each technology has also been attached for immediate reference and specific examination of the process operation and design.

COMPLETED PROJECTS

HALT - Hydrate Addition at Low Temperature

The HALT project was Edison's first clean coal project. It was installed as a 5 MW pilot at the Toronto (Obio) Plant.

Basically, the HALT process injects hydrated lime and then moisture directly into the flue gas ductwork downstream of the furnace and upstream of the dust collector. SO_2 in the flue gas reacts with the hydrated lime to form a solid, which is collected with the fly ash. Much of the HALT developmental work led to operating parameters and nozzle design used in a number of current duct injection processes.

The primary sponsor of the \$2.1 million HALT project was the U.S. Department of Energy. The prime contractor was the Dravo Lime Company.

Operation of the pilot unit started in November 1986 and continued until August 1987.

Conclusions from the HALT testing confirm the approach temperature is the single most important variable for optimum hydrate utilization and SO_2 removal efficiency. The Ca/S ratio was the second most important variable for optimizing process efficiencies and economics.

Figure 1 displays the Hydrate Utilization and removal efficiencies at various approach temperatures. With operating parameters optimized, a consistent removal of 60 percent SO_2 was achievable. The process also tested the efficiency of ESP particulate collection vs. baghouse collection downstream of the process. Both systems were successful in obtaining NSPS performance; however, there was a slight improvement of SO_2 removal with the baghouse arrangement.

<u>Conclusions</u>

The HALT process is a viable process and an excellent cost justifiable alternate for moderate SO_2 reduction in medium to high sulfur coal-burning boilers. Final results indicate that SO_2 removal of up to 60

percent was achieved with a 3.2 percent sulfur coal at a Ca:S ratio of 2.0 while maintaining optimum operating conditions. The process can be designed and operated on a continuous basis by proper installation and selection of the humidification nozzles. Preliminary leachate tests on the pilot disposal solids indicate that they meet RCRA limits for non-hazardous classification.

E-SOx - Electrostatic Precipitator SOx Removal

E-SOx is a post combustion retrofit technology for controlling sulfur dioxide emissions. It maximizes the use of existing plant facilities making the E-SOx process a relatively simplistic retrofit installation for low-cost, moderate SO₂ control.

E-SOx emission control technology represents an enhancement of an electrostatic precipitator (ESP) that involves reducing sulfur dioxide emissions and removing particulates. A flow diagram of the E-SOx process is presented in Figure 2. A lime slurry atomization system is added either immediately preceding the ESP or in the space created by removing the electrical internals from the first field of the ESP. Lime slurry is sprayed concurrently with the flue gas flow and provides for sulfur dioxide removal by reaction with calcium hydroxide. The flue gas evaporates the water in the slurry, resulting in a relatively dry solid product at the ESP inlet. Reaction products, unspent hydrated lime and fly ash are then collected in the ESP.

A 5 MWe equivalent field-pilot facility was constructed at the R. E. Burger Station of Ohio Edison to demonstrate the feasibility of the technology on a slipstream of flue gas from a coal-fired boiler. The facility was operated over about six months to develop process design parameters and demonstrate acceptable levels of removal for sulfur dioxide and particulates.

From the beginning, E-SOx technology has been considered a retrofit rather than a new plant control system. E-SOx does not provide a high level of sulfur dioxide removal relative to some alternative control processes such as wet scrubbing. But it does show promise as being extremely competitive economically on the basis of dollars per ton of sulfur dioxide removed.

The E-SOx emission control concept was originally developed and patented by the U.S Environmental Protection Agency (Sparks and Plaks, 1989). Further development and evaluation of the concept was performed under a grant from the Ohio Coal Development Office (OCDO) by a project team consisting of Babcock & Wilcox (B&W), U.S. Environmental Protection Agency (EPA), Southern Research Institute (SRI) and Ohio Edison. This development work included a pilot scale test for sulfur dioxide removal, ESP performance, gas flow computer model studies and pilot-scale atomizer evaluation and led to the design and operation of a demonstration-scale test facility.

The E-SOx 5 MW pilot was constructed in 1988 for a total project cost of 9.4 million including testing. Flue gas was first introduced through the facility in April 1989, followed by six months of testing over an approach temperature range of 30° F to 60° F and a range of stoichiometric ratios from 1.0 to 1.8.

<u>Conclusions</u>

SO₂ removals of 50 percent were achieved at approach temperatures of 28° F to 30° F and stoichiometric ratios of 1.3.

How well sulfur dioxide is removed in the E-SOx process is primarily a function of two control parameters: approach to saturation temperature and calcium-to-sulfur stoichiometric ratio.

The most influential operating variable is the approach temperature. This value is a measure of the difference between the flue gas temperature at the ESP inlet and the adiabatic saturation temperature of the flue gas. In general, for a fixed stoichiometric ratio, sulfur dioxide removal improves significantly as the approach temperature is reduced. However, operation below a practical limit of 25° F to 30° F may result in unacceptable deposition of unevaporated slurry in the spray chamber.

The economics of the process are enhanced as the stoichiometric ratio is reduced. Operation at a lower stoichiometric ratio also reduces the total particulate loading to the ESP. Therefore, it was desirable to achieve the required sulfur dioxide removal at the lowest possible stoichiometric ratio by operating at low approach temperatures.

The process design and economics provide a favorable SO_2 reduction for minimal capital costs and moderate (50 percent) SO_2 removal and create a dry product for easy handling and disposal with potential by-product utilization.

Clean Coal Fuels Management

Ohio Edison Company, Electric Power Research Institute (EPRI), Bechtel Group, Inc., B&W and OCDO teamed together in a Clean Coal Fuels Management Project to investigate the technical and economic feasibility of a novel coal cleaning system that combines existing technologies (conventional cleaning methods and an atmospheric fluidized bed boiler).

The system investigated utilizing an advanced coal cleaning system to produce two levels of coal quality: a deep-cleaned, low sulfur, high quality coal, and a high sulfur, poor quality coal rejected in the deepcleaning process. The low sulfur, high quality coal is lower in sulfur than can be achieved economically in present coal cleaning plants. This fuel was used by an existing boiler without SO₂ emission control equipment. The high sulfur, poor quality coal was sent to an atmospheric fluidized bed boiler.

One of the products of the \$1.1 million research project is a computer model that may be used by the State of Ohio, electric companies, coal producers and others to evaluate fuels management for their specific conditions.

Figure 3 represents a flow chart of the input coal and the three product possibilities as a result of the cleaning process. The computer program will calculate the percentages of the three products for any specific fuel the utility selects to enter, which allows the flexibility of predicting for current and future coal supplies.

This project was completed in 1990 and the computer program is available from EPRI. This project was the only Ohio Edison clean coal technology that is categorized as a pre-combustion process.

LIMB/Coolside - Limestone Injection Multi-Stage Burner

A \$47 million, full-scale demonstration of the LIMB technology was

conducted at Ohio Edison's Edgewater Plant in Lorain on a 104 MW boiler burning a nominal 3 percent sulfur coal.

LIMB involves upper furnace injection of hydrated calcitic lime, coupled with the use of low-NOx burners. The injected dry sorbent mixes with the boiler combustion gases and chemically removes the sulfur dioxide. The by-product then travels through the remainder of the boiler and is removed along with fly ash in the unit's existing dust collector.

Developed as a technology aimed at moderate levels of SO_2 and NOx control for relatively low-cost retrofit applications, LIMB operation at a Ca/S ratio of 2.0 was capable of achieving 55 to 72 percent SO_2 removal. The removal was dependent on the specific sorbent utilized and the degree of humidification employed. In conjunction with SO_2 removal, the performance of the XCL low-NOx burners was evaluated with an average emission rate of 0.48 lb. per mmBtu observed.

The Base LIMB program began in July 1987. The long-term operation of the LIMB process with humidification, a second phase of the project, began in September 1988 and continued for approximately 10 months. A process flow diagram of the complete LIMB/humidifier system is provided in Figure 4.

The results of this testing included the use of a commercial, hydrated calcitic lime treated with calcium lignosulfonate, an additive that appeared to improve SO_2 removal. Testing indicates that the modified sorbent increased SO_2 removal from 55 to 63 percent with minimal humidification, and from 65 to 72 percent at close approach to saturation, when operating at a Ca/S ratio of 2.0.

Since the SO_2 removal was particularly dependent upon the temperature at the injection point, particular attention was focused on operating variables that affected parametric optimization. These variables included injection at different elevations in the furnace, the momentum flux ratio (injection velocity and furnace penetration at a given load), the angle of injection (nozzle tilt), and boiler load. The results show that these parameters have little effect on SO_2 removal in the Edgewater boiler over most of the ranges tested which indicate that the system is insensitive to minor changes if the initial design parameters enable near-optimum operation.

The project also demonstrated that SO_2 removal could be enhanced by humidification of the flue gas. Humidification increased the SO_2 removal from 55 to 65 percent at a Ca/S ratio of 2.0.

For NOx reduction, the existing circular burners were replaced with B&W's XCL burners as part of the demonstration project. Baseline data indicated that 0.7 to 0.9 lb. per mmBtu NOx was reduced to an average of 0.48 lb. per mmBtu with unburned carbon averaging 1.54 percent. There appeared to be no interactive effects between sorbent injection and NOx reduction.

A third phase of the LIMB project was made possible by the U.S. DOE Clean Coal Technology Program, as a Clean Coal I project. Coolside is a lowcost retrofit technology similar to HALT. Data from this earlier project was used in the design. Dry lime is injected into the flue gas duct after the gas leaves the boiler. Then the flue gas is humidified with a water spray containing chemical additives to enhance SO₂ adsorption and electrostatic precipitator performance. Coolside testing started in July 1989 and was completed in February 1990. SO₂ removal of up to 70 percent was achieved.

The final phase of the program which involved testing different combinations of three coals and four sorbents was completed in August of this year.

This project was sponsored and funded by Ohio Edison, U.S. EPA, U.S. DOE, OCDO, B&W, Consolidation Coal, Radian and Stone & Webster.

<u>Conclusions</u>

The LIMB process impacts on boiler and plant operations are related primarily to the increased quantity of particulate matter that must flow through the boiler, ESP and ash handling equipment. The need for effective soot blowing is the single most important requirement when considering application of the technology.

LIMB technology is a process which requires low capital investment and is easily retrofitted to existing boilers. Although the removal efficiencies for SO₂ are lower than conventional and advanced scrubbers, the cost per unit of sulfur removed is much lower than for scrubbers.

PROJECTS IN PROGRESS

The next generation of clean coal projects which are currently in progress at Ohio Edison represent a generic principle of high removal efficiencies of both SO₂ and NOx. Coupled with this shared objective is the integration of little or no waste product generated. These attributes signify an economical emission control process when compared to commercially available scrubbers in combination with a NOx control technology plus the potential for a marketable by-product. Although the programs in progress are too premature to quantify the removal costs, the predictions of removal efficiencies and costs of equipment in place indicate viable alternatives to scrubbing systems and offer uniquely attractive processes for compliance with the Clean Air Act Amendments of 1990.

<u>NOXSO</u>

The NOXSO process is a dry flue gas treatment system that employs a reusable sorbent. The sorbent consists of sodium impregnated on a high-surface-area alumina. Flue gas exiting the ESP or baghouse is directed through a fluidized bed of sorbent which simultaneously removes SO_2 and NOX from flue gas. The spent sorbent is regenerated for reuse by treatment at high temperature with a reducing gas. This regeneration reduces sorbed sulfur compounds to SO_2 , H_2S and elemental sulfur. The SO_2 and H_2S are then converted to elemental sulfur in a Claus-type reactor. The sulfur produced is a marketable by-product of the process. Adsorbed NOX is decomposed and evolved on heating the sorbent to regeneration temperature. Regeneration of active NOX sorption sites is accomplished simply by heating the sorbent. The concentrated stream of NOX produced is returned to the boiler with the

combustion air. Figure 5 represents a diagram of the project.

Construction of a 5 MW Proof-of-Concept project began in July 1990 at Ohio Edison's Toronto Plant. The unit is designed to treat approximately 12,000 SCFM from either of two boilers burning approximately 3.5 percent sulfur coal. The process is designed to simultaneously remove 90 percent of the SO₂ and NOx in the flue gas. The regeneration process to reuse the sorbent material results in no waste products being formed, and the potential of improving the thermal efficiency of the boiler operation by returning hot gases laden with NOx as combustion air, bypassing the air preheater.

The \$9.5 million project is sponsored by U.S. DOE, OCDO, NOXSO, MK-Ferguson, W. R. Grace and Ohio Edison. Start-up activities have commenced with operating and design data being utilized to design and construct a fullscale demonstration of the NOXSO process.

The full-scale demonstration was selected in Round III of the U.S. DOE's Clean Coal Program and is currently being designed for installation at Ohio Edison's Niles Plant.

This project will provide the technical and economic data for a commercial installation along with availability and reliability information. The full-scale demonstration will be fully integrated into a cyclone-fired 108 MW boiler and will include two additional features that the pilot project will not be testing. These include the Claus Plant for sulfur recovery and the NOx recycle to the boiler furnace.

This \$66 million project includes all of the pilot plant co-sponsors and additional participation by EPRI, the Gas Research Institute (GRI) and East Ohio Gas. Engineering and procurement are scheduled for 1992 with construction to commence in 1993, followed by two years of testing and operation.

The attractive advantages to the utility operator in addition to the high removal efficiencies and lower costs than current commercial applications with similar emission reduction capabilities are the small footprint due to the tower design and the installation downstream of the utility equipment which minimizes changes to the current boiler operation. The other significant advantage is the fact that no waste products are produced. Due to the current and future water and waste regulations, the economic impact of eliminating all disposal costs while producing a saleable product results in a win-win situation.

SNRB - SOx-NOx-ROx-BOx

The SOX-NOX-ROX-BOX (SNRB) process, developed by B&W, is an advanced emission control process for the combined removal of SO₂, NOx and particulates from coal-fired boilers or processes.

The key to the SNRB process is a high-temperature baghouse in which simultaneous SOX, NOX and particulate removal occurs. SO₂ removal is accomplished by injecting a dry sorbent such as hydrated lime or sodium bicarbonate into the flue gas. NOX removal is accomplished in part by ammonia injection with a selective NOX reduction catalyst. Finally, the particulates and spent SOX sorbent are collected in a high-temperature baghouse. Figure 6 provides a flow diagram of the project. Construction of the 5 MW pilot project began in March 1991 at Ohio Edison's R. E. Burger Plant. The unit is designed to treat a slipstream from a coal-fired PC boiler burning a nominal 2.5 percent sulfur coal. Earlier tests have provided the project goals of 70-75 percent SO₂ removal at stoichiometric ratios of 2.0 to 2.5 and 90 percent NOx reduction at cost-effective NH₃/NOx stoichiometric ratios. Greater than 99.9 percent particulate removal is expected in the pulse-jet baghouse which utilizes a unique design of bag, bag cage and catalyst retainer. Removal efficiencies will be optimized at a baghouse operating temperature range of 700°F to 850°F.

The \$11.4 million project was selected in Round II of the U.S. DOE's Clean Coal Program. Sponsors of the project include B&W, U.S. DOE, OCDO, EPRI, Norton, 3M and Ohio Edison. Start-up and shakedown activities have commenced and parametric testing and operation is scheduled for 1992.

Besides providing the technical and operating data for a full-scale application, this project will provide commercial readiness of the technology because the baghouse utilizes commercial size bags (approximately 6-1/2" diameter, 20' length).

The economic attractiveness of this project is exemplified by the use of a single vessel for removals of all three pollutants. Additional advantages include simplification of operation due to minimal equipment requirement (low man-hours required for operation) and minimal dry waste product that is easily transported and has potential for by-product utilization. An additional potential benefit is the ability to operate the air preheater at a lower flue gas outlet temperature, thus improving heat recovery and boiler thermal efficiency.

SNOX - Wet Sulfur Acid from SO2 and NOx Reduction

The SNOX technology is a catalytic removal process capable of removing 95 percent of the SO_2 and 90 percent of the NOx from a coal-fired boiler. Flue gas upstream of the ESP is first processed through a bag filter for removal of the fly ash, then heated in an exchanger by the exiting gas stream to the required reaction temperature. A small amount of ammonia is added and the mixture is then processed through a NOx SCR for conversion of nitrogen oxides to nitrogen and water vapor.

Gas exiting the NOx reactor is heated further and then processed through the SO₂ reactor, in which SO₂ is converted to SO₃. The gas exiting the SO₂ converter is heat exchanged and then passed to a condensing tower, the key component of this technology. In the condensing tower, the gases are cooled to produce a high-concentration, commercial grade, sulfuric acid. Figure 7 provides a flow diagram of the SNOX process.

The SNOX project was selected in Round II of the U.S. DOE'S Clean Coal Program. This \$31.5 million project is the first domestic installation of a technology developed in Denmark and currently being tested in a project there and on an additional installation in Italy. Project sponsors in addition to the U.S. DOE include OCDO, Combustion Engineering, Haldor Topsoe, Snamprogetti and Ohio Edison. Construction on this project began in March of this year with startup activities commencing in December 1991 followed by an 18-month testing and operation phase. The SNOX project is treating approximately one-third of the flue gases from one of Ohio Edison's Niles Plant 108 MW cyclone-fired boilers, or the equivalent of a 35 MW demonstration.

This demonstration will validate the removal efficiencies and economic advantages of a domestic installation utilizing high sulfur coal. The advantages include high removal efficiencies without producing any waste products. Because of the exothermic properties and potential integration of recovered heat to the utility boiler, the process offers significantly lower O&M costs than commercially available technologies. The economics of the process are also enhanced with the production of a saleable by-product, highly concentrated sulfuric acid. Another distinct advantage is the location of the SO₂ converter downstream of the SCR which eliminates ammonia slip considerations allowing for maximum NOx removal capabilities. In addition, the process reduces CO and hydrocarbon emissions and actually improves efficiency with increasing sulfur content of the coal.

<u>REBURN</u>

An additional project at Ohio Edison's Niles Plant is the REBURN project, which is a NOx reducing, in-furnace technology utilizing natural gas as the reburn fuel.

REBURN technology involves creating a second combustion or "reburn" zone downstream from the main burners in a boiler. Combustion gases that result from burning a fossil fuel in the main combustion zone, move to the "reburn" zone where additional fuel, in this case natural gas, is injected. The injection of additional fuel creates a fuel-rich zone in which the NOx formed in the main combustion zone are converted to molecular nitrogen and water vapor which occur naturally in the atmosphere. Any unburned fuel leaving the reburn zone is subsequently burned to completion in a downstream burnout zone where additional air is injected. Reburning is especially attractive for cyclone-fired boilers and other wet-bottom boilers since low-NOx burners and most other low-NOx combustion technologies used on conventional boilers are not applicable to cyclone-fired and wet-bottom boilers. The overall goal of the program is to successfully demonstrate a 50 percent reduction in NOx emissions from a cyclone-fired boiler employing reburning technology. Figure 8 shows a schematic of the REBURN project.

Project participants include Combustion Engineering as the project manager and main contractor, along with U.S. DOE, U.S. EPA, GRI, EPRI, OCDO, Ohio Edison and the East Ohio Gas Company.

Mobilization for this \$10.3 million project occurred in March 1990, with boiler modifications completed during a planned boiler maintenance outage in June. Parametric testing began in late 1990 where testing results indicated a 60 percent reduction in NOx emissions.

Although the initial data was extremely promising, an unexpected phenomena was occurring in the boiler. Ash deposition had increased significantly along the rear wall starting at the gas injection location and continuing to higher elevations up to the slope wall of the boiler. This was theorized as a result of the recirculated flue gas which was used as a mixing medium for the natural gas and to keep the upper fuel injectors (UFI's) cool. The cooling effect on the rear wall was allowing the normal ash thickness to increase from 4-6" to 12-18".

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Combustion Engineering redesigned the natural gas injectors by fabricating e water-cooled, injection nozzle, which eliminates the recirculation of flue gas and reduces the boiler penetrations to approximately 6" diameter circles. This application reduces the number of boiler tubes requiring modification and eliminates the operation of a flue gas recirculating fan.

This modification was completed during a scheduled boiler maintenance outage starting in September of this year. Parametric testing has commenced to examine the NOx reduction utilizing the new natural gas injectors.

Advantages to this technology include a design that is the only feasible means for in-furnace NOx reduction for a cyclone boiler. However, the process is applicable for NOx reduction in a PC-fired boiler also.

The other striking advantages to the utility operator is the ease of installation, the ability for quick on/off operation and the proven advantage to operate the system without additional manpower requirements.

SORBTECH

Another combined removal technology at Ohio Edison is the Mag*Sorbent Technology developed by SORBTECH (formerly known as Sanitech). Mag*Sorbent is a dry, regenerable process utilizing a sorbent material capable of removing 90 percent of the SO₂ and 40 percent of the NOx from flue gas emissions. The sorbent is comprised of two inexpensive industrial minerals, magnesia and vermiculite.

The process involves a radial panel-bed adsorber which is retrofitted to the utility downstream of the particulate control device. The gases pass through a bed of approximately 12" of the sorbent material where the NOx and SO₂ are simultaneously removed. The sorbent is regenerated in a heating process where the SO₂ and NOx are driven off, and the sorbent is screened to remove the fine particles and returned as make-up to the adsorber. The Mag*Sorbents exhibit very high utilizations and need only to be regenerated 10 times for attractive process economics. There are no waste products generated by the process, and the spent sorbent has potential for by-product utilization such as soil enhancement or developments are occurring for possible regeneration of the sorbent constituents.

A 2.5 MW pilot demonstration was constructed at Ohio Edison's Edgewater Plant this summer. This is a scale-up from previous testing that was performed at Ohio Edison's Gorge Plant. This \$700,000 project is cosponsored by OCDO, SORBTECH and Ohio Edison. Start-up and shakedown of the equipment is scheduled to begin before the end of the year followed by a sixmonth testing program. Figure 9 shows a flow diagram of the project.

Advantages include the simultaneous high removal efficiency of the SO₂ combined with NOx removal, without creating a waste product. The results of this project will validate the process economics which appear to be about one-half the cost of commercially available equipment with comparable removal rates. The simplistic process and equipment integrated downstream of the utility's equipment provide the potential for low capital costs, low operating costs and ease of retrofit installation.

PROJECTS ON THE HORIZON

Land Application for Dry FGD By-Product

Air quality control regulations for sulfur dioxide have spurred the development of several dry FGD processes suitable for retrofit on moderate-tohigh sulfur coal burning utility generating units. These processes may generate enormous quantities of dry solid by-product material consisting primarily of calcium-based excess sorbent, reaction products containing sulfates/sulfites and fly ash. The major dry FGD processes being tested are:

- LIMB Lime injection in the boiler furnace downstream of the burners.
- DUCT INJECTION Lime or sorbent injection downstream of the boiler air preheaters in the lower flue gas temperature regions.

FBC - Fluidized bed combustors.

SPRAY DRYER FGD SYSTEMS

All of these processes produce a "dry" material that is removed in the particulate control equipment along with the fly ash.

The primary objective of the project is to study ways in which these materials can be used to offset other materials now being used for soil reclamation, agriculture uses and soil stabilization. The demonstration project will fully characterize the generated solid materials and determine the potential of applying these materials to various land surfaces. Beneficial and detrimental effects to the soil and possible environmental impacts related to the vegetation, water table and water runoff need to be studied and well understood.

The work for this project will be performed by Ohio State University with cooperation from the United States Geological Survey under the direction of Dravo Lime Company, who will act as the prime contractor, Ohio Edison Company and a steering committee made up of representatives from EPRI, U.S. DOE, Ohio EPA, Consolidated Coal Company and other utilities. The project will take 48 months to complete. The work will be performed at Ohio State University's main campus in Columbus, Ohio and at full scale demonstration sites selected from among active coal mine sites in Ohio.

FGD Gypsum Recovery

An integrated two-stage process has been developed that has the potential to cost-effectively recover saleable lime and sulfur from a gypsum that is a flue-gas desulfurization by-product. The first stage reduces the gypsum to calcium sulfide. This calcium sulfide is then transferred into the

. . second-stage reactor to produce a regenerated solid calcium oxide and a gas stream rich in sulfur dioxide. This calcium oxide can be collected in a cyclone, while the product gas is used to produce sulfuric acid. Elemental sulfur can be produced by use of the Claus process (or variations thereof).

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A program has been funded by OCDO, GRI, Ohio Edison, Columbia Gas and Consolidated Natural Gas to advance this technology toward commercialization. Battelle will be a subcontractor and will perform the majority of the experimental effort. A vital element in this commercial step is an A&E organization that can contribute to the transition from laboratory to pilot plant demonstration and ultimately design the commercial plant.

The overall project objective is to advance this technology toward commercialization. The specific project objective is to generate the data necessary to design a demonstration plant (50 to 100 tons/day) that will establish commercial feasibility of the FGD gypsum recovery process and be used as a large-scale development process. This large-scale developmental facility may also be used for expanded applications of the technology.

The process being developed at Battelle for the recovery of chemical values from by-product gypsum consists of two separate reactors used first to reduce the gypsum to calcium sulfide (CaS) and then in the second reactor, to roast the resulting sulfide with air to produce a gas stream rich in sulfur dioxide (SO2) which can be used to generate elemental sulfur or sulfuric acid and regenerated solid calcium oxide (CaO). The potential application of the Battelle FGD lime recovery process eliminates some of the problems inherent with other processes to convert gypsum.

The process is shown schematically in Figure 10. Wet gypsum from FGD systems, waste acid neutralization, or storage is calcined using waste heat from incineration of the Stage 1 reactor off gas and fed into the fluidized bed Stage 1 reactor.

In Stage 2, the concentrations are suitable for conversion to elemental sulfur or for conversion to SO3 as the first step in sulfuric acid manufacture.

Summary

All of these projects share the goal of bringing promising new technologies closer to commercialization.

There are only two options, today, in reducing emissions of sulfur dioxide from coal-fired power plants -- expensive, complex scrubbers, and switching to lower sulfur fuels.

Managers of businesses don't like constraints on their choices when it comes to serving their customers. Electric companies are no exception, and clean coal technologies allow flexibility in selecting options for the future. Ohio Edison wants to help realize the potential of these new technologies, help the Ohio coal industry and provide a medium to bring premier technologies closer to commercialization.

ACKNOWLEDGEMENTS

Rather than list specific individuals, I have alphabetically listed all the organizations that have contributed or are contributing to any of the clean coal projects/programs that involve Ohio Edison. These companies have an integral role in executing the projects and have, therefore, contributed to the development of this paper.

ABB Combustion Engineering ABB Environmental Systems Babcock & Wilcox Battelle Bechtel Group Columbia Gas Consolidated Natural Gas Consolidation Coal Dravo Lime East Ohio Gas Electric Power Research Institute Gas Research Institute Haldor Topsoe Minnesota Mining & Manufacturing MK-Ferguson Norton NOXSO Ohio Coal Development Office Ohio State University Radian Snamprogetti SORBTECH Southern Research Institute Stone & Webster U.S. Department of Energy U.S. TPA W. R. Grace



Figure 1

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Figure 2



CUAL CLEANING PROCESS



Figure 3


LIMB Process Flow Diagram



Figure 5



Schematic of the 5-MM, SWRB Field Demonstration Facility

Figure 6

The SNOX Project



Figure 7



SCHEMATIC OF REBURN PROCESS

Figure 8

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The SORBTECH Project



Figure 9

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Battelle's Gypsum Recovery Process Schematic

Figure 10

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Sanitech's 2.5-MWe Magnesia Dry-Scrubbing Demonstration Project

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ABSTRACT

The performance of a new regenerable sorbent, developed by Sanitech Inc., is being demonstrated in a 2.5-MWe pilot plant installation at Ohio Edison's Edgewater power plant in Lorain, Ohio. The granular sorbents, called "Mag*Sorbents," are 50 weight-percent magnesia and 50 weight-percent exfoliated vermiculite. A special heat-treatment step endows the sorbents with high sorption capacities. In earlier, smaller, pilot facilities, the new dry sorbents demonstrated excellent combined SO_2 , NO_x , and residual-particulate removal rates. During thermal regeneration with natural gas in the atmosphere, captured NO_x is converted to nitrogen and water, and the sorbed SO_2 comes off as a concentrated stream of elemental sulfur, SO_2 , and H_2S , for by-product production.

The objective of the present 2.5-MWe pilot plant program is to duplicate the previous high SO₂ removal rates and high sorbent utilizations at a larger scale, while demonstrating life-cycle process operation, with sorbent cycling continuously between the sorption and regeneration steps. The project is designed to accumulate the data necessary for a full 100-MW facility installation. To date, the Mag*Sorbent pilot plant has been designed and installed. It is currently undergoing shakedown testing.

INTRODUCTION

Sanitech, Inc. is scaling-up a unique, dry, regenerable acid-rain control technology for low-cost retrofit utility applications. This "Mag*Sorbent" process utilizes granular sorbents made from two inexpensive industrial minerals, magnesia (MgO) and vermiculite. In Sanitech's process, MgO is coated onto individual vermiculite exfoliates, which have been thermally expanded into small accordionlike structures. The Mag*Sorbents can be loaded to about 50 percent MgO by weight, so that process components are small and only low quantities of materials are circulated through the system. A special heat treatment before their use that makes the sorbents very reactive toward SO, and NO_x.

A special radial panel-bed filter is employed in the new process. In this filter, which is retrofitted before a utility's smokestack, dry sorbent in the form of a slowly-moving panel-bed removes greater than 90 percent of the flue gas SO_2 , compliance levels of NO_x , and much of the fine, residual particulates that pass through an existing electrostatic precipitator, all in one unit. The Mag*Sorbents exhibit very high utilizations and are thermally regenerated typically five to ten times, which results in very attractive process economics.¹ Because the system is regenerable, there are no wastes to dispose of, only marketable by-products.

PROCESS DEVELOPMENT

Sanitech began its work with the new sorbents in 1985. Since that time, it has carried on research and development programs with the assistance of the U.S. Environmental Protection Agency, the U.S. Department of Energy, and the Ohio Coal Development Office, advancing the technology. A major development occurred in 1987 when Sanitech researchers discovered that the new sorbents, after becoming saturated with SO_2 and NO_x , could be thoroughly regenerated by simply heating the materials in a slightly-reducing environment. During regeneration, the sorbed NO_x is converted to nitrogen and water, and much of the released SO, comes off as elemental sulfur.

Since 1987, Sanitech has been scaling up the Mag*Sorbent technology in steps. During 1988, it demonstrated combined SO_2 and NO_x removal in a small panel-bed filter on a 0.02-MWe slipstream of flue gas at Ohio Edison's Gorge power plant. During 1989, high SO_2 and NO_x removals were achieved on a 0.1-MWe slipstream.² In early 1990, the process was demonstrated at the 0.5-MWe level, with sorbent cycled between multiple sorption and regeneration steps.³

In recent months the process has been scaled up one step further. Equipment has been designed, constructed, and installed at Ohio Edison's Edgewater power station in Lorain, Ohio to treat a 2.5-MWe slipstream of flue gas.

SPECIAL SORBENT CHARACTERISTICS

Magnesia in the presence of moisture readily reacts with SO_2 to form $MgSO_3$ and $MgSO_4$. The MgO Wet Scrubbing Process, employed, for example, at Philadelphia Electric's Eddystone power plant, employs magnesia in the form of a wet $Mg(OH)_2$ slurry.⁴ Magnesia and magnesium hydroxide can also sorb SO_2 in a more convenient dry form, but they react at a slower rate.

Sanitech engineers discovered a way to increase the reaction rate of dry magnesia, while at the same time increasing the SO₂-sorption capacity of the material. They achieved this by (1) coating the magnesia onto individual expanded vermiculite granules, and (2) heating the combinations to 550°C in air. These procedures result in a sorbent with a large MgO surface area. Figure 1 shows electron photomicrographs of the surface of a typical Mag*Sorbent granule. At about 500°C, the already small magnesium hydroxide crystals on the vermiculite surfaces were found to

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recrystallize to magnesium oxide structures with larger active surface areas and advantageous pore size distributions. These recrystallized structures can be seen in the photomicrographs.

Kent State University surface chemists identified two mechanisms as responsible for the higher-than-expected utilizations of the sorbents.⁵ The two mechanisms are:

- The normally-expected chemical reaction between MgO and SO₂, which principally forms MgSO₃;
- 2. A physical phenomenon known as "capillary micropore condensation," where SO_2 complexes are physically captured and held by capillary forces within the micropores of the sorbent structure.

This second mechanism boosts sorbent utilization each cycle, resulting in lower process costs.

THE 2.5-MWe EDGEWATER PILOT PLANT PROJECT

A goal of the 2.5-MWe pilot-plant program currently underway is to demonstrate that the high SO₂-removal efficiencies and the high sorbent utilizations observed in earlier small pilot-plant facilities can be achieved at a large scale. A further goal is to demonstrate the new technology as a continuous process, where sorbent is continually cycled between sorption and regeneration steps. The project is designed to accumulate the data necessary for a full 100-MW facility.

The regenerable Mag*Sorbent technology is a straight-forward process. The flue gas simply passes through a thin panel of sorbent, then exits to the stack. The pilot plant consists of two principal circuits, a gas sorption circuit and a sorbent regeneration circuit, as shown in Figure 2. Three major components make up the sorption circuit: the sorber, a humidification spray, and a fan. The sorber, shown in Figure 3 before its installation, is a vertical cylindrical vessel through which a radial panel of sorbent flows slowly and continuously as a 12-inch-thick bed. The bed is supported between two stainless steel screens or louvered faces. Fresh sorbent is fed to the top of the sorber from hoppers above the unit. Saturated sorbent is removed continuously from the sorber discharge. The flue gas enters through the top-center of the vessel, radiates out through the radial panel of sorbent, and is channelled in the outer chamber to an exit duct and fan. Because the sorbents are granular and the sorbent panel is thin, pressure drops are low. This general sorber design has been used at the boiler-scale for years in the pulp and paper industry, among others.⁶ There, limestone chips are used instead of granular sorbents, because the objective is simply to take out particulates. The radial panel-bed design is very space-efficient, with a small retrofit footprint. A scaled-up design is shown in Figure 4.

The low-temperature chemistry of the process is advantageous for ease-of-retrofit. Humidification of the flue gas is accomplished by simply spraying water into the flue gas approximately 20 feet in front of the sorber. The added moisture also decreases the gas temperature, which improves SO, removal. However, an approach to saturation of at least 50 F degrees is maintained, to avoid any corrosion problems. The fan in the sorption circuit is employed principally to regulate the gas flow through the system. The regeneration circuit contains three principal components: the regenerator, a screening unit, and a condenser-burner system. The regenerator design selected for the Edgewater pilot plant has performed well in the past, although more efficient heat-transfer designs will probably be used in larger, commercial plants. The regenerator at Edgewater consists of two parts, a enclosed, rectangular, horizontal electric kiln and a continuous belt conveyor that passes through this kiln and carries the sorbent. The kiln is maintained at about 600°C. Regeneration can be carried out in air or in a controlled, reducing environment.

A screening station is employed after the regenerator to remove spent sorbent from the system during each regeneration cycle. Typically, 10 percent of the sorbent is expected to be removed with each pass. The removed materials include the smallest granules in the sorbent stream, including any fines that are produced through attrition. An addition of fresh make-up Mag*Sorbent is made to replace the removed material.

The condenser-burner system treats the off-gas from the regenerator when a reducing atmosphere is employed in regeneration. When air is employed in the regenerator, the off-gas typically consists of SO_2 , NO_x , nitrogen, oxygen, and H_2O . In the pilot plant, this off-gas is simply reintroduced to Edgewater's main flue-gas duct. In a full-scale plant, the concentrated off-gas would be processed into sulfur products. When a reducing-gas environment is employed in the pilot regenerator, the off-gas includes copious amounts of elemental sulfur and H_2S . The condenser is used to collect the sulfur in solid form and the burner is used to convert the H_2S back to SO_2 before the off-gas is released to the main flue-gas duct.

DEMONSTRATION TEST PLAN

The tests at Edgewater are being performed in four phases:

<u>Phase 1</u>. The first phase consists of equipment shakedown tests involving trials with individual equipment pieces making up the two circuits. Included in the shakedown tests are runs with both dry flue gas and humidified gas and regeneration trials with both an air atmosphere and a reducing atmosphere in the regenerator.

<u>Phase 2</u>. Parametric studies are being carried out in Phase 2. The effects of changes in the following variables on sorption performance are being evaluated:

- 1. Flue-gas face and space velocities
- 2. Sorbent flow rate
- 3. Approach to adiabatic saturation

- 4. Flue-gas temperature
- 5. SO, concentration in the flue gas
- 6. Sorbent composition
- 7. Sorber design.

Concurrent with the sorption performance studies, evaluations are being performed on how changes in the degree of sorbent saturation, sorbent processing rate, regeneration atmosphere, and regeneration temperature affect regeneration performance.

<u>Phase 3</u>. Upon completion of the parametric studies, a series of cycling runs will be performed. These runs are designed to demonstrate short-term, integrated sorption-regeneration operation of the system. The conditions and procedures that are found most favorable in the parametric studies will be employed.

<u>Phase 4</u>. A number of longer-term continuous runs, covering several days to several weeks of continuous operation, will also be performed. These runs will be operated at steady-state conditions to collect the operating data needed to scale-up the technology to the 50 to 100-MWe utility level.

Once a significant amount of spent sorbents have been generated, Premier Services Corp., the leading U.S. magnesia producer, will assist Sanitech in evaluating the potential of these materials as commercial by-products. The spent magnesia and vermiculite hold promise in soil conditioning and fertilizer markets, acid drainage neutralization, and as well as other value-added uses.

Based on the experience and data generated at the Edgewater facility, Sanitech will complete a full economic evaluation of the Mag*Sorbent technology at the end of the project.

ACKNOWLEDGMENT

Sanitech wishes to thank the Ohio Coal Development Office for co-funding this pilot-plant demonstration and the Ohio Edison Company for providing the host site.

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Figure 1. Electron Photomicrographs of a Typical Sorbent Surface at 10,000X and 40,000X Magnifications

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Figure 2. Sanitech/OCDO Pilot Plant



Figure 3. Photograph of Panel-Bed Sorber

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Figure 4. Commercial Design for Larger Facility

Application of Dow Chemical's Regenerable Flue Gas Desulfurization Technology to Coal-Fired Power Plants

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Abstract

The Dow Flue Gas Desulfurization Process is an advanced regenerable system with high SO2 removal efficiency, small footprint, and the ability to recover SO2-based by-products. The process uses a unique absorbent formulation developed by Dow that reacts reversibly and selectively with SO2, and has very favorable physical and chemical properties.

This paper characterizes the Dow Flue Gas Desulfurization (FGD) Process in terms of its developmental status, anticipated design, and overall economics relative to a number of competing FGD technologies. The design and cost information reported herein was completed by Stone & Webster Engineering Corporation under contract to Dow Chemical U.S.A. Dow prepared system design parameters, flow schematics, and a preliminary P&ID based on test results from the 1 MW pilot plant. Stone & Webster prepared a detailed material and energy balance and developed preliminary designs using power plant flue gas parameters identified in the EPRI report entitled *Economic Evaluation of Flue* Gas Desulfurization Systems.¹ Process equipment was sized based on the material balance; equipment costs were developed using budget quotations from equipment suppliers and in-house estimating data and methods. Economic analysis techniques applied to the competitive economic evaluation are consistent with EPRI assumptions and approaches used to evaluate the other FGD systems reported. The results of this analysis suggest the process compares favorably with commercial FGD systems.

Background

Dow has been a leader in acid gas treating since the early 1950's and currently has about 150 commercial units operating in the field that use a recirculating absorbent to remove an acid gas from a gas stream, recover the gas as a product, and recycle the absorbent to repeat the process. The Dow SO2 Removal process has similar unit operations in the same configuration. However, this sorbent has very different properties. In particular, this same absorbent molecule was designed and synthesized to react reversibly with SO2 and not react with other acid gases that might be present.

Currently, these research activities have progressed to the pilot plant stage and a 1 MW sized unit has been running since June. The data to date has validated the laboratory findings. The work remaining is to optimize operating parameters and costs, and to demonstrate the system on large scale gas streams. The process has shown sufficient potential such that Dow is preparing to begin engineering on multiple large scale (100 MW) demonstrations.

Process Design

Figure 1, Process Flow Schematic, illustrates the unit operations and major equipment required for Dow's regenerable FGD process. The process system design is similar to conventional gas sweetening processes used for H2S and CO2 removal in the gas and refining industries.

Economic Evaluation of Flue Gas Desulturization Systems EPRI GS-7193, Volume 1, February, 1991.

Flue gas (stream 1) exiting the electrostatic precipitator (ESP) or fabric filter passes through an existing ID fan (R-101) upgraded to provide the additional draft requirements of the retrofitted FGD system or the existing ID fan in series with a new booster fan (R-101). It is then quenched and scrubbed with water in the prescrubber (A-103) to remove most of the hydrochloric acid (HCI), some of the remaining fly ash, and a small amount of SO2 and SO3, which is present mainly as sulfuric acid mist. Makeup water (stream 2) is provided to replace evaporation and blowdown losses.

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Blowdown from the prescrubber (stream 3) is neutralized with caustic or lime and could normally be incorporated with coal pile runoff treatment or sent to an ash pond.

The prescrubbed flue gas (stream 4) passes through a high efficiency mist elimination system before entering the SO2 Absorber (A-101) where it is contacted with Dow's absorbent for SO2 removal. Scrubbed flue gas passes through another high efficiency mist elimination system before proceeding to the stack (stream 5). SO2 rich absorbent from the absorber proceeds to the Rich/Lean Absorbent Exchanger (E-103) where it is heated by hot lean absorbent.

The heated rich absorbent flows to the SO2 Stripper (A-102) where SO2 is thermally desorbed. The vapor phase of the SO2 stripper overhead (stream 10) proceeds to by-product recovery. Lean absorbent (stream 13) is cooled in the Rich/Lean Absorber Exchanger (E-103) and in the Lean Absorbent Cooler (E-102) with cooling water, and stored in the Lean Absorbent Surge Tank (T-102) prior to reentering the absorber. The Absorbent Surge Tank (T-102) may not be required if sufficient hold-up for the system can be provided in the bottom of the stripper.

The recovered SO2 stripper discharge gas flows through a Water Condenser (E-104) where it is cooled with cooling water, condensing most of the water vapor. The resulting sulfur dioxide rich gas is separated in the Water Recycle Drum (D-105) as recovered sulfur dioxide by-product (stream 11). The recycled water (stream 12), with an equilibrium amount of SO2, is pumped back to be added to the rich absorbent (stream 6) leaving the absorber (A-101).

As the absorbent recirculates between the SO2 absorption (A-101) and steam stripping (A-102) operations, it accumulates impurities that need to be removed. These impurities include fine ash particles, heat stable salts, and other soluble compounds. Filters will be used to remove ash particles from the absorbent. Heat stable salts are removed in a slipstream of absorbent using a proprietary Dow technology.

Process Development Status and Schedule

The purpose of this paper is primarily to report the comparison of this developmental technology, in its current state, to other technologies using recently published *EPRI FGD Economics*. It is felt that as the research continues, a comparison to existing technologies must be made and regularly updated to assure that a reasonable and viable process is emerging. An initial report on the process was presented at the AICHE conference in Houston earlier in this year.

The process chemistry can be generally characterized by the following reactions.

SO₂ + H₂O ↔ H₂SO₃ H₂SO₃ ↔ H⁺ + HSO₃⁻ R₃N + H⁺ ↔ R₃N+H The absorbent is a new compound and has been through the EPA evaluation procedures. The toxicology testing, both for the new compound as it would be delivered to a plant and as it exists in the process, has indicated that the material has the EPA designation of "essentially non-toxic". It has a very high boling point and therefore almost no material is vaporized and carried out with the scrubbed gas. The material is very stable so that virtually no therma' degradation occurs in the process. Reactivity with SO2 is very fast and complete such that removal to very low levels can be achieved with low scrubber circulation rates.

An aggressive schedule of development is being planned based on the favorable data collected to date. A 100 MW demonstration unit is anticipated to begin engineering in January, 1992. A second 100 MW project at a different site would begin in mid 1992. A 300 MW unit is planned beginning in 1993. The purpose of these first units would be to verify the process on a variety of coals at commercial scale, and to assure an understanding of the costs and operating parameters. This accelerated development program is intended to travel the learning curve associated with a new technology in a time frame that would allow the technology to be considered commercially for plants to be built in the latter part of the decade.

Design Basis

The designs presented in the EPRI study, and for the Dow FGD systems evaluated in this paper, are based on a 2.6% S Appalachian coal with a heating value of 13,100 BTU/lb, a chlorine content of .12% and 9.1% ash. This coal is consistent with the base coal specified in the 1989 EPRI Technology Assessment Guide.² The 300 MW power plant has a net heat rate of 9722 BTU/kWh, with a coal burn rate of 111.3 tons/hr. The raw flue gas stream from the ID fan is 3.19 million lb/hr, or 1.03 million acfm at 282° F.

The process design for this Dow FGD system application is based on an SO2 removal efficiency of 98%, and a prescrubber system designed to saturate the flue gas and remove 90% of the chlorides and 25% of the fine fly ash that survive a high efficiency electrostatic precipitator. Booster fan capacity of about 10 inches water is required for this configuration.

By-product Recovery Options

Three by-product recovery options were evaluated, including the production of sulfuric acid, elemental sulfur, and liquid SO2. Process designs, capital and operating costs were developed for each recovery option. Sulfuric acid production results in the highest capital cost; elemental sulfur production has the highest operating cost; while liquid SO2 has the lowest capital and operating cost. However, the relatively small market for liquid SO2 will limit the applicability of this option. Most utility applications are expected to require elemental sulfur production, primarily because of the ability to store by-product indefinitely should byproduct marketing and/or transportation difficulties interrupt the shipment of by-product from the plant. By-product systems to recover sulfuric acid and elemental sulfur are briefly described in the following sections.

Sulfuric Acid Recovery

Figure 2 presents a preliminary flow diagram of a sulfuric acid plant based on information provided by Monsanto.

²EPRI P-6587-L, <u>1989 EPRI Technology Assessment Guide</u>

The absorbent regeneration plant by-product, a water saturated SO2 gas, is the feed to a suffuric acid plant. The feed stream at approximately 18 psia and 213° F is first cooled to recover water that is recycled back to the regeneration plant. The SO2 gas is dried by contacting with sulfuric acid. The dried SO2 gas is heated and contacted with air in several vanadium pentoxide catalytic reactions. The cooled converter effluent is contacted with an aqueous acid stream to absorb SO3 from the gas stream and form sulfuric acid. This absorber overhead gas, consisting of a mixture of SO2 and air, is preheated against the hot feed stream. To reduce (recover) the remaining SO2 content of this overhead gas, the gas is passed through a secondary converter followed by a secondary absorber. The tail gas from the secondary absorber has approximately 45 lb/h of SO2 and must be returned to the flue gas upstream of the scrubber. The exothermic conversion of SO2 to SO3 provides the necessary feed preheat. At startup the catalyst bed must be preheated to the initial reaction temperature of 950° F to initiate the reaction. To achieve this initial catalyst bed. In normal operation, the SO2 is bypassed around the heater. The air preheat requirement applies to both the primary and secondary convertors.

Elemental Sulfur By-product Recovery

Figure 3 is a flow schematic for a sulfur recovery process provided by Allied Chemical.

Natural gas is heated by low pressure steam in a preheater and then mixed with the SO2 stripper overheads stream to raise the fluid temperature above the dew point of sulfur before entering the reduction process.

The sulfur dioxide, SO2, is reduced, in part, to form hydrogen sulfide, H2S, to a required ration of H2S/SO2 of 2/1 with some formation of sulfur.

The SO2 reduction is achieved in the catalytic reduction system. The reaction is exothermic and sustains the required reaction temperature. Elemental sulfur that is formed in the reactor system is condensed in an inclined shell and tube exchanger by generating low pressure steam. Sulfur is condensed and flows to the sulfur pit.

The residual process gas stream flows to the first stage of a two-stage Claus reactor system where an exothermic reaction occurs between the H2S and SO2 to form sulfur and water. The partially converted hot process gas is then cooled in a vertical steam generator to condense the sulfur which flows to the sulfur pit.

Unreacted process gas then flows to the second Claus reactor where H2S and SO2 forms additional sulfur. The sulfur is condensed in a second vertical steam generator and flows to the sulfur plt. The residual gas passes through a demister to recover entrained liquid from the tail gas stream. This tail gas stream can then be incinerated to oxidize any H2S to SO2, and recycled back to the water recycle drum, D-105. Some of the 50 psig steam generated is used to maintain liquid sulfur in the sulfur plt by means of a submerged coil. There is a net export of steam that can be used to supplement the SO2 stripper reboiler steam requirements, or the heating coil steam to the liquid sulfur storage tanks.

Competitive Analysis

Levelized costs were calculated using EPRI methodology and assumptions based on the EPRI GS-7193 report. The levelized (\$/ton) costs for the Dow FGD and several competing systems are summarized in Figure 4 for the two by-product cases shown, alongside several of the conventional and advanced FGD systems evaluated by EPRI. These represent values for a new 300 MW plant and do not include allowances for additional retrofit costs for adapting existing plants.

Conclusions

Based on the results of the technical and economic analyses completed for the 300 MW Dow FGD System, the following conclusions summarize the implications of the information summarized in this paper:

- 1. The overall economics of the Dow FGD Process appear favorable to the other FGD technologies evaluated to date by EPRI, primarily due to the value of by-products and the elimination of the solid waste disposal costs associated with throwaway systems. Capital and operating costs for the Dow FGD system with sulfuric acid or elemental sulfur recovery are lower than those for the limestone systems. These results are very sensitive to variations in the assumptions and methodology derived from the EPRI study.
- The Dow FGD system has many technical benefits compared to conventional and advanced limestone systems. Most dramatic is the fact that it is almost free of solids handling systems, which are more expensive to operate and maintain, and are less reliable than liquid systems.
- 3. Of the three by-product recovery systems evaluated, liquid SO2 is the most economic, followed by sulfuric acid and elemental sulfur. The economics of each by-product system are very sensitive to the capacity factor of the unit and by-product unit value.
- 4. The results presented in this paper can be compared directly with the economics published recently by EPRI for 15 other FGD technologies, as well as additional cases EPRI will publish early next year.

FIGURE 1. 300 MW FGD PROCESS

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FIGURE 2. SULFURIC ACID PLANT PROCESS

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FIGURE 3. ALLIED CHEMICAL SO2 REDUCTION PROCESS



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PILOT TESTING OF THE CANSOLV[®] SYSTEM FGD PROCESS

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ABSTRACT

Proof-of-concept pilot plant results are reported for a novel regenerable, retrofittable FGD technology. The process utilizes an amine based absorbent and in-duct scrubbing. The absorbent is regenerated by steam stripping to recover the SO₂ as a pure gas. The pilot plant processes 10,000 m³/hour (6,000 ACFM) of flue gas from utility boilers at Suncor's Oil Sands plant, which fires 7% sulfur petroleum coke. The pilot plant is a highly instrumented and versatile research unit that is skid mounted for relocatability. Statistically designed experiments were run over a wide range of independent variables, including 1,000-5,000 ppmv SO₂, L/G of 0.03 - 0.26 1/m³ (0.25 - 2.0 gal/MACF) and scrubbing temperatures of 20° - 60°C (70° - 140°F). The CANSOLV System achieved >95% SO₂ removal at low L/G ratios and scrubber residence times of less than 1 second and at a pressure drop of about 15 mm Hg (8"W.G). The results confirm that the CANSOLV[®] System is economically superior to the advanced wet limestone FGD processes, while delivering other benefits, such as small footprint, higher SO₂ removal and energy efficiency.

INTRODUCTION

The 1990 U.S. Clean Air Act is a recent event in the continuing world wide trend towards improving the environment of "Mother Earth". It is becoming widely recognized that mankind's ability to pollute is starting to exceed the capacity of natural processes to cleanse and remedy the air, water and soil contamination. The last 20 years have been a time of substantial progress in the control of sulfur oxide emissions resulting from the burning of sulfur bearing fuels and from industrial processes. Very substantial expenditures have been made in the development of FGD technology, but considerable room for improvement remains. The dominant DeS0_x technology today is limestone or lime based processes in various forms. While in general reliable and, in some forms, capable of high SO₂ removal efficiency, they produce large quantities of low value waste products, are expensive to build and operate and are difficult to retrofit in constrained sites due to the large equipment size.

Regenerable processes such as the Wellman - Lord or MgO process, avoid the waste product problem of calcium based chemistry, but they are significantly more expensive in terms of both capital cost and operating cost.

Research and development work by Union Carbide on a novel, regenerable, amine-based SO_2 scrubbing process has now progressed to proof-of-concept testing in a 2MW size field pilot plant. This paper reports initial results from that work.

PROCESS CHEMISTRY

Due to technical simplicity, aqueous scrubbing/regeneration cycles have been the basis of the most successful regenerable FGD processes such as the Wellman - Lord. In aqueous media, dissolved SO_2 undergoes reversible hydration and ionization reactions that can be summarized as:

$$SO_2 + H_2O = H_2SO_3 \tag{1}$$

$$H_2SO_3 = H^* + HSO_3$$
 (2)

$$HSO_3^* = H^+ + SO_3^=$$
(3)

The dissolution or equilibrium constants for steps (2) and (3) are reported as 1.54×10^2 and 1.02×10^{-7} at 18°C in dilute solution¹. The scrubbing capacity of water can be increased by adding a buffer or base to the absorbent which consumes hydrogen ions and causes reactions (1) - (3) to shift to the right.

Steam stripping regenerative processes in which the bases used are stronger than sulfite, degenerate to a sulfite/bisulfite scrubbing cycle, i.e. the effective base is sulfite.

$$2 \text{ NaOH} + SO_2 \rightarrow \text{Na}_2SO_3 + H_2O \tag{4}$$

$$Na_2SO_3 + SO_2 + H_2O = 2 NaHSO_3$$
(5)
Reaction (4) occurs in the initial contact of the base with SO_2 . Reaction (5) is the basis for scrubbing, being shifted towards the right in the absorber and being reversed by high temperature in the regenerator.

The sodium ion does not participate in the reaction, its role being to provide electrical neutrality to the solution. Reaction (5) can then be restated as (6), in order to highlight the essential process.

$$SO_3^- + SO_2 + H_2O = 2 HSO_3^-$$
 (6)

Any soluble cation can be used, as is sodium in the Wellman - Lord process, or a protonated amine (the triethanolammonium ion) in the UCAP process². The exact structure of the CANSOLV[®] FGD Process amine absorbent is proprietary.

The scrubbing/stripping reaction can be represented as:

$$R_{1} = R_{1} = R_{1}$$

$$R_{2} = N + SO_{2} + H_{2}O = R_{2} = N^{+} - H + HSO_{3}^{-}$$
(7)
$$I = R_{3} = R_{3}$$

The amine absorbent of the CANSOLV[®] FGD Process combines a low molecular weight and high concentration, resulting in a net removal of 25-100 g SO₂/1 (0.2 -0.8 lb. SO₂/USG), depending on the inlet SO₂ concentration, scrubbing temperature and % SO₂ removal desired.

The rate of SO_2 absorption into limestone slurries is limited by the slow dissolution of limestone, which can only be partly controlled by limestone grind fineness and slurry pH.

Since the CANSOLV FGD Process, as represented by Equation (7), is essentially an acid base reaction in a concentrated, homogeneous medium, its rate is very high. The limitation to mass transfer then becomes the gas side resistance, which can be minimized by proper scrubber design.

The high SO_2 capacity of the CANSOLV FGD Process absorbent and its high reactivity eliminate the need for absorbent recycle in the scrubber and permit operation at very low L/G ratios.

Practical SO₂ absorbents must be non-volatile in order to prevent equilibrium vapor phase losses with the flue gas. The aromatic amines of the Sulphidine and Asarco processes exhibit significant volatility and require removal from the treated flue gas stream by washing with dilute sulfuric acid³. This is both costly and complicated. The absorbent of the CANSOLV FGD Process is essentially nonvolatile (vapor pressure < 25 ppb).

Due to the special nature of the CANSOLV FGD absorbent, strong acids which either form in or are captured by the amine as Heat Stable Salts (HSS), may be present at high concentrations without limiting the amine solution's scrubbing capacity.

Heat stable salts form by reaction of the amine absorbent with acids that are either nonvolatile or too strong to be driven off in the steam regeneration step. These acids are introduced into the absorbent from the following sources:

- 1. Flue gas may contain SO₃ (produces H₂SO₄), HCl, HF, and NO₂.
- 2. SO_2 oxidation to SO_3 by oxygen.
- 3. Disproportionation of sulfite to sulfate and other sulfur species:

 $SO_3^- \rightarrow SO_4^- + \text{ other sulfur species}$ (8)

Many other reactions that produce strong acids are described in Reference 4.

PROCESS DESCRIPTION

The CANSOLV^{\bullet} Flue Gas Desulfurization process flow diagram is similar to the well known alkanolamine H₂S-CO₂ removal process and is depicted in Figure 1. Countercurrent multi-stage "in duct" scrubbing, utilizing air atomizing nozzles takes advantage of the absorbent's high reactivity and SO₂ capacity to effect up to 99% removal in a very compact and energy efficient manner.

The CANSOLV FGD absorbent is a homogeneous liquid throughout the process cycle and exhibits no tendency to precipitate solids. This results in several benefits:

- There is no equipment erosion, as with slurry processes;
- The SO₂ amine reaction that occurs in the homogeneous solution is fast. It therefore allows small contacting devices to be used in comparison to those needed for limestone systems;
- There is no scaling in the absorber or gas ducts;
- There are no significant solids handling problems.

The absorbent is non-volatile, stable both thermally and oxidatively and has good health and safety characteristics.

The process consists of a gas cooling and prescrubbing section, an SO_2 scrubbing section and a regeneration and solvent purification section.

The flue gas cooling and prescrubbing equipment reduces the temperature of the flue gas and removes most of the particulate matter and strong acids (SO₃, NO₂, HCl, HF etc.) The flue gas also leaves the prescrubber fully saturated with water.

Flue gas scrubbing is effected in-duct at flue gas velocities of up to 30-40 ft/sec. In the pilot plant, the high reactivity of the absorbent has allowed each of the three mass transfer stages to be only 8 feet long.

High speed interstage solvent collectors are used to recover the absorbent between stages and a final mist eliminator downstream of the scrubber removes amine to an insignificant level from the flue gas before it is sent to stack.

The regenerator is similar in design to regenerators in ethanolamine gas sweetening service. It is equipped with a steam heated reboiler to regenerate the amine and a vacuum pump to ensure that regeneration occurs at low enough temperatures to suppress the disproportionation of regenerable SO_2 into non regenerable SO_3 .

Strong acids in the flue gas, such as HCl and H_2SO_4 , which are not removed in the prescrubber, react with the absorbent to form heat stable salts. Additional salts are also formed in the amine solution when some of the dissolved SO_2 converts to SO_3 . The concentration of heat stable salts in the amine solution is controlled by taking a small, continuous purge stream of amine from the unit, purifying it chemically and returning it to the unit.

The only waste streams generated in the CANSOLV[®] FGD Process are:

- 1) the blowdown from the prescrubber water loop, and;
- 2) the sodium salt purge stream from the absorbent purification unit.

Effluent treatment techniques are site specific and depend on the composition of the flue gas and local environmental regulations that apply to the site. The small quantities of waste produced by the CANSOLV FGD Process, however, allow zero effluent discharge processes to be considered.

PILOT PLANT TESTING

Laboratory testing proved that the absorption and regeneration concepts of the process were sound. The commercial economics suggested by the lab data were sufficiently attractive to convince Union Carbide that further testing of the CANSOLV[®] FGD Process in a larger facility was justified. In May 1990, the Suncor Oil Sands Group Inc. in Ft. McMurray, Alberta agreed to work with Union Carbide to demonstrate the process at their plant and funds were secured to build it. The pilot plant design was heavily impacted by the need to: a) extract the data that will be needed to design and operate a larger facility and; b) to prove the viability and operability of the process in an industrial setting.

The pilot plant was designed to treat 6000 ACFM of flue gas emanating from the Suncor utilities boilers, which burn 7% sulfur petroleum coke as fuel. Three 70 MW_e boilers fire 2,300 tons per day of petroleum coke that is produced on site by the bitumen upgrading process. About 65 MW of electricity is produced by each boiler, while the balance of the steam is used for the extraction and upgrading of the bitumen to synthetic crude oil.

Properties of the coke are listed in Table I. Average flue gas conditions are given in Table II. The volume of flue gas treated in the pilot plant is about 3% of one boiler's output, roughly equivalent to about $2MW_e$. The pilot plant is of modular design and was shipped to Fort McMurray in December 1990. It was started up on February 25, 1991.

OPERATIONAL RESULTS

From startup through to June 22, 1991, a total of 2832 hours of operating time were available. The unit performed as follows:

	Flue Gas/Conditioning		Amine Regeneration		
Operating Time	2476 hrs	87%	2184 hrs	77%	
Planned Shutdown	168 hrs	6%	168 hrs	6%	
Adjust for Exps	0 hrs	0%	240 hrs	9%	
Mechanical S/D	<u>188</u> hrs		<u>240</u> hrs	9%	
Total	2832 hrs	100%	2832 hrs	100%	

The pilot plant operated very stably. When experimental plans allowed the operating conditions to be left unchanged for extended periods, there was very little work to be done to supervise the unit. In addition, when changes were required, the pilot plant achieved steady state operating conditions within about two hours of the change.

The pilot plant also permitted the reagent side to be isolated from the flue gas side so that minor maintenance could be performed with minimal disruption to the overall unit. The ability to "uncouple" the two systems allowed some maintenance of each system to be performed while the other was still on line.

INSPECTION FOLLOWING NINETY DAYS OF OPERATION

A seven day planned shutdown was taken to perform a general inspection of the unit after ninety days of operation. During this period, all corrosion coupons were pulled and several critical areas of the unit were inspected in detail. Both the coupons and the general inspection of the unit indicated that 316 stainless steel performed acceptably in amine and dilute acid service.

FLUE GAS SYSTEM

The flue gas cooling and conditioning system has proven to be very reliable. Outages of the flue gas system were caused by two failures of the flue gas emergency shutdown valve. The heat exchangers and the rotating equipment in the flue gas cooling and conditioning system have operated acceptably. Additional outages of the flue gas side occurred because the supply of flue gas quench water was unreliable. A change was made in the supply system and service was upgraded.

AMINE SYSTEM

The operation of the SO_2 absorption and regeneration sections was interrupted several times to repair seal and gear problems in the reflux pump. Most of the rotating equipment, including the reflux pump, was not spared in the pilot plant. This decision contributed to nearly 200 hours of amine side outage during the early operating period that could have been avoided. All other rotating and heat exchange equipment in the SO_2 absorption and regeneration system have operated acceptably.

PILOT PLANT EXPERIMENTATION - RESULTS

In excess of 15 independent variables characterize the operation of the CANSOLV^{Φ} System. Statistically designed experiments were run and the results were analyzed by regression analysis to generate a statistical model of the process. Of these variables, the inlet SO₂ concentration, the flue gas scrubber velocity and the inlet gas temperature served most to characterize the process's performance. Figure 2 illustrates the "experimental universe" that established the parameters for the experimentation work at the pilot plant.

The pilot plant was run at conditions within the experimental universe and SO_2 removals of between 90% and 99% were demonstrated. The results were proved and are reproducible. SO_2 removals up to 99% at any inlet SO_2 concentration can be obtained. The variability in the removal rates was impacted not only by the flow, inlet SO_2 concentration and temperature, but also by other variables such as L/G ratios, stripping rate etc. The SO_2 removal rate can thus be adjusted to almost any value through the adjustment of only a few of the critical values that impact the operation of the unit.

PROCESS ECONOMICS

Union Carbide commissioned a study by an independent engineering firm to compare the economics of several commercial processes to the CANSOLV[®] FGD Process. Four lime/limestone processes and one regenerable process were selected for comparison. A power plant consisting of 2 x 150 MW units was chosen as the basis for the study. The FDG capital costs were based on coal containing 4.1%, while the operating costs were generated on the assumption that 3.3% sulfur coal was normally used. The results are shown in Figure 3.

The study proved that when CANSOLV is compared with limestone processes in a high sulfur application, the results can be very favourable.

Generally, the CANSOLV^{\circ} System also is quite insensitive to variable coal sulfur compositions. The graph in Figure 4 shows how the cost for CANSOLV would vary with sulfur content.

Furthermore, considering that the CANSOLV FGD Process is still at a relatively early stage of optimization, it is not unreasonable to expect further improvement in process economics.

CONCLUSIONS

The early operation of the pilot plant has clearly shown that:

- SO₂ can be removed from flue gas to any desired level up to 99% by varying the L/G ratio of the solvent fed to the unit without exceeding an L/G ratio of about 0.26 l/m (2 USG/1,000 ACF) of gas.
- 2) The CANSOLV[®] System reagent is stable.
- 3) The CANSOLV System reagent absorbs SO₂ at high scrubbing velocities. SO₂ can be removed from the amine by steam stripping and the amine may be reused in the absorber.
- 4) The interaction of sulfur species in the system is easily controllable and does not impact significantly on the operability of the process.
- 5) The rate of heat stable salt formation in the system requires less than 1% of the circulated solution to be removed for treatment and subsequent reuse.

Pilot plant results have clearly indicated that CANSOLV technology represents a viable, low cost system for SO₂ emission control for coal fired power facilities. It has been demonstrated that the CANSOLV System can remove up to 99% of the SO₂ in the flue gas and that it represents a trouble free system for SO₂ removal.

ACKNOWLEDGEMENTS

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Table I

SUNCOR Petroleum Coke Analysis

Moisture	8% - 10%
Volatiles	10%
Fixed Carbon	84% - 87%
Sulfur	7%
Ash	3%
Ash Analysis (as oxides):	
Si	50.5%
Al	25.5%
Fe	7.5%
Ca	1.9%
v	5.5%
Others	9.1%

Table II

Average Flue Gas Conditions

Composition:	
$\overline{N_2}$	81%
$\overline{O_2}$	8%
CO ₂	11%
SO ₂	3600 ppm
Cl, F	Present
NO	175 - 375 ppm
Particulate	$0.06 - 0.11 \text{ kg}/10^3 \text{ kg flue gas}$
	(0.03 - 0.06 gr/SCF)
Temperature	475° - 550°F
Pressure	-2 mm Hg (-1" H ₂ O)

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Figure 1. CANSOLV[®] System Schematic



Figure 2. Flue Gas Conditions



Figure 3. Capital and Operating Costs CANSOLV® vs Other FGD Technologies



Figure 4. CANSOLV[®] Cost Sensitivity To % Sulfur in Coal

DRY DESULPHURIZATION TECHNOLOGIES INVOLVING HUMIDIFICATION FOR ENHANCED SO₂ REMOVAL

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1. ABSTRACT

The paper is in two (2) parts. The first part describes an In-Furnace Dry SO_2 Scrubbing Technology while the second part describes a Post Combustion Dry SO_2 Scrubbing Technology. Both technologies utilize enhancement features to improve overall sulphur removal efficiencies.

The first part of the paper describes the key design features and the results of lime injection into a furnace plus gas humidification upstream of the electrostatic precipitator. The desulphurization plant has been installed on a 65 MW (thermal capacity) stoker-fired boiler. The results cover desulphurization efficiency, the impact of the process on the boiler and electrostatic precipitator, ash utilization, and overall reliability. The flue gas humidification, in the conditioning reactor, result in an overall sulphur capture of better than 90% at high boiler load and a Ca/S stoichiometric ratio around 2.0. A desulphurization efficiency of approximately 65% was obtained with lime injection alone.

(The paper further describes the pertinent design features and the results of dry humidified hydrated lime in a fluidized bed reactor after the air heater and upstream of the fabric filter dust collector, or electrostatic precipitator). The desulphurization plant is installed on a district heating plant in the South of France with a capacity of 3 MW (thermal). The results cover the desulphurization efficiency at various Ca/S stoichiometric ratios and humidification levels. Results show that with an acceptable level of humidity in the reactor, an overall sulphur capture of better than 90% by weight, at a Ca/S stoichiometric ratio around 1.5 can be achieved.

2. INTRODUCTION

An "In-Furnace" process utilizes limestone injection directly into the furnace, with a conditioning-tower installed downstream. In contrast, a "Post-Combustion" system employs the injection of dry hydrated lime or lime powder into the flue gas stream downstream of the furnace and economizer. The "Enhanced-Dry" process activates the powder reagent reactivity by increasing its humidity or chemical reactivity prior to injecting the powder into the flue gas stream, downstream of the furnace and economizer.

The method of direct desulphurization discussed here is the absorption of sulphur by the basic sorbents $CaCO_3$ (powdered limestone) and $Ca(OH)_2$ (slaked lime). <u>Fig.1</u> shows the qualitative process of sulphur capture, plus that of any halogens present.

When $CaCO_3$ or $Ca(OH)_2$ is employed as the additive for pollutant capture, an endothermic decarbonation or dehydration reaction (calcination) takes place in the furnace in accordance with the following equations:

CaCO,>	$CaO + CO_2$	(1)
Ca(OH)2	CaO + H-O	(2)

The CaO particles react with oxides of sulphur and other pollutants like halogens according to the following exothermic reactions.

CaO	÷	SO ₂ +	1/2 Q ₂ >	CaSO4	(3)
CaO	+	HCl		$CaCl_2 + H_2O$	(4)
CaO	+	2 HF	>	$CaF_2 + H_2$	(5)
CaO	+	SO3	>	CaSO	(6)



Fig. 1: Schematic representation of direct Desulphurization process with Conditioning reactor

During direct desulphurization in the furnace the additive particles become covered with a compact layer of sulphate. Migration of the SO_2 deep into the pores and adequate diffusion velocity in the boundary layer can only be attained with very long residence times (minutes or hours), therefore, the core of the additive particle is not available for reaction with SO_2 .

In order to make this free CaO available for further sulphur capture, a conditioning reactor is employed downstream of the furnace. The prerequisite for applying this additional process for better sorbent utilization is the presence of free active CaO in the flue gas exiting from the boiler.

For the conditioning process, it is necessary to further humidify the flue gas. In order to accomplish this, water is injected into the flue gas at the reactor inlet. Considerable care has to be taken to achieve good atomization in order to ensure complete evaporation inside the reactor. As a result of the hygroscopic properties of the free CaO, the water vapour diffuses within the pores of the CaO core which is surrounded by a layer of CaSO₄. The free CaO in the pores then combines with the H₂O to form Ca(OH)₂. This exothermic reaction tends to progress outwards from the pores on the exterior of the particle, and is also encouraged by discontinuities and substitution molecules.

Since $Ca(OH)_2$ has a lower bulk density and a greater specific surface area than CaO, the resulting expansion of the hydroxide and the heat produced during slaking tends to split the material along the particle boundaries. At these break points a new surface capable of further reaction with the pollutants, is produced. During the first reaction there is slaking in order to form $Ca(OH)_2$, followed by the capture of sulphur dioxide.

$CaO + H_2O$	$Ca(OH)_{2}$	+	1.952 KJ/Kg CaO	(7)
$Ca(OH)_2 + SO_2 + H_2O + 1/2 O_2$	CaSO₄	•	2H ₂ O	(8)
$Ca(OH)_2 + SO_2 + H_2O$	CaSO ₃	-	2H ₂ O	(9)

At the fracture zones of the particle the free CaO takes part preferentially, in the sulphur capture reactions according to the following equations:

CaO	+	$SO_2 + 2 H_2O + 1/2 O_2$	CaSO ₄ .	2 H ₂ O	(10)
CaO	+	SO ₂	CaSO ₃		(11)
CaO	+	SO + 2 H-0	CaSO ₃ .	2 H ₂ O	(12)

A comparison of the reaction equilibrium constants show that for sulphur capture the conversation to calcium sulphate is the most favoured reaction.

Simultaneous with the absorption of sulphur dioxide, the HCl and HF concentrations in the uncleaned gas are also reduced. The chemical reactions involved are described by the following equations:

$Ca(OH)_2 + 2 HCl$	$CaCl_2 + 2H_2O$	(13)
CaO + 2 HCl	$CaCl_2 + H_2O$	(14)
$Ca(OH)_2 + 2$ HF	CaF ₂	(15)
CaO + 2HF	$CaF_2 + H_2O$	(16)

The achievable desulphurization efficiencies depend heavily upon the approach to the adiabatic saturation temperature of the flue gas.

The technical components of the conditioning process are a conditioning reactor, a flue gas side bypass and (possibly) a flue gas reheat system as shown in Fig. 2.

Preliminary experiments have shown that the degree of desulphurization achievable in the reactor substantially increases with the amount of water evaporated there. Thus, the aim is to run the conditioning reactor as close to the dew point as possible, ensuring that neither incomplete evaporation nor condensation on the reactor walls will occur.



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A retrofit with the direct desulphurization process in combination with a conditioning reactor, is recommended, especially for boilers equipped with electrostatic precipitators, is quenching the flue gas with water helps to upgrade the performance of the electrostatic precipitator.

3. <u>TEST BOILER</u>

The boiler shown in Fig. 3 is a stoker-fired unit with a thermal capacity of 65 MW. It fires a bituminous coal containing roughly 1 % sulphur with a net calorific value of approx. 29 MJ/kg. The unit is a 3-pass boiler, the furnace forming the 1st pass, with the 2nd pass containing superheaters and the 3rd pass the economizer. The superheater section and the economizer are equipped with sootblowers. Spray attemperation is included in the steam circuitry between the superheater section 1 and 2 as well as between 2 and 3 to bring the steam temperature down to 525° C.

The unit is equipped with a cold-side ESP mounted on top of the boiler with a nominal design specific capture area of $81.8 \text{ m}^2 / (\text{m}^3/\text{s})$. The ESP consists of two separately energized electrical fields in series. The particulate emissions are less than 50 mg/m³.

Bottom ash from the travelling grate is extracted dry and stored separately in a hopper.

The flyash from the ESP and the bend between the 2nd and 3rd pass is pneumatically conveyed to a storage silo from where it can be discharged either into trucks or railcars.

4. CONCEPT OF SORBENT INJECTION

Extensive investigations have shown that the following four key parameters mainly determine direct desulphurization:

- 1. Flue gas temperature at the point of injection of the additive.
- 2. Residence time of the flue gases in a definite temperature range.
- 3. Dispersion of the additive in the furnace.
- 4. Reactivity of the additive.

Previous investigations have shown that additive injection should not take place at a temperature higher than 1200° C and that the period required to cool the flue gases down to approx. 750° C should not be shorter than around 1 to 2 seconds. The shorter residence time applies to additives with a smaller particle size or larger specific surface area, e.g. Ca(OH)₂.

In order to determine the optimum sorbent injection level, the mean axial temperature profile in the furnace was computed with help of field measurements and heat transfer modelling, as shown in <u>Fig. 4</u>. With the aid of a sulphation model, in which the temperature at the point of injection and the residence time down to 750 °C play a major role, two injection levels at 10.8 m and 18.5 m were established. The injection nozzle spray direction can be adjusted over a range of + 30° to - 30° along the vertical axis of the furnace.

<u>Fig. 5</u> shows the residence time as a function of boiler load for the higher and the lower level and for three different angles of sorbent injection.



<u>Fig. 3:</u> Schematic diagram of test unit at Boehringer Ingelheim.



<u>Fig. 4:</u> Flue gas temperature profile along the axis of boiler furnace.



Fig. 5: Residence time of flue gas as a function of boiler load for higher and lower level of additive injection in the sulfation window.



Fig. 6: Schematic flow of direct desulphurization system.

The additive flow rate can be set manually to produce a constant molar ratio Ca/S at a particular load e.g. for test purposes. In the normal case when the boiler is operated according to the load demand, the additive flow rate is adjusted automatically with the help of a controller according to a function m = f (load) to achieve a required percentage of desulphurization. In addition to the input curve the additive flow can be automatically corrected so as not to exceed a given SO, emission level.

5. <u>Conditioning REACTOR DESIGN</u>

Fig. 7 shows in schematic form the arrangement of the conditioning reactor in the flue gas duct system. The damper is the bypass and can be set at intermediate positions between "open" and "closed", thus making it possible to route any desired flow through the conditioning reactor right up to the full flue gas flow.

The conditioning reactor is cylindrical and located in a vertical position. At full load, the flue gases are at a temperature of about 150° C and the residence time in the cylindrical section of the reactor is approx. 8 seconds. Flow through the conditioning reactor is from top to bottom.

The head of the reactor consists of a diffusor which diverges the flow cross-section to the diameter of the reactor. At the inlet to the diffuser, nine external twin-fluid nozzles, manufactured by Lechler, for the injection of water, are located in the flue gas duct cross-section (Fig. 7). The external mixture of water and atomization fluid allows either steam or compressed air to be used. The liquid (water) is fed in the middle of the sprayer and leaves the nozzle in the form of a hollow cone. The compressed air is fed through a co-axial pipe to the chamber, which is equipped with swirl inserts.

The atomizing nozzle is a prefilm type; that is the liquid is formed into a liquid sheet before it is hit by the high velocity swirled airstream. The prefilming of the water provides fine atomization due to the very thin water sheet.

The droplet size distribution (Sauter Mean Diameter) depends on the air to water ratio and on the water pressure. With higher water pressures it is possible to achieve finer droplets for a relatively low air consumption. This allows selection of the optimum design parameters for atomization.

The main advantages of a nozzle with external mixing and prefilming of the liquid are the higher amount of atomized water and the possibility of utilising steam instead of air. Because of the separate feeds of air and water flow to nozzle, they can be very simply controlled, by setting the required pressure for each medium.

The length and angle of divergence of the diffusor approximately match the range and spray angle of the nozzles, so that the water droplets are dispersed in the flue gas, at the outlet of the diffusor section. In the cylindrical part of the reactor the residual water is evaporated, and the secondary desulphurization described above, is effected.

The flue gas can be cooled down to within 10° C of the adiabetic saturation temperature at the conditioning reactor outlet. The amount of water sprayed is controlled, in order to set up a predefined temperature at the reactor outlet. It is important that the conditioning reactor is kept dry; that is, the water sprayed in must be fully evaporated. This can be achieved by the choice of a suitable length for the reactor and by limiting the droplet size of the water which is injected. In the present case, the objective is attained by making the cylindrical part of the reactor around 20 m long and limiting the maximum size of the droplets produced during atomization to 130 micron.



Fig. 7: Contitioning reactor arrangement.

This last measure involves high operating costs which might be reduced, in future, by using steam as the evaporating medium. One possible method of shortening the evaporating section for the droplets would be to use water heated to a maximum of 85° C for spraying purposes.

When the flue gases emerge from the bottom of the conditioning reactor, they are sharply deflected and at least part of the entrained particulate matter is ejected. The bottom of the reactor is conical to allow the solid material thus collected, to be drawn off to the fly ash storage silo.

In the rising clean gas duct, the flue gas is heated, if necessary, to be at a temperature of at least 88°C, upstream of the stack. Heating is provided by a tubular heat exchanger operated with saturated steam at a temperature of 193°C and a pressure of 13.5 bar. The amount of steam is controlled on the condensate side in accordance with the flue gas temperature downstream of the heat exchanger.

6. <u>RESULTS</u>

6.1 Direct Desulphurization

Desulphurization efficiency N, is defined as

$$N_{s} = \underline{SO_{toor} - SO_{2}}$$
(17)

SO_{2 theor}.

where $SO_{2 \text{ lasor}}$ is the maximum theoretical value calculated from the sulphur content of the fuel and SO_2 is the measured value during sorbent injection.

The molar ratio Ca/S is given by the amount of calcium injected into the furnace and the sulphur content of the fuel.

<u>Fig.10</u> shows the desulphurization efficiency as a function of the molar ratio Ca/S for boiler full load and a part load of 43%. These sulphur capture rates are obtained in the optimum operation mode. At a molar ratio Ca/S = 2 with the sorbent Ca(OH)₂, the sulphur capture achieved at full load is about 65% and at low load about 80%.

The sulphur capture curve in Fig.8 demonstrates the expected shape, which has been always round in the investigations. Mathematically such curves can be described with help of exponential functions. Theoretical considerations /1/ show that these sulphur capture curves can be closely represented by the mathematical function:

$N_{1} = 1 - e^{-} A^{-C_{m}S}$

The coefficient A represents the maximum achievable efficiency N_{α} , which is attained when the ratio Ca/S tends towards zero.

$A = N_{\alpha}$, when Ca/S ----> 0

since A is the slope of the tangent to the curve described by equation (18) when Ca/S = 0. The coefficient A can be seen as the characteristic of the direct desulphurization system and hence represents a simple way of quantifying the potential for sulphur capture in the system.

The optimal mode of operation for full and part load can be derived from $\underline{Fiq.9}$ with the aid of the coefficient.

Fig.9 summarized the desulphurization characteristic in relation to residence time. The effect of employing alternately the upper or the lower level and likewise the angle of injection $(-30_o, 0_o, and +30_o)$ can be clearly seen. It is also apparent that increasing the residence time will only improve desulphurization if the sorbent is reliably prevented from encountering excessively high temperatures. Increasing the residence time in the upper part of the permissible temperature range always has a very favourable effect on sulphur capture, leading to a steep rise in the value with increasing residence time. For example, at full load an increase in residence time of 0.3 sec., achieved by directing the nozzles downwards, produces A-value of 55% instead of 36%.

A drop in the value of the coefficient is observed when the residence time is increased, which indicates that the sorbent is being injected at too high temperature. This could, for example, be caused by injection in the tower plane at full boiler load.

6.2 Conditioning Reactor

An initial test series has been already run in order to establish the optimum conditions for sulphur capture while keeping the reactor dry.

For this purpose, the amount of water sprayed into the reactor has been increased in steps, with the Ca/S stoichiometry being maintained constant at Ca/S = 1.5. Since the evaporation heat for the water added was completely taken from the flue gas, the amount of water can be expressed as the difference between flue gas temperature at reactor outlet and the adiabatic saturation temperature for water in the flue gas. \Box . The maximum water flow to be evaporated by a given flue gas flow is given by \Box . - 0. At low values of Δ T, the Ca/S ratio was varied between 1.5 and 2.5. The result is shown in Fig.10.

For all stoichiometric Ca/S ratios, the desulphurization efficiency in the conditioning reactor N_{sq} increases as the temperature difference ΔT between the outlet and the adiabatic saturation temperature of the flue gas decreases. On the other hand, the Ca/S ratio strongly affects sulphur capture, at least at low values of ΔT . With Ca(OH)₂ at a Ca/S ratio - 2, 65% sulphur capture inside the conditioning reactor has been attained at 85% boiler load, resulting in an overall capture N_{sq} of more than 90%. At the same stoichiometric ratio but 70% boiler load, N_{sq} = 84% (N_{sq} = 98%) were measured. 43% load resulted in near 100% capture as the stack SO₂ monitor could no longer detect any SO₂.

During experiments with partial bypassing of the conditioning reactor and increase of residence time sulphur capture was not improved.

However, a certain influence of boiler load on the sulphur capture in the conditioning reactor was recorded: desulphurization $N_{s,q}$ improves at lower boiler loads. This is rather unexpected as the flue gas temperature at the reactor inlet is then also lower and the amount of water to be evaporated for a given oT is also lower. Consequently, the water burden in the flue gas decreases. Further experiments must be carried out to prove whether higher temperatures in the radiant section of the boiler at higher loads also make the sorbent less reactive, as far as desulphurization in the conditioning reactor is concerned.

Up to Ca/S = 2.5, increasing the stoichiometry significantly improves sulphur capture in the reactor. As desulphurization efficiency better than 90% is achieved at this ratio, a further increase of the Ca/S is not necessary.

Going down to less than about 15°C above the saturation point was found to cause condensation on the reactor walls. Thus, $\Delta T = 15$ °C is the limit to which the flue gas can be cooled within the conditioning reactor.



<u>Pig. 8</u>: Desulphurization efficiency η_S as a function of molar ratio Ca/S.



<u>Fig. 9:</u> Desulphurization. characteristics for different operating modes of the additive injection system.



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<u>Fig. 10</u>: Desulphurization, efficiency $\gamma_{S,Q}$ in the conditioning reactor as a function of approach to adiabatic saturation temperature A T with the molar ratio Ca/S as parameter.

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So far, only $Ca(OH)_2$ has been tested as a sorbent. However, it is also planned to conduct experiments with $CaCo_3$.

6.3 Operating Experience with Downstream Plant Components

Fouling of heating surfaces:

It has been observed that the deposits on convective heating surfaces are very loose and light and are easy to clean off with the installed sootblowers. As a result, the fouling remaining layer on the tubes after sootblowing is thinner than in the case of boiler operation without direct desulphurization.

No detrimental effects have been observed on the flue gas ducts, ID fan or stack.

Blectrostatic precipitator:

No unusual fouling or caking has been observed on the electrostatic precipitator during DDP operation.

The prescribed limiting value for dust emissions of 50 mg/m³ STP was a rule maintained during DDP operation as well.

Electrostatic precipitators which have a specific collecting area larger than 75 m_2 / (m^3 /s) (384 ft²/1,000 acfm) can comply with a limiting value for emissions of 50 mg/m³ STP (0,04 11/ 10⁶ BTU) under normal boiler and fly ash conditions.

CONCLUSIONS

Although long-term tests are on-going, the suitability of the combined direct desulphurization process with the conditioning reactor has been proven on an industrial scale.

The capture efficiency provided by a low-cost process involving relatively low sorbent consumption and by-product volume, noticeably exceeds that produced by the other direct desulphurization methods used so far.

7. PRINCIPLE OF THE PROCEDAIR ENHANCED DRY

The principle used by Procedair in its "dry" systems is the absorption of the gaseous pollutant by a powdery material uniformly dispersed within the flue gas stream. The efficiency of the process is a function of the true contact between reagent and the polluted gas, and this has been mastered over many years with the Procedair Venturi Reactor Tower. This however, is not the only factor involved, and for FGD the efficiency has been "enhanced" by the humidification or conditioning of the reagent with a piece of equipment called a conditioning drum patented by Procedair in 1985.

The conditioning of the reagent, hydrated lime in this case, has two favourable effects:

- Cracking of the lime particles with a resultant increase in the solid-gas contact surface,
- Reduction in the temperature of the flue gas being treated.

The pilot/experimental plant which was installed during 1985 was on a municipal heating system boiler plant at Gardanne (France) which incorporated 3 MW thermal power. This plant was operated until 1988 when it was judged that sufficient data and experience had been accumulated to develop and standardise the equipment and to be able to predict and guarantee performance levels.

The original objectives of the program were set to achieve a 90% SO_2 reductioln with a Ca/S stoichiometric ratio of around 2. (equivalent to levels achieved with Spray Dryer Technology). In fact the test demonstrated a superior performance with 95% SO_2 reduction at Ca/S ratios of 1.3.

8. <u>SYSTEM DESCRIPTION</u> (Fig.11)

8.1 Possible Gas Pre-Conditioning

The flue gas may be conditioned prior to the FGD stage, if necessary, to reduce its temperature, in order to achieve with humidified reagent the optimum temperature in the filter stage.

In accordance with the degree of cooling required, one of the following methods could be used :

- Slight dilution with ambient air
- Evaporative cooling
- Heat exchanger
- Heat recovery.

8.2. FGD_Stage

The FGD stage is a compact vertical up flow reactor tower which is comprised of a venturi throat at its base followed by a diffuser section and reactor column, with an external return section.

The reagent, after being humidified in the conditioning drum, is injected into the throat of the venturi. The reagent injected is a mixture of fresh material and the partly used reagent collected in the filter. The velocity of the flue gases in the throat and the reactor column are critical design prints as is the overall residence time in the reactor column and external return section.

It is essential that the reagent is injected into the flue gas stream in a manner which ensures a dispersion which is as homogenous as possible. Its quality is a function of the quantity of recycled product and the injection characteristics. The resultant concentration in the stream is an important parameter.

8.3 Filtration Stage

The loaded flue gas stream passes into a modern generation pulse Jet filter unit which separates the reaction products from the gas stream. The scrubbed gas is exhausted via the main draught fan to the stack and the reaction products are evacuated from the filter hopper by a live bottom screw conveyor.

This partly used reagent and ash are conveyed, either mechanically or pneumatically, to an intermediate holding hopper fitted with product agitation and twin discharge screws. These screws, in conjunction with the level probes in the holding hopper, control the flow of product to the conditioning drum and/or to discharge.





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The product directed to discharge is automatically replaced by fresh reagent and dust.

The use of a fabric filter enhances the efficiency of the system as the reaction of the SO, with the powdery reagent continues as the gas passes through the dust cake built up on the filter surface. It also ensures that very low particulate emission levels can be achieved, certainly superior to those required by legislation.

Conditioning Drum 8.4

The original design of the conditioning drum was extensive and required considerable detailed thought, in order to ensure that:

- The fresh and recycled reagent were homogenously mixed,
- _ The water was uniformly atomised and dispersed.
- _ The product was uniformly humidified.
- The action of the drum did not agglomerate the particles.

Whilst the original design proved to be correct, there was continual development for the first three years, which contributed to the improved operational results ln year four.

9. GARDANNE FGD PILOT PLANT CHARACTERISTICS

The plant handles a fixed volume of 6000 NM³:/H or 10 000 AM³/H at 180°C and is capable of taking the flue gases from 2 or 3 boilers, due to the recirculation system.

The coal burnt at Gardanne contains 6% sulphur and 8% ash.

-	average weight of sulphur	:	12 kg/h
-	sulphur content in the gas	:	1.2 to 2.5 g/NM^3
-	dust content in the gas	:	200 mg/NM^3
-	reagent used	:	Commercial extra fine hydrated lime 90 to 95%, purity. Specific surface (BET) 15 m/g.
-	average fresh lime consumption	:	30 to 45 kg/h
-	averge filter pressure drop	:	130 - 140 mm WG
-	fresh lime silo	:	30 m ³
-	discharge skip	:	6 m ³

There is a 100% variation in this figure due to the operational variations of the boilers and it is relatively low due to high excess combustion air amounts and high recirculation rates at low duty.

10. EXPERIMENTAL RESEARCH PROGRAMME RESULTS

The programme consisted basically of :

- Defining the operational ranges of various parameters compatible with a reduction efficiency equal to or greater than 90%:
- Gas temperature
- Reagent volume and Ca/S ratio
- Reagent recycling rate
- Reagent humidification rate
- Pressure drop across filter Testing 4 different reagents.
- Verification of the test results by an official organisation IRCHA.

10.1 Reduction Efficiency Against Ca/S Ratio

A series of curves (Fig.12) summarise the percentage reduction in SO_2 against the stoichiometric ratio for various operating conditions.

The SO_2 reduction efficiency can be read directly as a function of the stoichiometric ratio Ca/S expressing the reagent consumption, e.g.:

For an inlet concentration of 2.0 g/NM³ of sulphur and in optimum FGD conditions,

	Efficiency b	Sulphur Emission mg/NM3		Sulphur Emission mg/NM3	
Ca/S fatio	Billeney b	Net at 13.5% 02	Corrected to 6%		
1 1.2 1.5	85 96 99	300 80 20	160 40		

The average temperature at the inlet to the FGD stage was 180°C.

These figures have good reliability factor; as a dual continuous SO_2 measurement instrument was installed upstream and downstream of the equipment; this allowed for simultaneous measurements and monitoring in real time of the variations observed, as a function of the operating parameters.

10.2 Influence of Reagent Recycling

The recycling of used reagent in the system plays an important role in the reduction efficiency. The rate of recycling originally envisaged based on previous dry scrubbing experiences has been slightly increased.

10.3 Influence of Reagent Humidification

The addition of water is essential for high SO_2 reduction. This is a fact which was quickly established but the quality of spray atomization and distribution also play a role. Modifications to the drum design resulted in increased reduction efficiencies.

10.4 Influence of Gas Temperature

Tests have shown that the operation should be close to the minimum temperature compatible with no condensation taking place in the filter.

An increase in this temperature relates to a slight decrease in reduction efficiency. This is, however, of lower influence than a decrease in the resultant moisture content.

For example, and in broad terms, a 20° C rise in gas temperature or a 1% decrease in moisture content will both translate to a 5 to 7% efficiency loss.



Results - Gardanne Process

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Fig. 12: Percentage reduction in so2 against the stoichiometric ratio for various operating conditions

10.5 Alternative Reagents

A week of tests was set for each of the following alternative reagents:

- Calcium
- Coal soot from Gardanne laden with calcium
- Quick lime
- Magnesian lime (CaO : MgO)

The first two can not be adapted but the last two are possibilities since the results were only slightly less than the stoichiometric equivalent.

However, quick lime is more difficult to adapt : (mechanical handling and operator protection).

The magnesian lime requires special grinding and probably transport from considerable distance which affects its economic viability.

11. INDUSTRIAL APPLICATIONS

The system, as developed is judged to have considerable potential of all industrial and smaller sized utility installations. These are not limited to coal fired or incineration plants. One particular plant which has recently been brought onto line, is the treatment of the flue gases coming from Borosilicate glass furnace.

For this application, the operating parameters and gas composition are as given in the table in Fig. 13. The gas composition relates to using natural gas as the fuel, but the use of No. 2 fuel oil as an alternative was to be considered and accounted for in the design.

Apart from a guaranteed reduction of 90% ln SO_2 , the system was also required to attain a 90% reduction in Fluorides and a reduction in all chemically formed condensables (borates) or matter issuing from the stack, to achieve an opacity of less than 6%.

The complete installation (Fig.14) comprised:

- A: stainless steel evaporative quench tower to reduce the gas temperature from 870°C to 250°C, with possibility to supplement with ambient air dilution before and after the quench tower
- A Procedair vertical venturi reactor tower
- A Procedair off-line cleaned pulse jet filter with on maintenance facility.
- A used reagent recycling system to the conditioning drum and a waste reagent pneumatic conveying system.
- A fresh reagent silo and handling system feeding the conditioning drum.
- The main I.D. fan and exhaust stack.

The installation has been operating since May 1991 with EPA proving trials being carried out in October 1991, which demonstrated compliance with the contract guarantees.

The visible emissions from the furnace have been eliminated and with comparison is possible with the plume being emitted from the second untreated furnace.

12. CONCLUSION

The Gardanne pilot plant enabled valuable experience to be gained on the influence and interaction of several operational parameters. It demonstrated that the high SO_2 reduction efficiency normally associated with wet type systems, can be achieved with a basically dry system, with its operational and reliability advantages.

The following basis was used for design of the APC system:

Operating Conditions		Maximum	<u>Minimur</u>	
•	Gas Flow to System, NM ³ /Hr	21,000	14,000	
•	System Inlet Temperature, °C	880	880	
lacksquare	Furnace Pressure, in. MM W.G.	50 .	6.0	

FLUE GAS ANALYSIS (at inlet of system)

25.0
50.0
7.5
17.5
280
700
300
650
10

DESIGN PERFORMANCE LIMITS

•	Particulates, mg/NM ³	30
٠	HF, ppmdv @ 7% O ₂	45
•	SO ₂ , ppmdv @ 7% O ₂	200
٠	Opacity	< 6% *

* Includes all chemically-formed condensibles (Borates) or matter issuing from the stack.

Furnace pressure will be controlled within $\pm 25^{\circ}$ W.G. under normal operating conditions.

Fig. 13: Process design conditions





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The reagent used by preference in the system is commercial hydrated lime which is relatively easy and safe to handle, and needs no treatment or preparation on site. Since 95% efficiency is obtainable, at Ca/S ratio close to 1.2:1 stoichiometry reagent consumption is minimised which makes for economic acceptability, this is unusual for a completely dry system.

Due to the geographical location of Gardanne in the south of France, the municipal heating system was not run in the summer months, which extended the time of running the pilot plant and obtaining all the data necessary. This, however, had the effect of worsening potential corrosion and operational problems as the plant was shut down and restarted each season, without any particular or special procedures.

We have toi report that surface corrosion on the interior walls of the reactor tower and filter unit, which were unprotected, was evident, but the amount of corrosion was judged to be less than that which would have been expected for a filter system on untreated flue gas.

The system does not create an effluent problem, and very serious opportunities exist for using the waste product in other processes.