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Proceedings: 1991 SO₂ Control Symposium

Volume 4. Session 7

For Sponsors:

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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/NO_x) 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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16. ABSTRACT The proceedings document the 1991 SO ₂ Control Symposium, held December 3-6, 1991, in Washington, DC, and jointly sponsored by the Electric Power Research Institute (EPRI), the U. S. Environmental Protection Agency (EPA), and the U. S. Department of Energy (DOE). The symposium focused attention on recent improvements in conventional SO ₂ control technologies, emerging processes, and strategies for complying with the Clean Air Act Amendments (CAAA) of 1990. It provided an international forum for the exchange of technical and regulatory information on SO ₂ control technology. More than 800 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. In 11 technical sessions, speakers presented 111 technical papers on development, operation, and commercialization of wet and dry FGD, clean coal technologies, and combined sulfur oxide/nitrogen oxide (SO _x /NO _x) processes.		
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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:

<u>Session</u>	<u>Subject Area</u>
I	Opening Remarks by EPRI, EPA 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 SO _x /NO _x Technologies
6A	Wet FGD Operating Issues
6B	Clean Coal Demonstrations/Emerging Technologies
7	Poster Session - papers on all aspects of SO ₂ 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 Administrator, 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

AGENDA

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 Administrator, 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.

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

- 2-1 Scrubbers: A Popular Phase 1 Compliance Strategy, P.E. Bissell, 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 Engineers & Constructors
- 2-6 Strategies for Meeting Sulfur Abatement Targets in the UK Electricity Supply Industry, W.S. Kyte, PowerGen
- 2-7 Compliance Strategies for Future Capacity Additions: The Role of Organic Acid Additives, C.V. Weilert, Burns & McDonnell Engineering Co.
- 2-8 IPL Petersburg 1 & 2 CAAA Retrofit FGDs, C.P. Wedig, Stone & Webster Engineering Corp.
- 2-9 Evaluation of SO₂ Control Compliance Strategies at Virginia Power, J.V. Presley, Virginia Power

Session 3A Wet FGD Process Improvements

Session Chair: David R. Owens - EPRI

- 3A-1 Overview on the Use of Additives in Wet FGD Systems, R.E. Moser, EPRI
- 3A-2 Results of High SO₂ Removal Efficiency Tests at EPRI's HSTC, G. Stevens, Radian
- 3A-3 Results of Formate Additive Tests at EPRI's HSTC, M. Stohs, Radian Corp.
- 3A-4 FGDPRISM, EPRI'S FGD Process Model-Recent Applications, J.G. Noblett, Radian Corp.
- 3A-5 Additive Enhanced Desulfurization for FGD Scrubbers, G. Juip, Northern States Power
- 3A-6 Techniques for Evaluating Alternative Reagent Supplies, C.V. Weilert Burns & McDonnell Engineering Co.
- 3A-7 Factors Involved in the Selection of Limestones for Use in Wet FGD Systems, J.B. Jarvis, Radian Corp.
- 3A-8 Magnesium-Enhanced Lime Reaction Tank Design Tests at EPRI's HSTC, J. Wilhelm, Codan Associates

Session 3B - Furnace Sorbent Injection

Session Chair: Brian Gullett - EPA

- 3B-1 Computer Simulation of Reacting Particle-Laden Jet Mixing Applied to SO₂ Control by Dry Sorbent Injection, P.J. Smith, The University of Utah
- 3B-2 Studies of the Initial Stage of the High Temperature CaO-SO₂ Reaction, I. Bjerle, University of Lund
- 3B-3 Status of the Tangentially Fired LIMB Demonstration Program at Yorktown Unit No. 2: An Update, J.P. Clark, ABB Combustion Engineering Systems
- 3B-4 Results from LIMB Extension Testing at the Ohio Edison Edgewater Station, T. Goots, Babcock & Wilcox

Session 4A - Wet FGD Design Improvements

Session Chair: Richard E. Tischer - DOE

- 4A-1 Reliability Considerations in the Design of Gypsum Producing Flue Gas Desulfurization Plants in UK, I. Gower, John Brown Engineers & Constructors Ltd.
- 4A-2 Sparging Analysis for FGD Systems, M. A. Twombly, ARINC Research Corp.
- 4A-3 Increasing Draft Capability for Retrofit Flue Gas Desulfurization Systems, R.D. Petersen, Burns & McDonnell Engineering Co.
- 4A-4 Development of Advanced Retrofit FGD Designs, C.E. Dene, EPRI
- 4A-5 Acid Rain FGD Systems Retrofits, A.J. doVale, Wheelabrator Air Pollution Control
- 4A-6 Guidelines for FGD Materials Selection and Corrosion Protection, H.S. Rosenberg, Batelle
- 4A-7 Economic Comparison of Materials of Construction of Wet FGD Absorbers & Internals, W. Nischt, Babcock & Wilcox
- 4A-8 The Intelligence & Economics of F.R.P. in F.G.D. Systems, E.J. Boucher, RPS/ABCO

Session 4B - Dry FGD Technologies

Session Chair: Michael Maxwell /Brian Gullett/Norman Kaplan - EPA

- 4B-1 Poplar River LIFAC Demonstration, T. Enwald, Tampella Power Ltd.
- 4B-2 1.7 MW Pilot Results for Duct Injection FGD Process Using Hydrated Lime Upstream of an ESP, M. Maibodi, Radian Corp.
- 4B-3 Scaleup Tests and Supporting Research for the Development of Duct Injection Technology, M.G. Klett, Gilbert/Commonwealth Inc.
- 4B-4 A Pilot Demonstration of the Moving Bed Limestone Emission Control Process (LEC), M.E. Prudich, Ohio University
- 4B-5 Pilot Plant Support for MDI/ADVACATE Commercialization, C. Sedman, U.S. EPA
- 4B-6 Suitability of Available Fly Ashes in ADVACATE Sorbents, C. Singer, U.S. EPA
- 4B-7 Mechanistic Study of Desulfurization by Absorbent Prepared from Coal Fly Ash, H. Hattori, Hokkaido University
- 4B-8 Results of Spray Dryer/Pulse-Jet Fabric Filter Pilot Unit Tests at EPRI HSTC, G. Blythe, Radian Corp.
- 4B-9 Results of Medium & High-Sulfur Coal Tests on the TVA 10-MW Spray Dryer/ESP Pilot, T. Burnett, TVA
- 4B-10 Evolution of the B&W Durajet™ Atomizer, S. Feeney, Babcock & Wilcox
- 4B-11 Characterization of the Linear VGA Nozzle for Flue Gas Humidification, J.R. Butz, ADA Technologies, Inc.
- 4B-12 High SO₂ Removal Dry FGD Systems, B. Brown, Joy Technologies, Inc.

Session 5A - Wet Full Scale FGD Operations

Session Chair: Robert L. Glover - EPRI

- 5A-1 FGD System Retrofit for Dalhousie Station Units 1 & 2, F.W. Campbell, Burns & McDonnell Engineering Co.
- 5A-2 Zimmer FGD System, W. Brockman, Cincinnati Gas & Electric
- 5A-3 Results of an Investigation to Improve the Performance and Reliability of HL&P's Limestone Electric Generating Station FGD System, M. Bailey, Houston Lighting & Power
- 5A-4 Full-Scale Demonstration of EDTA and Sulfur Addition to Control Sulfite Oxidation, G. Blythe, Radian

- 5A-5 Optimizing the Operations in the Flue Gas Desulfurization Plants of the Lignite Power Plant Neurath Unit D and E and Improved Control Concepts for Third Generation Advanced FGD Design, H. Scherer, Noell, Inc.
- 5A-6 Organic Acid Buffer Testing at Michigan South Central Power Agency's Endicott Station, B. J. Jankura, Babcock & Wilcox
- 5A-7 Stack Gas Cleaning Optimization Via German Retrofit Wet FGD Operating Experience, H. Weiler, Ellison Consultants.
- 5A-8 Operation of a Compact FGD Plant Using CT-121 Process, Y. Ogawa, Chiyoda Corp.

Session 5B - Combined SO_x/NO_x Technologies

Session Chair: Mildred E. Perry - DOE

- 5B-1 Simultaneous SO_x/NO_x Removal Employing Absorbent Prepared from Fly Ash, H. Tsuchiai, The Hokkaido Electric Power Co.
- 5B-2 Furnace Slurry Injection for Simultaneous SO₂/NO_x Removal, B.K. Gullett, U.S. EPA
- 5B-3 Combined SO₂/NO_x Abatement by Sodium Bicarbonate Dry Injection, J. Verlaeten, Solvay Technologies, Inc. (124)
- 5B-4 SO₂ and NO_x Control by Combined Dry Injection of Hydrated Lime and Sodium Bicarbonate, D. Helfrich, R-C Environmental Services & Technologies
- 5B-5 Engineering Evaluation of Combined NO_x/SO₂ Controls for Utility Application, J.E. Cichanowicz, EPRI
- 5B-6 Advanced Flue Gas Treatment Using Activated Char Process Combined with FBC, H. Murayama, Electric Power Development Co.
- 5B-7 SO₂/NO_x Control using Ferrous EDTA and a Secondary Additive in a Combined Lime-Based Aqueous Scrubber System, M.H. Mendelsohn, Argonne National Laboratory
- 5B-8 Parsons FGC Process Simultaneous Removal of SO_x and NO_x, K.V. Kwong, The Ralph M. Parsons Co.

Session 6A - Wet FGD Operating Issues

Session Chair: Gary M. Andes - EPRI

- 6A-1 Pilot-Scale Evaluation of Sorbent Injection to Remove SO₃ and HCl, J. Peterson, Radian Corp.
- 6A-2 Control of Acid Mist Emissions from FGD Systems, R.S. Dahlin, Southern Research Institute
- 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 Facility, A.F. Jones, Radian Corp.
- 6A-5 CEM Vendor and Utility Survey Databases, J.L. Shoemaker, Engineering Science, Inc.
- 6A-6 Determination of Continuous Emissions Monitoring Requirements at Electric Energy Inc., V. V. Bland, Stone & Webster Engineering Corp.
- 6A-7 Improving Performance of Flushless Mechanical Seals in Wet FGD Plants through Field and Laboratory Testing, F.E. Manning, BW/IP International Inc.
- 6A-8 Sulcis FGD Demonstration Plant Limestone-Gypsum Process: Performance, Materials, Waste Water Treatment, E. Marchesi, Enel Construction Department

Session 6B - Clean Coal Demonstrations

Session Chair: Joseph P. Strakey - DOE

- 6B-1 Recovery Scrubber Cement Application Operating Results, G.L. Morrison, Passamaquoddy Technology
- 6B-2 The NOXSO Clean Coal Technology Demonstration Project, L.G. Neal, NOXSO Corp.
- 6B-3 Economic Comparison of Coolside Sorbent Injection and Wet Limestone FGD Processes, D.C. McCoy, Consolidation Coal Co.
- 6B-4 Ohio Edison's Clean Coal Projects: Circa 1991, R. Bolli, Ohio Edison

Emerging Technologies

- 6B-5 A Status Report on Sanitech's 2-MWe Magnesia Dry Scrubbing Demonstration, S.G. Nelson, Sanitech Inc.
- 6B-6 Application of DOW Chemical's Regenerable Flue Gas Desulfurization Technology to Coal Fired Power Plants, L.H. Kirby, Dow Chemical
- 6B-7 Pilot Testing of the Cansolv System FGD Process, L.E. Hakka Union Carbide Canada LTD.
- 6B-8 Dry Desulfurization Technology Involving Humidification for Enhanced SO₂ Removal, D.P. Singh, Procedair Industries Inc.

Session 7 - Poster Papers

Session Chair Charles Sedman - EPA

- 7-1 Summary of Guidelines for the Use of FRP in Utility FGD Systems, W. Renoud, Fiberglass Structural Engineering, Inc.
- 7-2 Development and Evaluation of High Surface Area Hydrated Lime for SO₂ Control, M. Rostam-Abadi, The Illinois State Geological Survey
- 7-3 Effect of Spray Nozzle Design and measurement Techniques on Reported Drop Size Data, W. Bartell, Spraying Systems Co.
- 7-4 High SO₂ Removals with a New Duct Injection Process, S.G. Nelson, Jr. Sanitech, Inc.
- 7-5 Combined SO_x/NO_x Control Via Soxal™, A Regenerative Sodium Based Scrubbing System, C.H. Byszewski, Aquatech Systems
- 7-6 The Healy Clean Coal Project Air Quality Control System, V.V. Bland, Stone & Webster Engineering Corp.
- 7-7 Lime/Lime Stone Scrubbing Producing Useable By-Products, D. P. Singh, Procedair Industries Inc.
- 7-8 Modeling of Furnace Sorbent Injection Processes, A.S. Damle, Research Triangle Institute
- 7-9 Dry FGD Process Using Calcium Absorbents, N. Nosaka, Babcock-Hitachi K.K.
- 7-10 Clean Coal Technology Optimization Model, B.A. Laseke, International Technology Corp.
- 7-11 SNRB Catalytic Baghouse Process Development & Demonstration, K.E. Redinger, Babcock & Wilcox
- 7-12 Reaction of Moist Calcium Silicate Reagents with Sulfur Dioxide in Humidified Flue Gas, W. Jozewicz, Acurex
- 7-13 Commercial Application of Dry FGD using High Surface Area Hydrated Lime, F. Schwarzkopf, Florian Schwarzkopf PE.
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Session 7
POSTER PAPERS

**SUMMARY OF GUIDELINES
FOR THE USE OF FRP IN UTILITY FGD SYSTEMS**

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ABSTRACT

In recent years, Fiberglass Reinforced Plastic (FRP) has demonstrated successful performance as the material of construction for FGD systems. Excellent corrosion resistance, high reliability, low maintenance and attractive initial cost give FRP the potential for extensive use in future FGD systems.

Despite its potential, successful use of FRP has been hampered by a lack of clear standards for design and fabrication. Many utility companies are inexperienced in purchasing FRP equipment, and there has not been adequate information available to project engineers and managers in order to control quality.

EPRI is presently developing a guideline of value to power industry purchasers of FRP equipment used in FGD systems. The guideline provides a basic understanding of FRP composite material and design issues, as well as an overall strategy for quality control. This paper will briefly discuss this guideline.

Fiberglass Reinforced Plastic (FRP) has great potential for service in the process environments found in Flue Gas Desulfurization (FGD) systems. It has very good resistance to corrosion and seismic damage, is light weight, and is easily maintained. In many cases, FRP is lower in its initial life cycle costs than alternative materials.

These attributes have made FRP a desirable material in Flue Gas Desulfurization.

FRP's distinctive characteristics make it unique from the standpoint of materials and structural engineering. The lack of practical engineering knowledge at the level of the end-user is probably the greatest drawback to this material. Proper design and quality control are critical in custom, high performance FGD equipment made of advanced materials like FRP, and it is difficult to assure adequate performance without knowledge of the related engineering. Unfortunately, there are few good sources of information relating to application of FRP in FGD service.

EPRI is in the final stages of preparing and offering a document which covers most of the information that an owner needs in order to undertake and manage an FRP project. Background and specific information are presented in such a way that end-users will understand not only the options available to them but also the basis for sound decisions.

This paper provides a summary of the topics addressed in the upcoming EPRI guidelines. The information presented in the guidelines will be specifically limited to the design and fabrication of equipment built entirely from fiberglass and intended specifically for utility FGD systems. Furthermore, this guideline will consider only the wet process slurry systems for SO₂ removal. The three main processes of this type utilize limestone, lime, or alkaline fly ash as reagents.

POTENTIAL APPLICATIONS OF FRP IN FGD SYSTEMS

The corrosion resistance of FRP makes it a good candidate for use in the construction of FGD equipment where the inlet quenching systems limit continuous operating temperatures to 220°F or less. Since no two systems are exactly alike, the physical and chemical conditions of each system must be analyzed on a case by case basis to optimize the use of FRP materials. FRP laminates can be tailored to meet the conditions present in each zone of the FGD process. This is accomplished by controlling resin selection, laminate construction and flexibility, type of glass reinforcements, addition of fillers and methods of cure.

The main factors that affect the suitability of fiberglass as a construction material for FGD systems include: The continuous temperature of the process, the type of process (alkaline fly ash systems are more abrasive than others), the chemical composition of the gas stream (coal, sulfur, fluoride, and chemical content), the source of make up water, the reheat methods employed and the operation and maintenance policies. The use of FRP may also be influenced by the addition of chemicals to the process stream to enhance SO₂ removal or to reduce the build-up of hard deposits.

BASICS OF FRP

Laminated composites consist of several individual layers of reinforcement bonded together by saturating with a resin matrix. Lamination is used to combine the special characteristics of each layer and optimizes the overall, or "composite" properties and performance of the laminate. An example of a familiar laminate is plywood, which gains its strength and stability from the alternating grain orientation and grade of its various plies.

FRP laminates consist of glass reinforcing filaments embedded in a matrix of chemically resistant thermoset resin. Thermoset resins are unsaturated liquid polymers that react in the presence of a catalyst by cross-linking their molecular chains to form a solid mass. The FRP composites obtain their high tensile strength from the glass reinforcement and chemical resistance from the surrounding thermoset resin matrix.

One of the advantages of FRP composite materials is that the physical and chemical resisting characteristics can be custom designed for various applications through careful selection of the type of resin, the orientation and placement of the glass reinforcements and through the inclusion of organic and inorganic fillers and other additives. By modifying these various attributes, the FRP designer has great versatility in determining strength and stiffness, resistance to corrosion and abrasion, durability, and high temperature performance.

FRP structures are largely immune to many of the electromechanical corrosion mechanisms present in FGD systems that eventually destroy corrosion resistant metal alloys through stress corrosion cracking, intergranular corrosion, pitting and crevice corrosion. In addition, FRP composites are not chemically affected by the majority of chloride and sulfite trace elements found in FGD systems that have been shown to increase the susceptibility of stainless steel to pitting and stress-corrosion cracking.

On the other hand, FRP composites have lower operating temperatures than metallics. The maximum recommended operating temperature for FRP in gas stream applications is generally in the range of 300° to 400° F. Repeated temperature cycling over a period of time may lead to the formation of defects in the laminate such as cracks in the resin matrix, subsurface blistering, breakdown of glass to resin bonds, or a reduction of physical properties.

FRP composites generally have higher coefficients of expansion than metallics, which must be taken into consideration in the structural design of the equipment. Abrasion may also require special consideration in some areas of the FGD system. The properties of most FRP laminates vary with direction due to the oriented nature of the glass reinforcement, so it is practical to design a cost effective FRP composite to meet the special conditions found in FGD systems.

There are three main fabrication processes employed to produce fiberglass corrosion-resistant equipment for industrial service. These processes are hand lay-up, filament winding and field winding. Where a choice exists, the method of fabrication should be specified by the engineer to best satisfy the laminate requirements.

FRP EQUIPMENT DESIGN

The proper design of FRP equipment entails complexities beyond the typical issues confronting designers. The special nature of the FRP composite is easily overlooked, even by competent engineers. In addition to familiarity with the general principles of equipment design, there are two major areas of specialized knowledge that are critical.

Possibly the most important and most frequently misunderstood design issue is that of physical properties, including the various failure modes under different types of loads. The physical properties vary widely with the materials and fabrication methods employed, and analysis is complicated by the bi-modular behavior of many laminate types. In addition, the long-term success of FRP equipment will require developing a failure criteria based on parameters other than ultimate strength; FRP equipment may be damaged by severe operating environments at a stress level that is well below ultimate stress.

Another requirement for FRP design is an understanding of appropriate design and analysis procedures. Too often, analytical techniques developed for traditional materials are extended to use with composites.

There are many design guides and standards which have been developed to aid the engineer in designing FRP equipment. These guides and standards have been developed over the many years of growth in the FRP industry, and, with the increase in research, available technology, and the experience of design engineers, they naturally vary in completeness and approach.

It should be recognized that specifying any particular document does not ensure that the equipment will be designed properly. In other words, compliance with a design standard does not necessarily mean that the design will be adequate for the intended service. It is essential that the design engineer be experienced with and knowledgeable of the attributes of FRP, understanding the special nature of laminates and their fabrication techniques. Sound engineering judgment and the ability to accurately analyze the structural properties of FRP laminates and their application to FGD service are necessary to obtain equipment adequate for long term service.

The design specification for FRP equipment should provide adequate engineering details to allow the design methodology and completeness to be thoroughly reviewed. The "design package" should include a complete set of engineering calculations and detailed construction drawings and specifications, which will ensure that assumptions made during design are valid.

PROCUREMENT STRATEGY

There are several main players which can be involved in procuring FRP equipment. The ultimate user of the equipment (Owner) and the builder of the equipment (Fabricator) are always involved, and, on smaller projects, may handle all required functions without additional assistance.

In many cases, however, one or more additional parties are included in the procurement chain. An engineering firm is often responsible for global design of an expansion or modification. This firm may have total responsibility, or the Owner may retain responsibility for some portions, such as major pieces of equipment.

Whether the engineering firm is involved or not, certain kinds of specialty equipment may be procured as "packages". Many firms exist to provide the process, engineering, and equipment for these subsystems, retaining responsibility for the proper performance of the process as well as the equipment. In most cases, these process companies have the FRP equipment fabricated to their own specifications, then resell the equipment as a part of the system package.

Any one of the parties mentioned can optionally employ an independent engineering firm for the detailed design of the equipment.

The design of the FRP equipment can be divided into two segments, typically performed by different parties. The configuration of the equipment is dependent on the overall design of the system and process. The Owner, engineering firm or process company normally provides this level of design, determining design criteria such as temperatures and pressure.

The second element of the design is the detailed design, which includes the structural engineering, material selection, and development of specific construction details and procedures. The fabricator of the equipment historically has provided the detail design for FRP equipment, based on the configuration or process design which has been provided to them. Fabricators often work to specifications provided by the Owner, engineering firm or process company, but these specifications vary widely as to quality, completeness and approach.

Relying on the fabricator for detailed design is an approach used widely in the purchase of all types of industrial equipment, and is not unique in the procurement of FRP equipment. Unlike equipment fabricated from traditional materials such as steel, however, FRP fabrication practices and equipment can vary widely among suppliers.

In a few cases, owners have developed in-house expertise with regard to FRP equipment detail design and specification. This practice is most common in the chemical industry, where FRP equipment usage is high and a basic understanding of plastics may already exist. Development of in-house FRP design expertise or standards has been limited to a handful of major companies, and is not common among major engineering firms and process companies.

There are two distinct approaches normally taken by buyers of FRP equipment, differing in the allocation of design responsibility between the buyer and the supplier. To a large extent, equipment is purchased on a "performance" basis, meaning that the supplier provides the detailed design as a part of the purchase and is responsible for assuring that it performs as intended. Since true long-term performance cannot be measured initially, it is often difficult for an Owner to know whether the equipment will prove adequate in long-term service.

The alternative approach is for the buyer to provide a detailed design of the equipment prior to requesting bids, removing the design responsibility from the supplier. The Owner's "descriptive" specification reflects decisions as to how conservative the design should be, and further allows competitive bids on a single predetermined design.

In reality, most specifications fall somewhere between the two extreme approaches, with the owner making some of the decisions and specifying as such, while leaving much of the design responsibility with the supplier. When additional parties are involved in the procurement chain, each party normally assumes some portion of the design responsibility. Owners can exercise greater control over the long-term success of FRP equipment by active involvement in the design decisions which affect quality.

QUALITY MANAGEMENT

In order to have the longest possible service life from FRP equipment, attention must be paid to the quality issues in several areas. In general, these include:

- Process design and identification of design criteria
- Appropriate material selection and equipment design
- Fabrication quality
- Verification of design and fabrication (testing)
- System maintenance

The Owner can establish procedures that allow for control of the key decisions affecting quality. In order to accomplish this, it is important to become acquainted with the special nature of FRP and the complexities of analysis and fabrication. The Owner should adopt an appropriate procurement strategy that allows subcontractors to provide equipment or services in a manner which promotes quality.

One of the first important steps an Owner can take to assure overall quality of the FGD equipment is to insure that appropriate design criteria are established. The party responsible for the process design of the equipment would normally develop these parameters to be used for equipment design. In order for the equipment to be designed efficiently and procured for the lowest possible cost, the criteria must be realistic and accurate. A qualified designer using methods accurate for composite analysis will include adequate design (safety) factors to assure long term adequacy based on realistic criteria.

While it is important to state conservative values (criteria) such that potential service extremes are taken into account, this should be identified in terms of frequency. This allows the designer to incorporate these criteria into the design process in an appropriate manner. It is generally best to incorporate the necessary safety factor at the time of detail design.

A natural tendency exists at all levels of design to be somewhat conservative with each design decision. When this happens in the determination of the design criteria, the impact can be magnified dramatically as each progressive level of design is accomplished. Overstating design criteria is wasteful, in that final designs can become excessively conservative and expensive. In the extreme case, overly conservative design criteria could cause a decision to change materials completely when it would not otherwise be necessary. The party responsible for process design should be made aware of the special nature of FRP composites. It may be possible to modify the process somewhat in order to bring service conditions into a more suitable range for FRP.

Even the highest level of effort applied to the design and engineering of FRP equipment will have little bearing on the success of a project unless all phases of fabrication and installation are carried out by competent, experienced people in accordance with an established quality management program. An effective quality management program will evaluate the vendor's expertise, define the fabrication activities to be performed and establish levels of inspection required to assure vendor compliance with the project specifications, engineering drawings, and related contract documents. The intent of the program is to prevent deficiencies in fabrication and to assure that the level of reliability designed into the equipment is actually achieved in the fabrication and installation process.

Inspection levels are established by the power plant after a careful evaluation of the need for, and the extent of control desired. The level of need for controlling quality is based on the level of consequence if the equipment were to fail. Equipment critical to plant operation, operator safety or significant environmental concerns receive the highest inspection priority.

Quality management programs, as they relate to fabrication and installation of FRP FGD equipment, encompass four main themes:

- Qualifying Vendors
- Vendor's Quality Control Program
- Owner's Quality Assurance Program
- Qualifying Inspectors

SYSTEMS MAINTENANCE

Fiber reinforced plastic equipment used in FGD applications is subject to demanding thermal and corrosive conditions. These conditions, when properly considered and accounted for in the equipment design and materials selection, will be pushed to its limits of performance due to elevated temperature upsets or unexpected chemical concentrations in portions of the FGD system.

FRP is often specified where maximum corrosion resistance in aggressive environments is required. When used in FGD systems, it is normal and expected that FRP equipment will degrade over a period of time and that periodic inspection and regular maintenance will be required to assure system reliability.

These factors point to the need for a comprehensive inspection and maintenance program designed to ensure the long term use and uninterrupted availability of the power plant. A recommended approach to maintaining FRP is through a predictive maintenance (PM) inspection program combining routine, scheduled inspections with a detailed reporting system for tracking, documenting and recording defects. With good, current knowledge of equipment condition, maintenance needs can be projected and developing problems can be dealt with on a planned basis.

Predictive maintenance and repair decisions involve subjective risk. The object is to evaluate the probability of equipment failure and consequence of failure if repair or replacement is not done versus the cost of the repair if it is done. If unnecessary repairs are specified, costs will be high for little or no gain. If repairs are delayed and the equipment becomes unserviceable, costs for operational losses and reduced service life will be high also. Finding the balance between risk and cost is the challenge facing the inspector and engineering specialist.

The least risky choice is to repair all defects when they are found. For defects repaired with a small effort or cost, this is reasonable. If the cost of the repair is great, however, the inspector is in a position to evaluate the probability of damage if the repair is delayed. If the probability of further damage is low, the cost of repair might well be delayed or avoided for the intended life of the equipment.

By making a detailed comparison of current and previously documented defects, a trend can be established that will allow the plant to track degradation and help predict the point at which the equipment must be

replaced or repaired. In addition, previous inspection documentation is invaluable for predicting if a defect will penetrate through the corrosion liner and into the structural wall before the next scheduled inspection.

The primary elements of a successful PM program are: Planned inspection intervals, quantitative documentation of defects, knowledgeable evaluation, and carefully administered repairs. The intent of PM is to detect problems in their early stages, so maintenance costs and the threat to safety and reliability caused by unexpected failure of equipment are reduced.

An effective PM program for FRP will include the following elements:

- A regularly scheduled program for interior and exterior inspection, with frequency of inspection based on the age and condition of the equipment, severity of service, and history of previous defects.
- The use of inspection tools and methods suited to FRP materials for determining surface hardness, extent of subsurface defects, corrosion liner thicknesses, and overall condition of FRP laminates.
- A system for documentation and reporting that allows inspection findings to be chronologically updated so that changes in the condition of the equipment can be tracked and, based on long term trend evaluations, future maintenance needs projected.
- Inspection personnel who have the ability to interpret the significance of specific defects, who are knowledgeable and experienced in the inspection of FRP equipment, and who are capable of recommending appropriate repairs.
- A defined plan for repairs, if repairs should become necessary, including the specification of materials and methods of repair and verification of compliance through inspection.

The need for ongoing inspection of FRP FGD equipment cannot be over emphasized. Inspection is as important for assuring long term, uninterrupted use of the equipment as the original design and engineering used to build it.

COMPLETE GUIDELINES

The final Guidelines for the Use of FRP in Utility FGD Systems will address each of the above subjects in far greater detail, providing power plant owners with useful information in purchasing and controlling quality of FRP equipment. Appendices will serve as a further valuable resource, identifying relevant terms, current industry standards and information obtained from the manufacturers of resins.

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**DEVELOPMENT AND EVALUATION OF HIGH-SURFACE-AREA
HYDRATED LIME FOR SO₂ CONTROL**

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ABSTRACT

A process for producing high-surface-area (HSA) hydrated lime has been developed at the Illinois State Geological Survey (ISGS). The process has been optimized in a batch, bench-scale reactor and has been evaluated as being technically feasible and economically attractive. The "know how" is available to tailor properties of hydrated limes for specific SO₂ removal applications. A patent application covering the process was filed with the U. S. Patent Office in 1990. An integrated, continuous lime hydration process optimization unit (POU) capable of producing 20-100 pounds of HSA hydrated lime per hour has been designed, constructed, assembled and tested. The POU will provide engineering and scale-up data for rapid commercialization and transfer of the technology to lime industries.

SO₂ removal efficiencies of five ISGS HSA hydrated limes with surface areas ranging from 40 to 60 m²/g were evaluated in pilot-scale dry sorbent injection test facilities in Consolidation Coal Company's Coolside unit, in Research-Cottrell EST's boiler economizer system, and in the U. S. EPA/Acurex innovative furnace reactor under furnace sorbent injection conditions. Calcium utilization data were also obtained at economizer temperatures in a differential flow reactor at U. S. EPA/Acurex. The ISGS HSA hydrates showed up to 84% SO₂ removal (Ca/S=2) under furnace sorbent injection conditions (a 22 m²/g commercial hydrates removed 60%) and up to 80% calcium conversions under boiler economizer conditions (59% for the commercial hydrate). Tests at Research-Cottrell EST under boiler economizer conditions showed 64% SO₂ removal (Ca/S=2) for a 48 m²/g HSA hydrate compared to 45% for its commercial counterpart. Under Coolside conditions (Ca/S=2, 25 °F approach to adiabatic saturation) the system SO₂ removals ranged between 67 and 81% for the HSA hydrates. The commercial hydrate removed about 50% SO₂.

INTRODUCTION

Dry sorbent injection (DSI) processes which inject hydrated lime powders to adsorb SO_2 from stack gases can be preferred for small and older power plants because these processes are easier to install, require less space and have lower projected capital cost than wet scrubbers using lime- or limestone-water slurry. The Electric Power Research Institute (EPRI) estimates that 450 power plants east of Colorado, 150 MW or less in size and accounting for 35,000 MW total capacity, could benefit by installing DSI systems (1).

The operating costs of DSI processes depend primarily on the expense and performance of the sorbents used. The SO_2 -capturing performance of commercial hydrated lime in these processes is generally less than 30% of its theoretical capacity, representing less than 60% SO_2 removal at Ca/S ratio of 2 (2, 3, 4). A more active sorbent that achieves substantially higher SO_2 removals than commercially available hydrated limes would make these processes suitable for more power plants, especially those burning high-sulfur coal. The reduction in sorbent needed to achieve a given emissions level lowers not only the cost of sorbent, but also expenditures for storage, handling and disposal depending upon comparable delivered sorbent costs.

A major objective of past research has been to identify sorbent properties that enhance SO_2 capture in various DSI processes. Because the chemistry and physics of SO_2 capture vary from one process to another, the properties of hydrated lime which are desirable for a specific SO_2 removal application may not be desirable for other applications. For example, in furnace sorbent injection (FSI) process, hydrated limes with high surface area, small particle size and large pores are desired (5,6). In duct injection/humidification (Coolside), hydrated limes with high surface area and porosity are preferred (7,8). In boiler economizer process, a balance between surface area and particle size is needed to achieve maximum SO_2 removal (9). In a boiler economizer process, the product not only should have a high surface area (above $40 \text{ m}^2/\text{g}$) but also particle diameters of 2 microns or less. If the particle diameter is large (above 2-5 microns and depending on SO_2 concentration) $\text{Ca}(\text{OH})_2$ reacts mainly with CO_2 rather than SO_2 since the latter reaction is controlled by film diffusion (in a typical flue gas generated by burning high sulfur coal, the concentration of CO_2 is 30 to 50 times greater than that of SO_2). Thus, it is desirable to provide calcium hydroxide having high surface area, high porosity, and small particle size for use in DSI processes.

Commercial hydrated limes typically have surface areas in the range of $10\text{-}25 \text{ m}^2/\text{g}$, mean particle diameters of $1.7\text{-}10$ micrometers, and pore volumes in the range of $0.1\text{-}0.25 \text{ cc/g}$. Several investigators have prepared small quantities of lime hydrated having surface areas in the range of $35\text{-}50 \text{ m}^2/\text{g}$ by using an aqueous alcohol solution (10, 11). Rheinische Kalksteinwerke GmbH, Wuelfrath, has developed and patented a process for the manufacture of alcohol-water hydrated lime (WUELFRA-sorp) having surface areas in the range of about $35\text{-}55 \text{ m}^2/\text{g}$ (12). A production plant with a capacity of 6 tons of WUELFRA-sorp per hour is currently in operation. Reportedly, small quantities of hydrates having surface areas as high as $80 \text{ m}^2/\text{g}$ have been obtained by calcining (dehydrating) commercial hydrated lime and rehydrating it using an alcohol-water hydration method (13).

ISGS HYDRATION PROCESS

Since 1986, the Illinois State Geological Survey (ISGS), a division of the Illinois Department of Energy and Natural Resources (ENR), has been developing a process to produce high-surface-area (HSA) hydrated lime with far more activity for adsorbing SO_2 than commercially available hydrated lime. HSA hydrate prepared by the ISGS method has considerably higher surface area and porosity, and smaller mean particle diameter and crystallite size than commercial hydrated lime. A patent application covering the process was filed with the U. S. Patent Office in 1990. Research Corporation Technologies (Tucson, AZ), a marketing and licensing organization, has accepted the responsibility for patent prosecution, marketing, and licensing of the ISGS process.

In the ISGS process, lime is hydrated at atmospheric pressure with an aqueous solution of a reagent (one-step process) followed by an optional post-hydration wash step (two-step process). The one-step process is capable of producing a hydrate with surface areas ranging between 35 and 50 m^2/g using commercial quicklimes as feed materials. Higher surface area hydrates, above 50 m^2/g , can be made using the two-step process. With either the one-step or the two-step hydration methods, hydrates with even higher surface areas (up to 85 m^2/g) can be made using specially-prepared quick limes.

During the past five years more than 500 experiments have been conducted to optimize the ISGS hydration process and identify key parameters influencing hydrate properties (14, 15, 16, 17). These tests were conducted both at gram quantities in a laboratory-scale unit and in 5-7 pound quantities in a bench-scale batch hydrator. The dependence of the hydrate properties (surface area, porosity, particle size and crystallite size) important for SO_2 capture on operating conditions including hydration temperature, contact time, type and quality of lime, quantity of water and reagent, and the amount of reagent used in the post-hydration wash step have been investigated. Based on the results of these tests, optimum conditions for producing HSA hydrates from different limes have been determined. Typical properties of HSA hydrates prepared by the ISGS method and hydrates available commercially are compared in Table 1. In addition to their considerably higher surface area and porosity, the ISGS hydrates have smaller mean particle diameter and crystallite size than commercial hydrated lime.

ECONOMIC EVALUATION OF THE ISGS HYDRATION PROCESS

In 1989, a technical and economic evaluation of the ISGS hydration process was conducted by Arthur L. Conn and Associates, Ltd. to determine the probable cost and the suitability of the ISGS hydrate for manufacture on a commercial scale (18). This preliminary study was performed on the basis of a lime hydration plant large enough to handle the demand of a 1000 MW coal-fired power plant site using a 12,000 Btu/lb Illinois coal containing 3.5% sulfur. The study concluded that the process to manufacture HSA hydrates by the ISGS method is technically feasible and that conventional commercial equipment should be applicable. The projected cost of production of the ISGS HSA hydrated lime was evaluated to be only marginally greater than the cost of currently available, commercial hydrated lime. The cost benefit gained by the large increase in SO_2 adsorption capacity for HSA hydrates far outweighs this small increased sorbent cost.

SO₂ REMOVAL PERFORMANCE OF ISGS HYDRATES IN DSI PROCESSES

Sorbents

The samples tested included five HSA hydrates prepared according to the one-step ISGS process, WUELFRAcorp, and a commercial hydrated lime. For the pilot-scale DSI tests reported in this paper, more than 1000 pounds of five HSA hydrates were prepared in the batch, bench-scale hydrator. The chemical analyses and the physical properties of the test sorbents are presented in Table 2 and 3. The surface areas of the HSA hydrates ranged from 40 to 60 m²/g compared to 22 m²/g for the commercial hydrate. The surface area of the WUELFRAcorp sample tested was about 40 m²/g. Mean particle diameters of the HSA hydrates were between 2.3 and 4.5 micrometers compared to 15 micrometers for the WUELFRAcorp and 20 to 25 micrometers for the commercial hydrates. The storage history of the WUELFRAcorp prior to shipment to the ISGS was not known. The sample could have lost some reactivity while in storage.

Test Facilities

Pilot-scale DSI tests were performed with several ISGS hydrates to evaluate their SO₂-removal efficiencies under typical conditions of burning high-sulfur coals. Pilot-scale tests were performed in Consolidation Coal Company's 100-kW Coolside pilot unit (Library, PA); in Research-Cottrell EST's 146-kW, boiler economizer furnace (Irvine, CA); and in U. S. EPA/Acurex 14-kW, Innovative Furnace Reactor under FSI conditions (Research Triangle Park, NC). Boiler economizer tests were also performed in a bench-scale flow reactor under differential conditions with respect to SO₂ concentration at U. S. EPA/Acurex Corporation.

Furnace Sorbent Injection Tests

The SO₂ removal performances of the hydrates under furnace sorbent injection conditions are shown in Figure 1 and Figure 2. The fuel used in these tests was natural gas doped with SO₂. In Figure 1, SO₂ removal is plotted as a function of Ca/S ratio for the ISGS HSA31 hydrate, and the commercial hydrate at 1042 and 1127 °C. The performance of the commercial sorbent was more temperature dependent than for the HSA31 hydrate in the temperature range studied. The ISGS HSA31 hydrate removed 53% SO₂ at Ca/S=1 and about 85% SO₂ at a Ca/S=2, independent of furnace temperature. The commercial hydrate, at Ca/S=2, captured about 58% at 1042 °C and 68% at 1127 °C. In Figure 2, SO₂ removal for the HSA1, HSA2, HSA3, WUELFRAcorp and the commercial hydrates at 1200 °C are shown. The ISGS HSA hydrates, regardless of surface area, captured about 84% SO₂ at a Ca/S=2 compared to about 75% for the WUELFRAcorp, and about 60% for the commercial hydrate. At Ca/S=1, only the ISGS HSA hydrates had SO₂ removal greater than 50% (ranged from 53 to 60%).

Boiler Economizer Tests

The SO₂ removal performance of HSA30 hydrate and the commercial hydrate is shown in Figure 3. These data were obtained by Research-Cottrell EST. The fuel used was natural gas doped with SO₂ (3000 ppm). The SO₂ removals obtained at 540 °C are plotted as a function of Ca/S ratio in Figure 3. At a Ca/S ratio of 1, the HSA30 captured 39% SO₂ compared to 28% for the commercial sorbent. At a Ca/S=2, HSA30 captured 64% SO₂ compared to only 45% for the commercial hydrate.

The calcination utilization data obtained at economizer temperatures in the differential flow reactor at the U. S. EPA/Acurex is shown in Figure 4. The conversion of calcium to calcium sulfite (or sulfate) is shown for the test sorbents. Calcium conversions achieved were 80, 75 and 51% for HSA1, HSA2 and HSA3, compared to 61% for the WUELFRA-sorp and 59% for the commercial hydrate. The highest SO₂ removal was observed with the HSA1 (50 m²/g) suggesting that there maybe an optimum hydrate surface area for maximizing SO₂ capture under boiler economizer conditions.

Coolside Tests

The results of Coolside tests conducted at Consolidation Coal Company are shown in Figure 5. The common conditions were 300 °F inlet flue gas temperature, 1500 ppm inlet SO₂ content (dry basis), and 125 °F adiabatic saturation temperature (corresponding to 25 °F approach to adiabatic saturation temperature). The flue gas flow rate was set at 175 scfm, which provided a 2.0 second humidifier residence time. The SO₂ removals reported include capture both in the humidifier and the baghouse.

Figure 5 shows the effect of the Ca/S molar ratio on system (Humidifier + baghouse) SO₂ removal in the pilot unit tests. The error bars represent one standard deviation. Points without error bars have standard deviations smaller than the plotting symbol. The highest SO₂ removal was observed using HSA2. The average system removals were 33, 53 and 81% at 0.5, 1.0 and 2.0 Ca/S, respectively, using HSA2. This represents 154, 71 and 62% (relative) higher SO₂ removal than the commercial hydrated lime. Sorbents HSA1 and HSA3 showed lower SO₂ removal than HSA2, but higher removal than the commercial hydrated lime at similar Ca/S ratios. At 0.5, 1.0 and 2.0 Ca/S ratios SO₂ removals were 28, 47 and 67%, respectively (representing 115, 52 and 34% relative improvement over commercial hydrate), using HSA1, and 30, 44 and 65%, respectively, using HSA3 (representing 131, 42 and 30% relative improvement over commercial hydrate). Using the best performing commercial hydrated lime, the SO₂ removals were 13, 31 and 50% at 0.5, 1.0 and 2.0 Ca/S, respectively.

Optimum Hydrate Surface Area for SO₂ Capture in DSI Processes

Figure 6 show the effect of hydrate surface area on SO₂ capture (at Ca/S = 2.0) under different DSI conditions. These data were obtained from Figures 1-5. It is seen that there is an optimum surface area of hydrate for maximum sulfur capture in each of the three systems. Under FSI conditions, HSA hydrates with surface areas ranging between 40 to 60 m²/g showed the highest SO₂ capture (about 85%). The SO₂ removal for the WUELFRA-sorp

and the commercial hydrate were 78% and 60%, respectively. Enhanced performance of the ISGS HSA hydrates could be related to their smaller particle size, higher surface area, and greater pore volume than for the other hydrates. Pore volume analyses of raw sorbents indicate the volume of pores between 0.01 and 0.1 micrometers was substantially higher for the HSA1 and HSA2 hydrates than for commercial hydrated lime. Pore volumes of hydrated limes are expected to correlate with the pore volumes of the corresponding calcines formed during calcination of hydrated lime. Due to the increase in molar volumes when converting from CaO to CaSO₄ (16.9 vs. 46.0 cm³/mole), pore plugging is known to limit the sulfation reaction. Sorbents with a high volume of larger pores are expected to capture more SO₂.

Under boiler economizer conditions, the calcium utilizations for HSA1, HSA2, HSA3, WUELFRA_{sorp} and the commercial hydrate were 80%, 75%, 51%, 61% and 55%, respectively. The maximum SO₂ removal was observed for the 50 m²/g HSA1 hydrate. Under Coolside conditions the SO₂ removal increased with increasing surface area and was 67% for HSA1, 85% for HSA2, 65% for HSA3, and 50% for the commercial hydrate.

Based on the data shown in Figure 6 and Table 3, the optimum hydrates for maximizing SO₂ removal under FSI or boiler economizer conditions appear to have surface areas in the range of 40 to 50 m²/g, mean particle diameters below about 1.5 micrometers (as measured by sedigraph), and pore volumes above about 0.25 cc/g. Hydrates with surface areas above 50 m²/g would likely be more effective for capturing SO₂ if their particle size could be significantly reduced (i.e., to less than 1 micrometer).

Hydrated limes having optimum properties for SO₂ removal in the Coolside process have surface areas of at least 55 m²/g (e.g. about 60 m²/g), mean particle diameters of below about 5 micrometers, and pore volumes above about 0.3 cc/g. For the Coolside process, particle size of hydrates appears to be of secondary importance.

PROCESS OPTIMIZATION UNIT

In November 1990, the ISGS received a grant from the Illinois Department of Commerce and Community Affairs under the Governor's Challenge Grant Program to build and operate an integrated, continuous lime hydration process optimization unit (POU) capable of producing 20-100 pounds of HSA hydrated lime per hour. The goals of the program are to generate design, construction, and operation data necessary for the private sector to scale-up the process to a commercial level, produce samples for further testing and to evaluate the economics of the process.

The POU has been designed, constructed and assembled. The mechanical operability tests of the individual units have been performed and baseline data have been obtained. Seven shakedown tests, a total of 40 hours of operation, have successfully been performed with the hydration reactor. The mechanical operability and performance of the reactor has been demonstrated in these tests. The results of the shakedown tests with the hydration reactor have indicated that there are no serious problems with continuous operation and scale-up of the process and that the quality of the hydrated lime is not affected. Process conditions for optimizing product based on the type of dry sorbent injection processes are being investigated. This "know-how" will help to tailor properties of hydrated lime products for specific SO₂ removal applications.

ACKNOWLEDGEMENTS

This work was funded in part by grants from the Illinois Coal Development Board and the Illinois Coal Industry Committee through the Center for Research on Sulfur in Coal and the Illinois Department of Commerce and Community Affairs. The authors thank Dr. Gullett at U. S. EPA, Mr. Bruce at Acurex Corporation, Dr. Yoon and Dr. Withum at Consolidation Coal Company, and Mr. Bortz at Research-Cottrell EST for obtaining DSI test data reported in this paper.

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Table 1

Typical properties of commercial and ISGS hydrated lime

	<u>ISGS</u>	<u>Commercial</u>
Surface area (m ² /g)	35-85	10-20
Mean particle diameter (micrometer)	0.5-2.5	1.5-5
Crystallite size (angstroms)	140-160	220
Pore volume (cc/g)	0.25-0.6	0.1-0.25

Table 2

Chemical analysis of test sorbents

Sorbent	Ash	Carbon	Hydrogen	CO ₃	CaO	Ca(OH) ₂ (by TGA)	Wt% moisture
HSA-1	74.35	1.03	2.80	NA ^a	73.85	89.2	1.0
HSA-2	74.49	1.22	2.82	2.93	71.28	86.2	0.4
HSA-3	74.75	0.90	2.82	1.60	73.44	91.6	0.8
Commercial	75.42	0.41	2.70	1.51	72.62	93.0	1.0

^a not available

Table 3

Physical properties of hydrates tested for SO₂ removal

<u>Sample ID</u>	<u>BET Surface Area (m²/g)</u>	<u>Pore Volume^c (cm³/g)</u>	<u>Particle Size (micrometers)</u>
HSA1	50	0.24	0.7 ^a (3.5) ^b
HSA2	60	0.36	0.8 ^a (3.5) ^b
HSA3	40	0.18	1.1 ^a
HSA30	48	NA ^d	(4.5) ^b
HSA31	47	NA ^d	(2.3) ^b
WUELFRA _{sorp}	40	NA ^d	(15) ^b
commercial hydrate	22	0.16	17-25 ^a (22) ^b

^ameasured by Sedigraph Particle Size Analyzer

^bmeasured by Microtrac Particle Size Analyzer

^cpores smaller than 0.25 micrometers

^dnot available

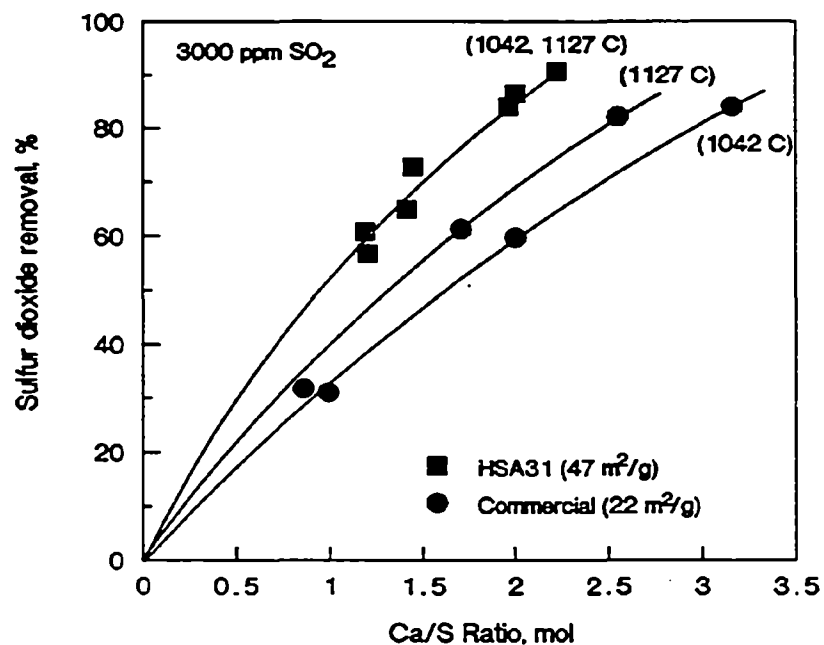


Figure 1. Comparison of FSI sulfur dioxide removals for commercial and HSA31 hydrate.

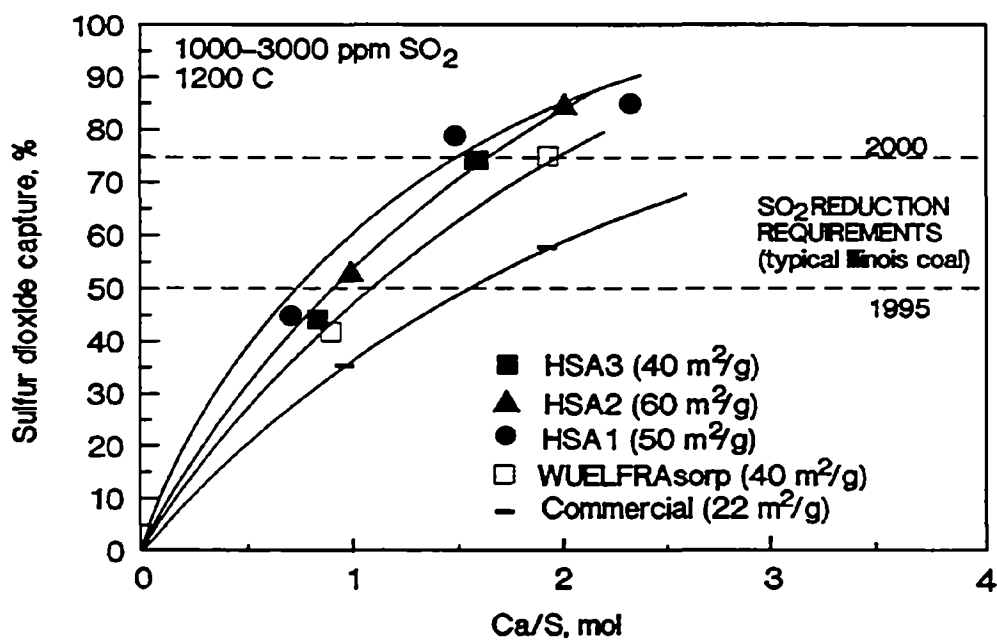


Figure 2. Comparison of FSI sulfur dioxide removals for ISGS HSA, commercial and WUELFRA sorb hydrates.

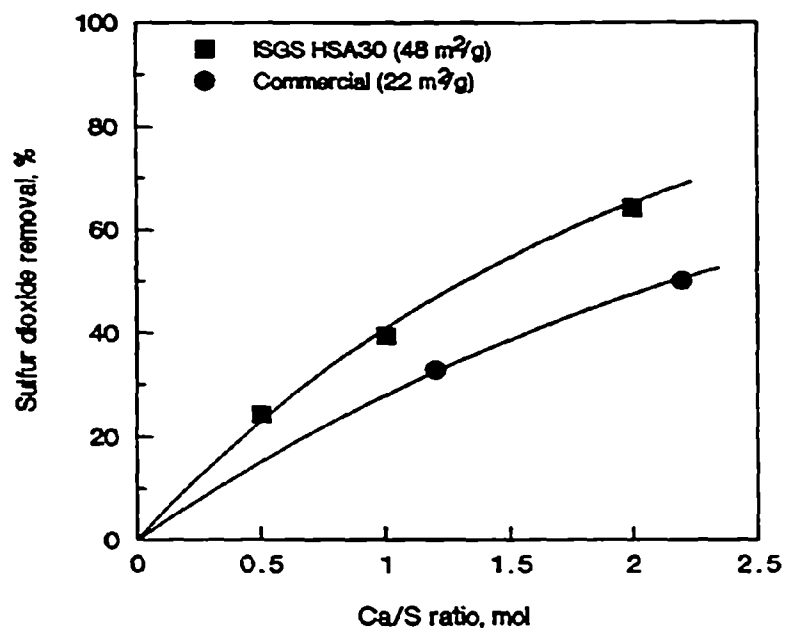


Figure 3. Comparison of pilot-scale boiler economizer sulfur dioxide removals for commercial and HSA30 hydrates.

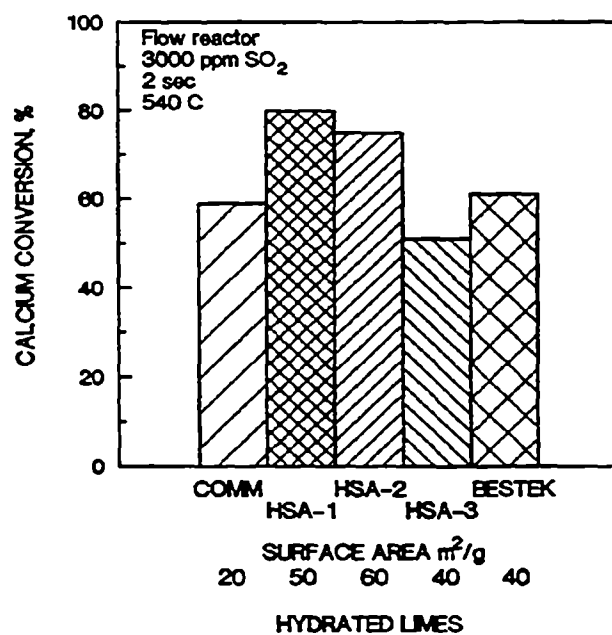


Figure 4. Comparison of boiler economizer calcium conversions for ISGS HSA, commercial and WUELFRAAsorp hydrates

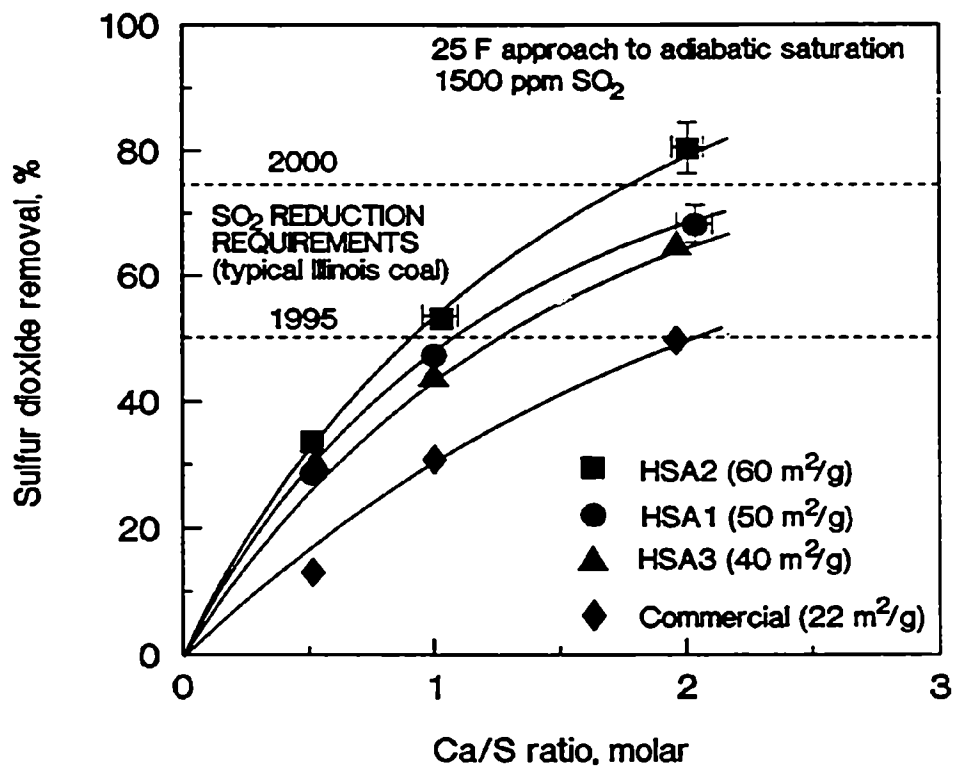


Figure 5. Coolside sulfur dioxide removals (humidifier + baghouse) for commercial and ISGS HSA hydrates.

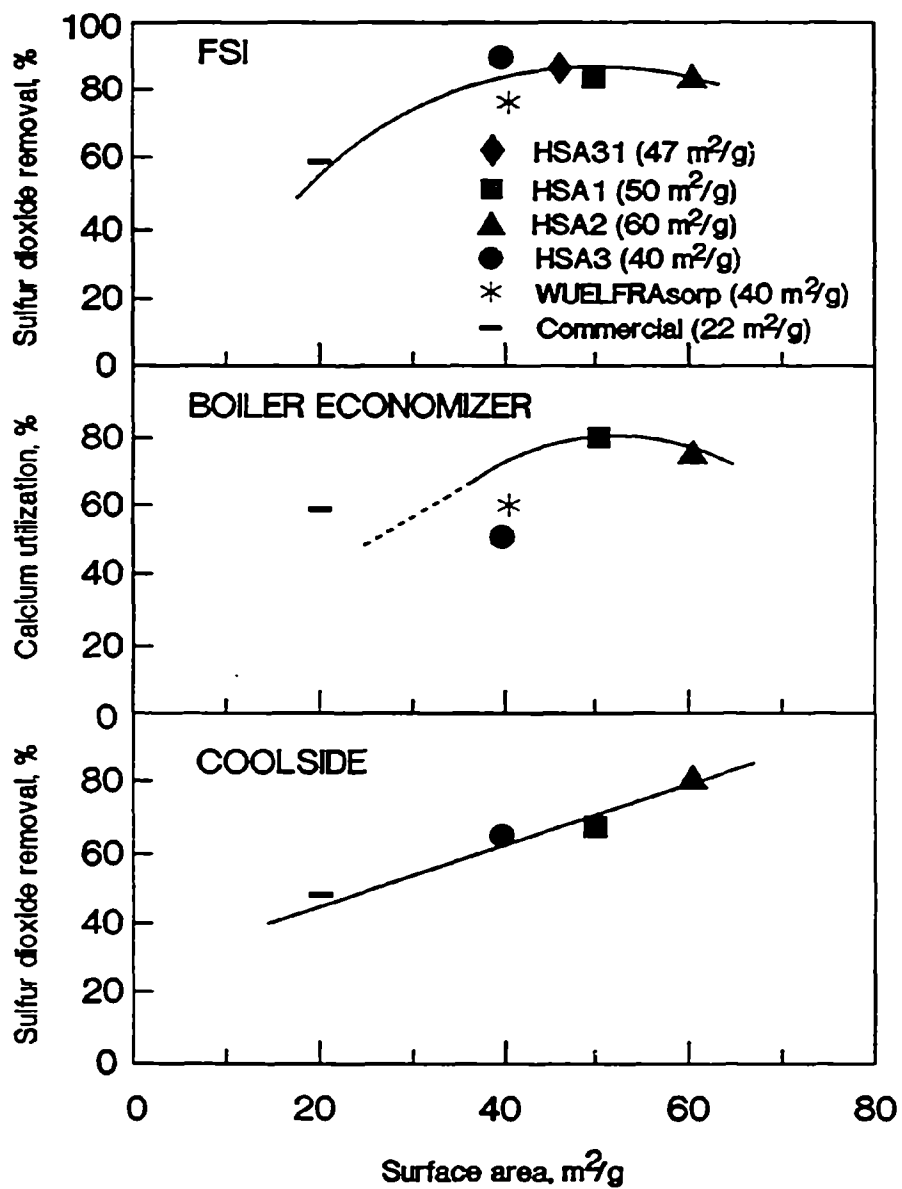


Figure 6. Sulfur capture for hydrates as a function of surface area .

**EFFECTS OF SPRAY NOZZLE DESIGN
AND MEASUREMENT TECHNIQUES ON REPORTED DROP SIZE DATA**

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ABSTRACT

Accurate spray nozzle drop size data is a critical component in the field of flue gas desulfurization (FGD). Nozzle manufacturers have worked independently responding to drop size requirements as specified by scrubber designers. Typically, a Volume Median Diameter drop size of 2500 microns is specified regardless of flow rate, operating pressure, or nozzle design.

In order to accurately assess drop size performance for a given nozzle, the method for testing should be fully understood. The type of instrument, method of collection, manner of interpretation of raw data, and reporting techniques all have a strong influence on the results.

This paper provides an overview of common drop size measurement techniques, emphasizing the importance that nozzle design has on resulting drop size as well as other factors such as capacity and pressure. Also, some of the more commonly used methods and instruments used for drop size data collection and the importance of repeatability of test results when comparing data from different sources is discussed. Finally, a critical look at reporting techniques and their potential affect on drop size data is presented.

EFFECTS OF SPRAY NOZZLE DESIGN

DISCUSSION

Let's first examine measurement techniques. The American Society for Testing and Materials (ASTM) recognizes two different types of drop size sampling techniques known as spatial and temporal (also known as flux-sensitive).

The spatial technique (i.e. spatial distribution) is implied when a collection of droplets occupying a given volume are sampled instantaneously (see Fig. 1). Generally, spatial measurements are collected with the aid of holographic means or high speed photography. This type of measurement is sensitive to the number density in each class size and the number of particles per unit volume.

The flux technique (i.e. flux distribution) is implied when individual droplets that pass through the cross section of a sampling region are examined during a interval of time. Flux measurements are generally collected by optical measurements that are capable of sensing individual drops.

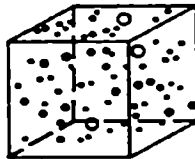
The flux distribution may be transformed to a spatial distribution by dividing the number of samples in each class size by the average velocity of the drop in that size class. If all drops in a spray are moving at the same velocity the flux and spatial distribution are identical.

However, the spray will generally exhibit differences in drop velocities that vary from class size to class size. In addition, these differences depend on the type of nozzle, capacity and spraying pressure.

SPATIAL vs. FLUX SAMPLING

SPATIAL

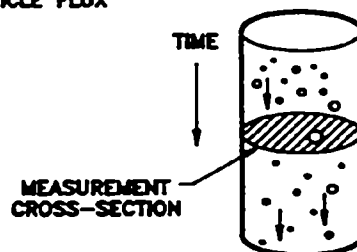
- AVERAGED OVER FINITE VOLUME
- INSTANTANEOUS SAMPLE
- SENSITIVE TO RELATIVE NUMBER DENSITY $N(d)$, PARTICLES/VOLUME



MEASUREMENT
VOLUME

FLUX (TEMPORAL)

- TIME AVERAGED
- SENSITIVE TO PARTICLE FLUX



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Fig. 1

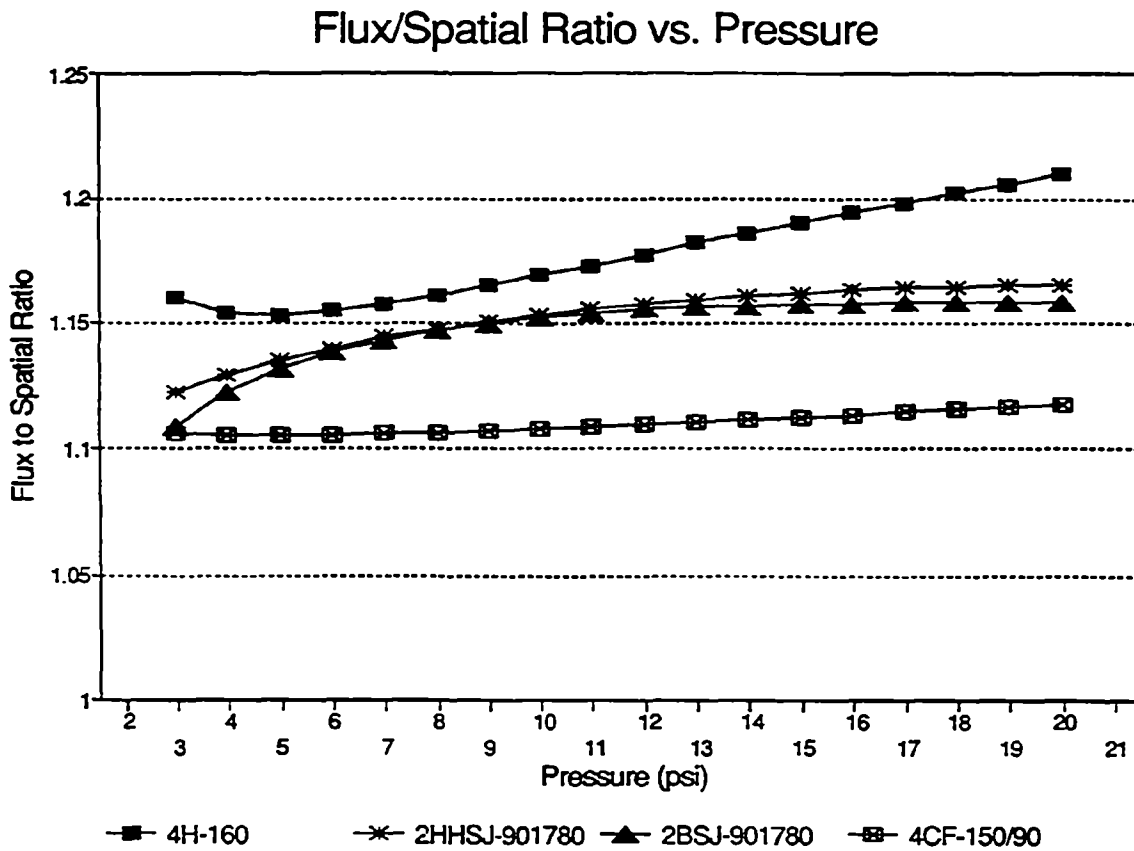


Fig. 2

Fig. 2 clearly shows the relationships between the spatial and flux samples for the nozzle listed at the indicated conditions. This data does not suggest that a relationship between the two methods is fixed, or that a certain correction factor could be developed.

The flux/spatial comparative drop size ratio relationship will vary with pressure and approaches unity at a condition where all droplets would be traveling at the same velocity. Therefore, it is important to combine measurement techniques and equipment for measuring drop diameters, and for the spatial measurement technique, to reconcile the drop size distribution by applying velocity correction values to each class size in the distribution.

In Example 1, while the same nozzle is used, the spatial data without velocity correction consistently indicates smaller drop sizes.

Example 1
4CF-150-90 WhirlJet® Hollow Cone Nozzle,
150 GPM @ 7 psig, 90° Spray Angle

<u>Pressure (PSIG)</u>	<u>Flux</u>	<u>Spatial</u>
3	3910	3490
5	3470	3050
7	3150	2750
10	2820	2450
15	2520	2170
20	2410	2070

The selected range of the instrument will also effect the end results. In Example 2 the same nozzle was tested using ranges of 100 to 6200 microns and 200 to 12,400 microns. For the first range, droplets larger than 6200 microns were discarded. While droplets larger than 6200 microns are few in number they will be a sizeable percent of the volume of liquid sprayed. Comparing the spatial samples we see a difference of 400 microns or 14.6 percent.

Example 2
4CF-150-90 WhirlJet®
VMD in Microns

Pressure (psig)	Range 6200	
	Flux	Spatial
7	2690	2340
7	Range 12,400	
	Flux	Spatial
7	3150	2740

In this example, the difference between the 6200 upper bound spatial data (2340) and the 12,400 upper bound flux data (3150), is 810 microns or a 25.8 percent difference for the same nozzle and pressure. In comparing nozzles of similar design, from different manufacturers, unless the sampling technique and range are known, evaluating the drop size performance of the two designs becomes subjective if not invalid.

With measurement techniques addressed, let's look at four common nozzle designs used in FGD applications and review the importance of flow rate and pressure when considering drop size.

Nozzle Selection		
<u>Nozzle</u>	<u>Description</u>	<u>Flow Rate</u>
4H-160 FullJet®	90° full cone spray pattern	160 GPM at 7 psi
2HHSJ-901780 SpiralJet®	90° full cone spray pattern	178 GPM at 10 psi
2BSJ-901780 SpiralJet®	90° hollow cone spray pattern	178 GPM at 10 psi
4CF-150-90 WhirlJet®	90° hollow cone spray pattern	150 GPM at 7 psi

The above nozzles have the same spray angle but the flow rates are given at the rated pressure established by the manufacturer for each nozzle design. Drop size tests are often conducted at the rated pressure. If a 150 GPM flow rate is required then three of the four nozzles must be operated at lower than rated pressures which will result in larger drop sizes. A proper comparison can only be made if drop size data is collected for all four nozzles at the same flow rate and pressure.

Figure 3 indicates that the four nozzle designs also produce four distinctly different volumetric spray distribution patterns which influence the composite drop size populations.

The FullJet nozzle, in this case the 4H160, has an internal vane which causes a swirling of the fluid, creating a cone shaped pattern. Typically this type of nozzle design produces a full cone pattern with larger droplets, yet will show a fairly wide overall drop size range.

The SpiralJet® nozzle (2HHSJ-901780) creates a pattern by shearing off portions of a column of water as it passes through the inside of the spiral. This type of nozzle is typically made with two deflective angles on the spiral which creates a cone within a cone spray pattern with the two edges of the cones having the largest droplets.

The hollow cone WhirlJet® nozzle (4CF-150-90) forms a spray by having the fluid enter tangentially from an inlet into a circular chamber exiting through a smaller concentric orifice. This method of spray formation can create a wider overall spray pattern and potentially a smaller droplet size for the same flow rate and pressure.

The hollow cone SpiralJet® nozzle (2BSJ-901780) uses shearing forces to turn the solid column of water into a hollow cone spray pattern. Spray formation is similar to the full cone SpiralJet except that only a single deflection angle is used.



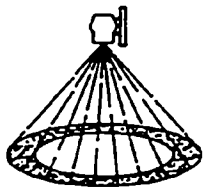
4H-160 FullJet®



2HHSJ-901780 Full
Cone SpiralJet®



2BSJ-901780 Hollow
Cone SpiralJet®



4CF-150-90
WhirlJet®

Fig. 3

VMD Data for 12400 Micron Range			
Pressure (PSIG)	Flow Rate GPM	FLUX	SPATIAL
4H-160 FullJet®			
3	106	4750	4090
5	137	4180	3630
7	160	3880	3350
10	189	3600	3080
15	225	3330	2790
20	260	3160	2610
2HHSJ-901780 Full Cone SpiralJet®			
3	98	4330	3900
5	127	3880	3420
7	150	3600	3150
10	178	3340	2900
15	218	3060	2640
20	252	2870	2480
2BSJ-901780 Hollow Cone SpiralJet®			
3	98	4100	3700
5	127	3590	3250
7	150	3300	2980
10	178	3020	2720
15	218	2730	2460
20	252	2550	2280
4CF-150-90 WhirlJet®			
3	98	3910	3490
5	127	3470	3050
7	150	3150	2750
10	179	2820	2450
15	220	2520	2170
20	254	2410	2070

Fig. 4

Figure 4 further illustrates how design can effect drop size. Note that each spray pattern provides a range of drop sizes. This range varies with spray nozzle type, capacity, spraying pressure, and to a lesser extent, spray angle.

Now, let's look at some of the more commonly available methods and instruments available for drop size data collection. Since repeatable test results are essential in comparing nozzle performance data, it is essential to use testing procedures that take into account all the potential variables in the sampling technique for both methods and instrumentation.

By spraying water into a pan of oil and shuttering the spray, it is possible to count and size individual droplets using a microscope. This technique is still used by some researchers. Problems involve drop coalescence, inadequate sample size and the fact that very small droplets will be deflected away from the oil by air currents at the surface due to the spray velocity. Also, larger droplets can and do break up from impacting the surface.

The same type of method is used when spraying a dye onto a stationary card or water on to liquid sensitive paper. Again, the small drops might be deflected away from the target and the large drops can break-up from the impact. Data collected by these "intrusive" methods depends on a number of uncontrolled variables making such test results generally non-repeatable.

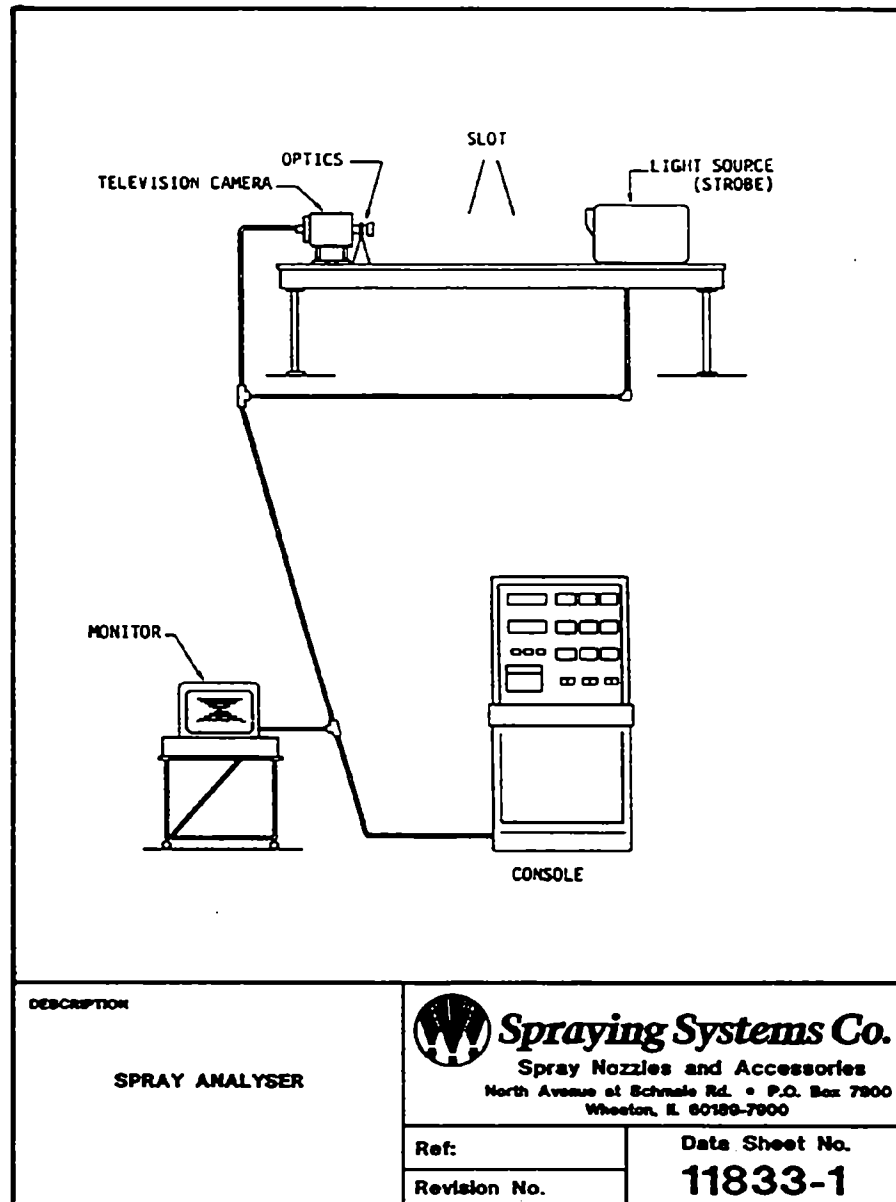
While drop size data was being collected in the early 1950's using methods such as flash photography, probably the first real breakthrough in droplet sizing technology was the development in 1961 of an automated imaging analyzer (Fig. 5).¹

Basically, the Electronic Imaging Analyzer incorporates the spatial measurement technique using a strobe light to illuminate the spray and record the image with a vidicon tube. The image is scanned and the droplets are sized and separated into different classes. Resulting data can be mathematically corrected using velocity data to give a flux distribution. Sources of error early in the development of this device included blurring, depth of field variations, and vidicon tube saturation. These sources were recognized and corrected.

The imaging type analyzer is still actively promoted by some nozzle manufacturers. The limited availability of this type of instrument, however, prevents independent researchers and other interested members of the drop size analyzer community from verifying data arrived at from a particular test or comparing performance from similar designs.

More recently the development of commercially available drop size analyzers makes it feasible to verify drop size results by independent sources. This new breed of analyzers incorporates lasers, special optics and digital circuitry to minimize imaging error. Some of the most commonly recognized manufacturers of laser measurement instruments include Malvern, Particle Measuring Systems (PMS), and Aerometrics.

¹The Electronic Imaging Analyzer was developed at Spraying Systems Co. by Dr. Verne Dietrich and built by the Dage Division of TRW, Michigan City, Indiana. The design was awarded U.S. Patent 3275733 in September of 1966 and is currently in its second generation.

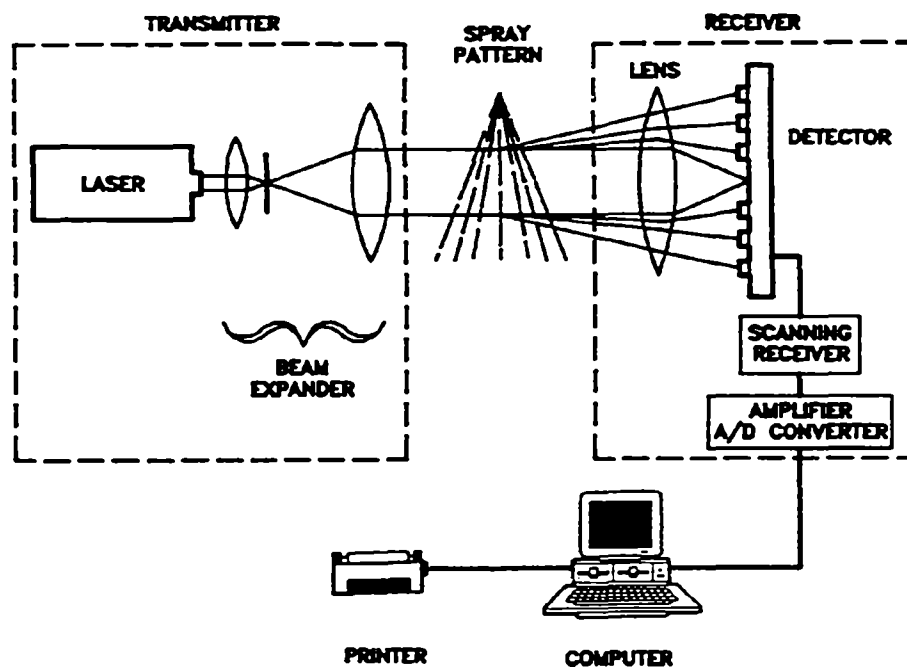


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Fig. 5

COMPONENTS OF THE MALVERN PARTICLE ANALYZER



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Fig. 6

The Malvern Analyzer which is considered a spatial sampling device, utilizes the principle that a spray droplet will cause laser light to scatter (Fig. 6) through an angle dependent on the diameter of the droplet. The scattered light intensity is measured using a series of semicircular photo diodes. Theoretically, the distance of the individual photo diodes from the centerline of the laser and the light intensity functions are all that are needed to calculate the droplet size distribution. A curve-fitting program is used to convert the light intensity distribution into any of several empirical drop size distribution functions. Since the Malvern has some self diagnostics, potential sources of error are easier to identify. The instrument must be aligned and calibrated periodically using reticle slides with known etched drop distributions.

Perhaps the biggest source for error with this type of instrument is multiple light scattering. If the spray is too dense, there is a possibility that the scattered light from one droplet might be scattered again by other drops further down the beam axis. The Malvern is equipped with a "obscuration level" indicator which can be used to determine if the spray is too dense, but such a determination is often difficult. To circumvent this in the lab the technician typically moves the nozzle farther away or uses special shielding to permit only a portion of the spray to enter the sample area.

Particle Measuring Systems, also known as PMS, produces both diffraction type instruments and imaging type instruments known as Optical Array Probes. The PMS Optical Array Probe (Fig. 7) is a flux sampling instrument. As the droplets pass through the sampling plane, the droplets are sized and counted providing information which can be used to determine velocity. The two dimensional grey scale OAP can provide droplet measurement in two ranges, 100 to 6200 microns and 200 to 12,400 microns, and is currently the most sophisticated offered by PMS.

The PMS OAP Grey Scale probes applies advanced technology utilizing extensive self diagnostics. These probes will reject drop images which are out of focus or which do not meet a series of other acceptability tests automatically. Problems with PMS units usually center on improper calibration or maintenance. The optics tend to get wet easily, and cleaning and alignment require some skill. Also, dense sprays tend to overload the circuitry and sample area reductions are often necessary. Sample area correction factors and drop distribution curve fitting equations are needed and are left up to the operator to include in the analysis.

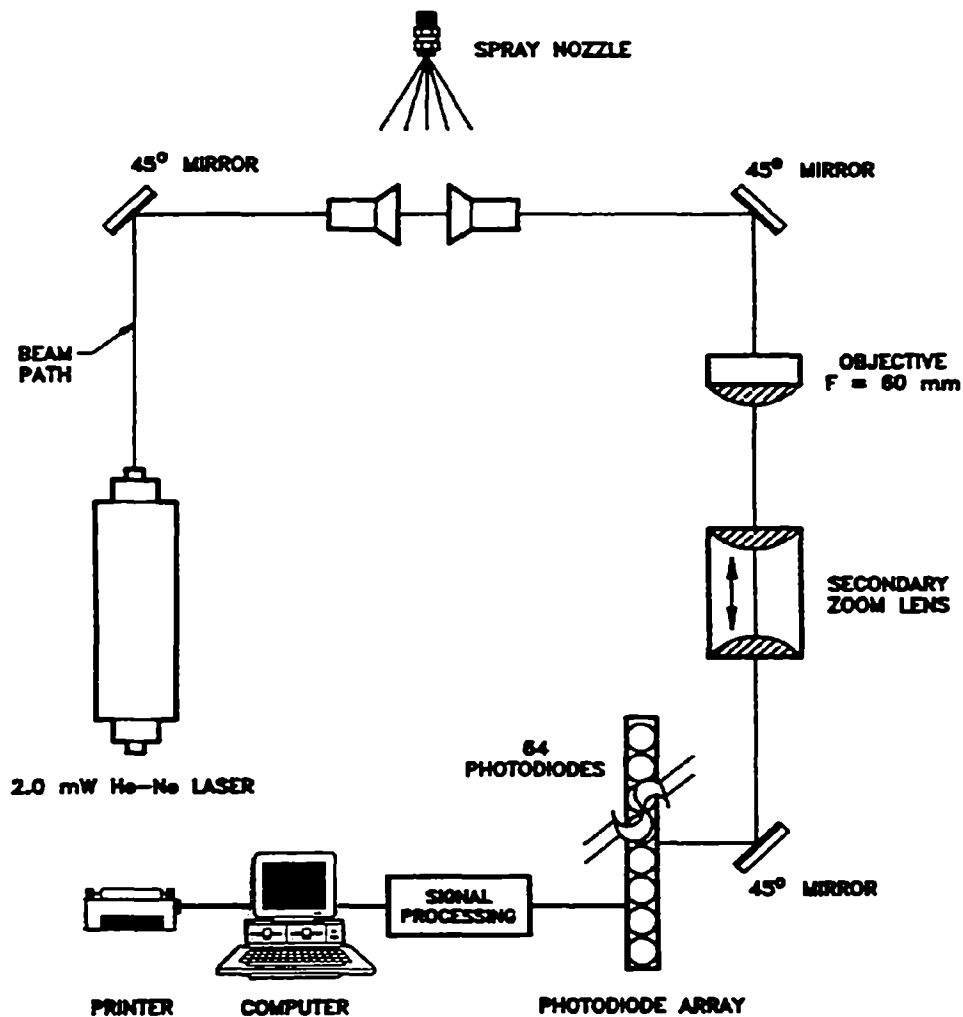
The Aerometrics Phase Doppler Particle Analyzer or PDPA (Fig. 8) is a point sampling device and is a flux-sensitive instrument. Point sampling refers to an instrument that focuses on a portion of the total spray pattern and requires targeting several test points within the spray in order to obtain a composite sample of the spray flux distribution.

The PDPA uses a low power laser that is split into two beams by utilizing a beam splitter and a frequency module. The two laser beams intersect again into a single beam at the sample volume location. When a drop passes through the intersection region of the two laser beams, an interference fringe pattern is formed by the scattered light. Since the drop is moving, the scattered interference pattern sweeps past the receiver aperture at the Doppler difference frequency which is proportional to the drop velocity. The spatial frequency of the fringe pattern is inversely proportional to the drop diameter.

Aerometrics offers an optional fibre optic probe which isolates the instrument from the spray and eliminates the potential for error due to vibration caused by direct contact with larger capacity sprays.

Other drop sizing instruments which are commercially available, generally use lasers and operate on principles which we've previously discussed.

OPTICAL SYSTEM DIAGRAM FOR AN OPTICAL ARRAY SPECTROMETER PMS MODEL OAP-2D GA2



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Particle Measuring Systems, Inc.
Boulder, Colorado

Fig. 7

COMPONENTS OF THE AEROMETRICS PDPA

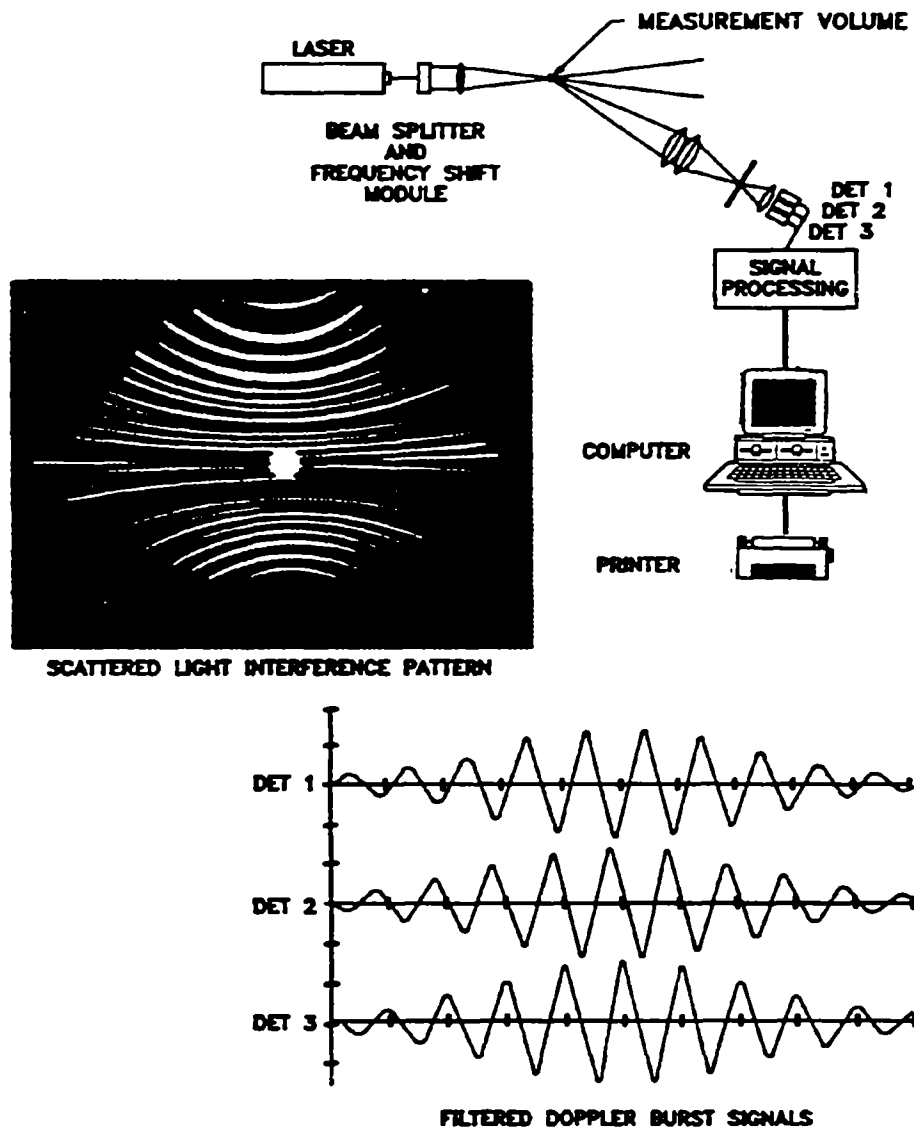


Fig. 8

Reprinted by permission of
Aerometrics Inc.,
Sunnyvale, California

In the application of these instruments if small regions of the spray are examined, as with the PMS or Aerometrics, it is important to test several points within the spray in order to obtain a combined result which is representative. Ideally, the combined drop size distribution will also be weighted relative to the volumetric flow at the various sampling points. This step is critical and is often ignored. In some situations, the effect is small, as with air atomizing or Whirljet® type nozzles. In other nozzle designs, improper weighting can affect the results by as much as 50%.

The distance that the nozzle is located from the sample region and the orientation also have an effect on the data collected. Smaller droplets will be entrained into the air flow pattern created by the nozzle and will show up in increasing concentrations as the distance from the nozzle increases in the regions of higher entrained air flow. Also, very small drops may evaporate completely before they get to the sampling region. Therefore, in order to provide accurate comparisons between nozzles of different design each nozzle test should be conducted at several locations reflecting the spray flux distribution and normalized to reflect the whole drop size population. However, a standardized procedure for obtaining composite data has not been established at the present time.

All of the issues mentioned so far can lead to differences in the data obtained, even if the instrumentation is in perfect working order. However, proper calibration and maintenance of the measuring equipment can't be overlooked. A great potential for error exists when everything seems to be working fine but something is just slightly out of adjustment. Properly scheduled calibration tests are important, particularly in labs where many people use the equipment.

While instrumentation issues are of great importance, the reporting method is the greatest potential source of bias for drop size data. This directly effects those responsible for evaluating nozzle performance and making recommendations. There are a number of formats used for reporting drop size data. When evaluating data, particularly from different sources, it is extremely important to know the type of instrument and range used, the sampling technique, and the percent volume for each size class in order to make for valid data comparisons.

Following the procedure as outlined by the ASTM Standard E799 (Fig. 9) provides an exact method used for collection and reporting. In this example the drop size data is tabulated using the ASTM standard, and an empirical (Rosin-Rammler) curve fitting formula is then applied to further classify each drop size as a percent of the volume.

To verify if the correct instrument range was used the ASTM guidelines state that the largest drop size reported should make up less than one percent of the volume of the spray flux. Looking again at Fig. 9, under percent volume undersize, we see that the largest drop size reported was 5333 microns or 0.2 percent of the volume. This verifies that a large enough collection range was used and assures the accuracy of the test.

REPRESENTATIVE DROP SIZES & DISTRIBUTION

4CF-150/90 WhirlJet

20 PSI

07-25-1990

-Dropsize Analyzer: PMS-OAP-2D-GA2 (12400 μm max)

-Sampling Method: Flux (TEMPORAL)

-All values computed utilizing the procedures for determining spray characteristics as outlined by ASTM (standard E799).

UPPER BOUND = 5332.65 (μm)

LOWER BOUND = 317.46 (μm)

DROP DIAMETER (μm)	PERCENT VOLUME UNDERSIZE	(BOUNDED CURVE) PERCENT COUNT UNDERSIZE	
317	0.20	0.00	
368	0.31	8.58	
427	0.47	16.95	
496	0.71	25.13	
575	1.08	33.10	
667	1.65	40.86	
774	2.50	48.39	
898	3.80	55.68	
1041	5.74	62.69	
1208	8.63	69.37	
1401	12.87	75.66	
1626	18.98	81.46	
1886	27.48	86.64	
2188	38.77	91.06	
2538	52.72	94.56	
2944	68.13	97.06	
3416	82.55	98.57	
3963	93.05	99.28	
4597	98.29	99.51	
5333	99.80	99.55	
		TOTAL CURVE (μm)	BOUNDED CURVE (μm)
(ARITHMETIC MEAN)	D_{10} :	0	1039
(SURFACE MEAN)	D_{20} :	0	1263
(VOLUME MEAN)	D_{30} :	0	1484
(SURFACE/LINEAR MEAN)	D_{21} :	1294	1536
("EVAPORATIVE" MEAN)	D_{31} :	1619	1774
(SAUTER MEAN)	D_{32} :	2026	2050
(DeBROUGERE [HERDAN] MEAN)	D_{43} :	2503	2514
(VOLUME MEDIAN DIAMETER)	$D_{V0.5}$:	2470	
(NUMBER MEDIAN DIAMETER)	$D_{N0.5}$:	804	[BOUNDED]
(DIAMETER AT Max. dVOLUME/dDIAMETER)	D_{VOL_MODE} :	2414	
(RELATIVE SPAN $[(D_{0.9}-D_{0.1})/D_{V0.5}]$)	RSF:	1.0075	
(COEFF. OF VARIANCE $[(D_{V0.5}/D_{N0.5})]$)	CV:	3.0737	

Fig. 9

BETE DROPLET ANALYSIS SYSTEM

COMPOSITE REPORT
 TEST DATE 4/19/84
 TESTS INCLUDED: 1247 1248 1249
 PRESSURE 10.0 PSI
 CENTERLINE DIST 60.00 INCHES
 AZ. ANGLE 50.0 DEG
 CYL. ANGLE 60 - 300 DEG

NOZZLE: 3 FWT 4460120

DIAMETER (MICRONS)	DROPS	% OCCURRENCE	% SURFACE AREA	% VOLUME	CUM % VOLUME	CLASS CHECK
125.9 - 158.5	529	4.33	0.20	0.02	0.02	0.000
158.5 - 199.5	1013	8.30	0.58	0.07	0.08	0.000
199.5 - 251.2	1639	13.42	1.38	0.19	0.27	0.000
251.2 - 316.2	1457	11.93	1.90	0.32	0.60	0.000
316.2 - 398.1	1588	13.00	3.27	0.70	1.30	0.001
398.1 - 501.2	1233	10.10	3.93	1.05	2.35	0.001
501.2 - 631.0	1345	11.01	6.59	2.19	4.54	0.003
631.0 - 794.3	1206	9.88	9.53	4.02	8.56	0.005
794.3 - 1000.0	858	7.03	10.69	5.66	14.22	0.006
1000.0 - 1258.9	539	4.41	10.67	7.12	21.33	0.008
1258.9 - 1584.9	363	2.97	11.23	9.37	30.70	0.011
1584.9 - 1995.3	208	1.70	10.36	10.95	41.64	0.013
1995.3 - 2511.9	137	1.12	10.64	14.05	55.69	0.016
2511.9 - 3162.3	50	0.41	6.09	10.09	65.78	0.012
3162.3 - 3981.1	27	0.22	5.43	11.54	77.32	0.013
3981.1 - 5011.9	13	0.11	3.76	9.61	86.93	0.011
5011.9 - 6309.6	5	0.04	2.31	7.41	94.34	0.008
6309.6 - 7943.3	2	0.02	1.42	5.66	100.00	0.006
12212		100.00	100.00	100.00	100.00	

AVERAGE DIAMETERS (MICRONS) :

ARITHMETIC MEAN = 547.61
 SURFACE MEAN = 722.28
 VOLUME MEAN = 959.87
 SAUTER MEAN = 1695.21
 WEIGHT MEAN = 2734.28
 VOLUME MEDIAN = 2306.22
 SAMPLE SIZE CHECK = 0.03

MAXIMUM DIAMETER = 6910.21
 MINIMUM DIAMETER = 155.73
 TOTAL DROPS IN SAMPLE = 12212
 TOTAL OUT OF FOCUS = 1824
 TOTAL FRAMES IN SAMPLE = 600
 AVL. DROPS PER FRAME = 20.35
 DEVIATION = 0.76

RELATIVE SPAN = $(5526.00 - 852.48) / 2306.22 = 2.03$

Fig. 10

²Bete, Solving Corrosion Problems, Paper No. 19, 1984. (Reproduced with permission from "Solving Corrosion Problems in Air Pollution Equipment," National Association of Corrosion Engineers, Houston, TX, 1984. Copyright NACE.)

In (Fig. 10)² while a similar format was used, the type of analyzer and range are not reported. Examining the percent volume, if the largest drop size class makes up a larger percentage of the total volume the upper limit of measurement may be too low. Therefore, a VMD droplet size which is substantially smaller than is actually occurring in the spray flux may be reported.

When using a curve to report drop size data such as volume median diameter ($D_{v0.5}$) vs. pressure, enough data points should be reported when the curve is plotted to aid meaningful interpolation of data between data points. Since performance variations between different pressures are not necessarily linear, comparing Figure 11A and 11B, a small difference in pressure may produce a significant change in trending the median drop size. In any case such a graph should be used to supplement a more complete reporting format, not as a substitute.

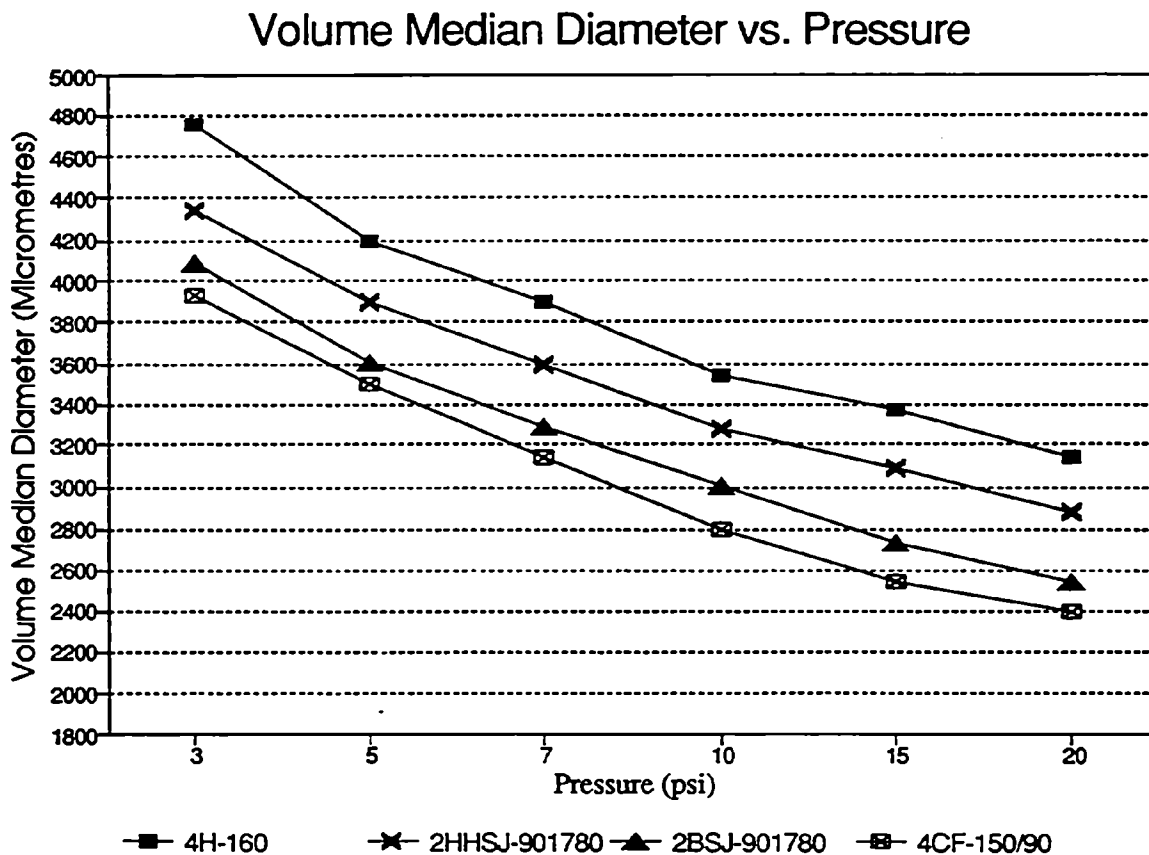


Fig. 11A

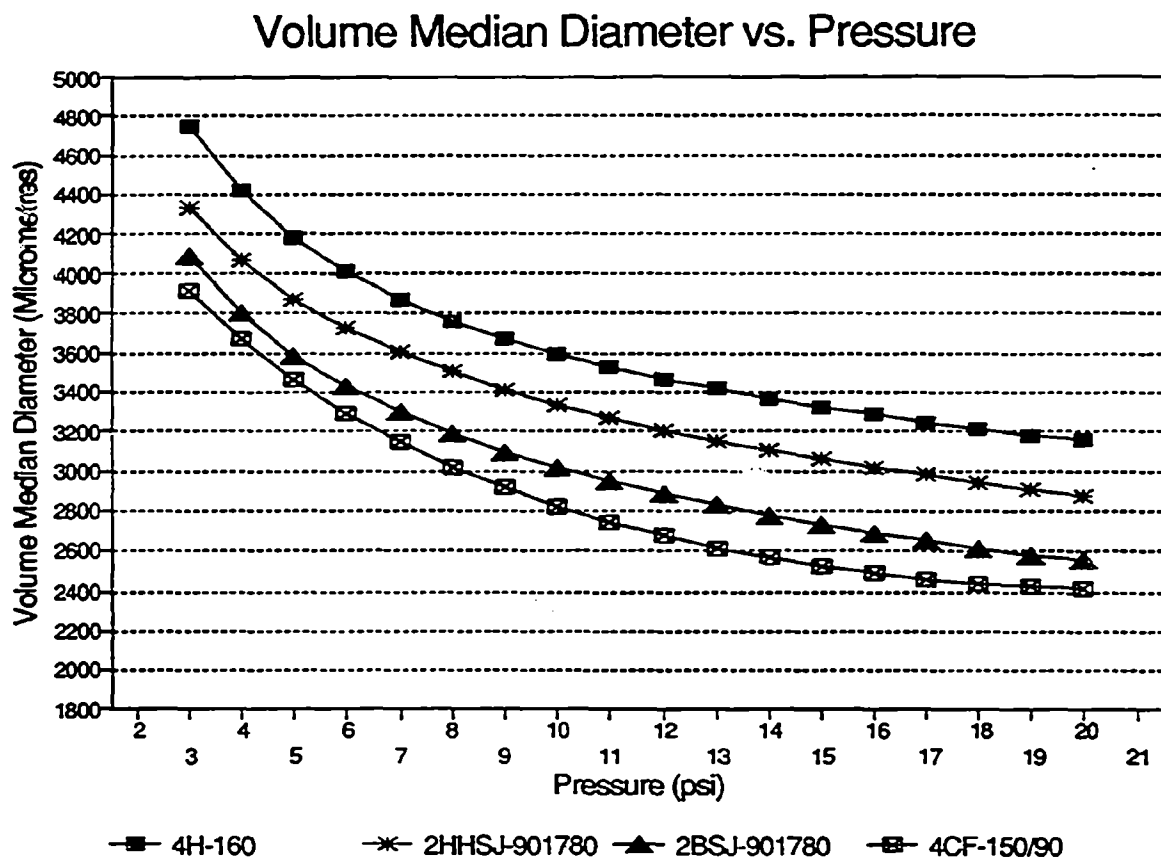


Fig. 11B

CONCLUSION

Providing accurate drop size data is the responsibility of the nozzle manufacturer. It is also apparent with the wide range of nozzle designs and capacities that no single instrument or technique is universal. Accurate data collection requires a dedicated facility which uses commercially available instruments and offers the potential for verifying test results. Most of all, a trained staff familiar with the latest calibration and collecting techniques is essential for reporting the results of any test.

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High SO₂ Removals with a New Duct Injection Process

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ABSTRACT

Sanitech has developed a new sorbent material specifically formulated for retrofit duct-injection applications. These lime-based sorbents are tiny enough to be entrained in the flue gas stream, yet large enough to be easily removed once saturated with sulfur dioxide. The sorbents distribute their reactive lime species over the large internal surface area of an inexpensive, sponge-like mineral support, which carries with it the optimum amount of moisture needed for acid-gas removal. Laboratory runs suggest the potential for greater than 90% SO₂ removal and 60% net lime hydrate utilizations for duct-injection retrofits with a small, high-ratio baghouse, enabling sorbent recycle. Plans are now being made for scaled-up demonstrations.

These "sponge-sorbents" hold particular promise for economical application at many older, moderately-utilized, power plants and those plants with existing particulate-control problems or potential toxic-emission problems.

INTRODUCTION

The initial promise of sorbent injection technologies, both furnace-injection and duct-injection, was that they would cost very little to install on coal-burning power plants. In practice, however, weak sorbent performance has plagued these technologies, with unassisted SO₂ removals of typically 40% to 60%; and low sorbent utilizations, of from 20% to 40%. Moreover, particulate-control problems have resulted. A removal efficiency of only 50% will not allow a plant to burn medium- or high-sulfur coal and still meet the 1.2 lb SO₂/MM Btu requirement of the 1990 Clean Air Act. Utilizations of only 30% mean that net sorbent costs will be high and that huge amounts of unused reactants, mixed-in with ESP fly ash, will require waste disposal.

Sanitech has developed a new duct-injection sorbent specifically formulated to solve these problems. For over four years, the company has been scaling-up a dry, regenerable magnesia technology which utilizes expanded industrial minerals -- granular vermiculite or perlite -- as reactant supports. The company has recently discovered how to endow less expensive calcium-based supported-sorbents with the same high reactivity and performance as magnesia and do so with even cheaper grades of the support materials. While not regenerable, the calcium sorbents are recyclable.

These proprietary sorbents are made from very fine, inexpensive, almost waste-grades of vermiculite or perlite. The tiny sorbents, called "sponge-sorbents," can be injected into a humidified flue gas stream after the electrostatic precipitator and then be captured on a fabric filter, where additional SO₂ removal takes place, much like the Electric Power Research Institute's HYPAS concept.¹ The sponge-sorbents are hundreds times smaller than Sanitech's regenerable, magnesia-based, panel-bed "Mag-Sorbents,"² yet they are still over a thousand times larger than typical fly ash or lime injectant particles. Consequently, a very small baghouse can be used for collection -- a "microbaghouse" -- which operates at a high air-to-cloth ratio (A:C). With this extra, but lower-cost, particulate collection device in line, the plant can avoid an otherwise-needed ESP-upgrade, or could incorporate a furnace-injection or second duct-injection front-end process as well.

SPONGE-SORBENT CHARACTERISTICS

The interrelated keys to the performance of sponge-sorbents are their size, moisture capacity, and recyclability.

Sorbent Size and Shape

Fine sponge-sorbents are simple to prepare. Very fine vermiculite or perlite, such as #5 vermiculite ore, is thermally expanded in the traditional, automated manner, where it increases in volume by a factor of about ten. Vermiculite expands like an accordion, exposing hundreds of thin mica plates; perlite pops like an exploding onion, similarly exposing a high internal macro-surface area. These expansions allow for a very high loading of reactive species, in this case hydrated lime, with a resulting sorbent composition of approximately 60 wt% $\text{Ca}(\text{OH})_2$. The material is then thermally activated and moistened before use. See the process flow diagram in Figure 1.

The key to the sorbents' application and low capital cost requirements is their size. The sorbents are about 0.20 millimeters on a side: small and light enough so that they can be entrained in the gas stream, yet large enough so that they present no problems in being removed from the gas once saturated. Fly ash and traditional lime injectants are thousands of times smaller than the sorbents. Fly ash frequently has a mass mean diameter of from 10 to 20 microns; hydrated lime particles, injected dry or as a slurry, generally average 5 microns in diameter. Particulate removal efficiency and cost are usually inversely proportional to particulate size. It is much easier and cheaper to separate a single, saturated 0.20 mm diameter sponge-sorbent from the gas stream than 40,000 equivalent, but tiny, 5-micron lime particles.

Because sponge-sorbents are so large, it may be possible to use fabric filters that are less than one-fourth the size of those required to filter out the usual 5-micron particles. Such high-ratio baghouses have been used historically to capture sawdust or perlite particles, which, like sponge-sorbents, are large and porous and result in low pressure drops. The Electric Power Research Institute is looking at high-ratio pulse-jet baghouses as retrofit back-ups to aging, marginal ESPs. They may also see use with furnace sorbent injection retrofits.

Traditional baghouses, or increases in ESP specific collector area (SCA), are major capital cost items. Consequently, if practicable, a high-ratio baghouse could cut the capital cost of a sorbent-injection retrofit by 70% or more. Because many of the fines that pass through the existing ESP will impinge upon and be captured by the sponge-sorbents, this device may also help aging, low-SCA ESPs meet tighter PSD, toxics, or PM-10 particulate emission regulations. In preliminary microbaghouse trials, Sanitech has seen significant fine-particulate captured by the sponge-sorbents, although this ability has yet to be quantified.

Moisture Capacity

The key to sorbent performance is water. It has long been known that the higher the amount of evaporated water in the flue gas, that is, the lower its approach to adiabatic saturation, the better the lime sorbent utilization and SO₂ removal. A high interaction between sorbent and injected humidification water has also been shown to result in better performance. Scavenging, that is injecting dry hydrated lime before humidification sprays to maximize water droplet-lime collisions, results in greater performance than lime injection after humidification, although utilizations are still low.³ Injecting lime and humidification water together in a liquid slurry, of roughly 5 to 20% solids, produces even better results: about 60% SO₂ removal with 35% utilization,⁴ although in this case the excess water causes the calcium hydrate crystals to agglomerate, decreasing the ultimate performance.

Because of their sponge-like mineral supports, the new sorbents can be heavily loaded with water, yet remain free-flowing and only moist to the touch. When exposed to the gas stream, they carry their water tightly with them, right along with the widely-exposed lime. The optimum quantity of water is exactly where it is needed. As the water evaporates into the flue gas from the sponge supports, the sorbents are preferentially cooled, dropping the wet-bulb temperature in the micro-vicinity of the sorbents and accelerating SO₂ sorption. Because much of the necessary water for gas cooling is evaporated from the moist sorbents themselves, the humidification requirement of the flue gas stream is significantly reduced.

Recyclability

The key to sponge-sorbent economics is their ability to be recycled. Fine lime particles injected into flue gas streams typically form a sulfated shell around an unutilized core that renders them largely useless for further sulfur capture. Sponge-sorbents, on the other hand, can be recycled by simply remoistening and reinjecting them into the gas stream until their ultimate utilization is reached. Because sorbent injection is after the ESP, flyash is not recycled along with the sorbents.

In practice, a significant amount of the baghouse-collected sorbent would be combined with a small amount of fresh, make-up sorbent, and re-entrained. The spent portion of the collected sorbent can be abraded back into its two constituent components. The dry, well-saturated lime sulfate fraction would go to disposal, as is customary. Because it is twice as utilized as typical lime injectants, however, only half the waste material is produced. The low-grade mineral supports can be either recycled back to be made into new sponge-sorbents or used in agricultural soil-conditioning or reclamation markets. If necessary, they can be easily compressed for more compact disposal. Thus, this new SO₂ removal process requires no water processing and has no other waste streams.

RECENT IN-DUCT LABORATORY TESTING

Sanitech recently initiated in-duct testing of the sponge-sorbents. These trials were carried out during three days of testing at the U.S. Environmental Protection Agency's 40-acfm duct-injection facility at the Air and Energy Engineering Laboratory in Research Triangle Park, N.C. This facility, which has been used in the development of the ADVACATE process, has been described elsewhere.⁵ Acurex Corporation, the site contractor, ran the trials.

The baghouse at this facility, unfortunately, was sized at a typical air-to-cloth ratio of approximately 3 feet-per-minute. This low face velocity was only sufficient to keep about one-half of the sponge-sorbent material on the bags. Half of the sponge-sorbents' reactive species immediately dropped to the baghouse hopper, becoming unavailable for SO₂ removal. Nonetheless, the results achieved in these runs were very promising.

Most important were the recycle runs, which simulated expected utility practice. Partially-saturated sorbent from previous runs was backmixed with a small amount of fresh sorbent, at a 4:1 weight ratio, remoistened, and reinjected into the gas stream. The recycle ratio used, on a total reinjected-solids basis, was less than that of the ADVACATE process. The saturation of the backmixed sorbent, however, was a little less than a true simulation of steady-state. The inlet concentration of SO₂ was 1500 ppm and the baghouse inlet was maintained at a 20°F approach to adiabatic saturation.

The recycle results are shown in Figure 2. The stoichiometric injection ratio represents the fresh lime that must be purchased per cycle -- the important determinant for cost calculations. Particularly noteworthy was the 88 percent SO₂ removal observed at a fresh-lime-consumption stoichiometry of only 1.5:1. This translates to a sorbent utilization of 59 percent.

These results were promising because:

- Due to the limited testing time, the tests were run without a prior parametric determination of the optimum operating conditions for the new sorbents in this system;
- Half of the sorbents' reactivity was not available for SO₂ removal in this baghouse, as it would with a custom-designed, high-ratio baghouse; and
- Higher removal rates for the ADVACATE process have been observed when it has been tested at larger scales than the limited-mass-transfer, 2-inch-diameter-duct apparatus used in these runs.⁶ Better performance might be similarly extrapolated when sponge-sorbent injection is scaled up.

ECONOMICS AND MARKET APPLICATIONS

Initial results suggest a potentially low-cost process. By boosting lime utilization, the fine, inexpensive vermiculite supports more than pay for themselves, while providing a dry, retrofitable method of 90-percent SO₂ removal. Early cost estimates of sponge-sorbent retrofit costs range from about \$300 to \$650 per ton of SO₂ removed, depending on the assumptions. If the fabric filter costs are not attributed to SO₂ control, the cost is significantly less. Costs are most sensitive to the plant operating factor, whether the use of a high-ratio microbaghouse is possible, and the possibility of support reuse and resale. As this technology is further developed and scaled-up, more thorough cost analyses will be made.

An obvious market niche for this technology are those plants that are already experiencing particulate control problems. To the extent that the added fabric filter used for sponge-sorbents recycle avoids the cost of an electrostatic precipitator replacement or upgrade, the sulfur-removal costs are largely only for the sorbent variable costs. This technology may also make sense as a polishing filter with another SO₂-removal process or for units where toxic emission control are needed.

FUTURE EFFORTS

Development efforts have continued since the small-scale tests. Plans are being made for megawatt-scale pilot plant runs and possible host sites are being sought for an eventual full-scale demonstration.

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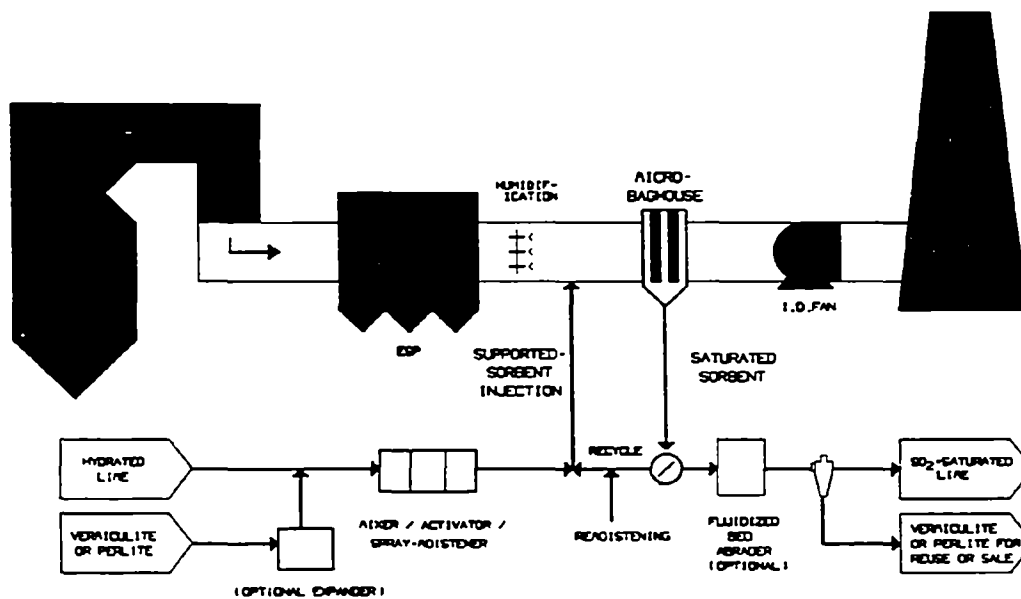


Figure 1. Sponge-Sorbent Flowsheet

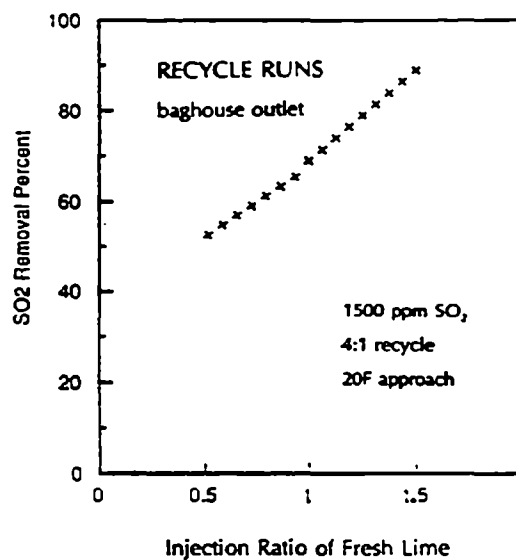


Figure 2. Sponge-Sorbent Performance

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**Combined SO_x/NO_x Control Via Soxal™,
A Regenerative Sodium Based Scrubbing System**

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ABSTRACT

AQUATECHTM Systems, a business unit of Allied-Signal Inc., proposes to demonstrate the technical viability and cost effectiveness of the SOXAL combined SO_x/NO_x control technology on a 2-3 MW equivalent flue gas slipstream from Niagara Mohawk Power Corporation's Dunkirk No.4 Steam Station. The No.4 Boiler is a 100 MW coal-fired utility boiler currently burning coal. This demonstration will be funded primarily by the US Department of Energy-PETC and Allied-Signal Inc. with in-kind contributions both from Niagara Mohawk Power Corporation and cofunded by NYSERDA and ESEERCO. The SOXALTM process combines high efficiency sulfur dioxide removal and improved NO_x removal from flue gas using a sodium based scrubber solution and regeneration of the spent scrubber liquor using AQUATECH Systems' proprietary bipolar membrane technology. The SOXAL process is applicable to both utility and industrial scale boilers using either high or low sulfur coal.

INTRODUCTION

Commercially available flue gas treating options for sulfur dioxide removal include both throwaway and regenerative processes. The limestone scrubbing process is the most commonly used throwaway process; however, it is cumbersome to operate because of the tendency of the scrubbing solution to scale in process equipment. In addition, large amounts of limestone reagent are consumed and the calcium containing sludge formed in the sulfur removal reactions requires extensive landfill area for disposal.

Double alkali processes have been developed to address the operational concerns of limestone scrubbing systems. In these processes the flue gas is scrubbed with a soluble sodium based salt solution. Lime or limestone is then used to convert the spent sodium bisulfite solution to calcium sulfite and sulfate for disposal while regenerating the sodium scrubbing solution for recycle to the flue gas scrubber. The use of these sodium based systems has greatly improved scrubber reliability; however, large amounts of lime or limestone reagent are consumed, sodium reagent losses are higher than anticipated, and substantial amounts of calcium containing sludge are generated that require landfill disposal.

The Wellman-Lord process combines the operational advantages of sodium based flue gas scrubbing processes with a thermal decomposition step to regenerate the spent sodium bisulfite solution for recycle to the flue gas scrubber while producing a salable sulfur byproduct. The sodium sulfate formed in the system, however, cannot be easily regenerated and results in a net waste stream even in the best operated units. The formation of sulfate also restricts the use of the Wellman-Lord process to those boilers using high sulfur coal where oxidation in the scrubber is less extensive. Perhaps the greatest disadvantages of the Wellman-Lord process are its high capital and operating costs relative to other flue gas treating systems.

The SOXAL process is an extremely promising flue gas treating system that effectively avoids the operating and economic disadvantages of the competitive flue gas treating systems. It uses highly effective sodium sulfite scrubbing solution to remove greater than 90% of the sulfur dioxide contaminant in the flue gas with a minimum of operating problems. The scrubbing solution is regenerated for recycle in a relatively simple electrochemical process using a patented bipolar membrane system. The first stage membrane stack regenerates the sodium bisulfite solution, while the second stage membrane stack regenerates the sodium sulfate as caustic and dilute sulfuric acid. The first stage regeneration step recovers a concentrated stream of sulfur dioxide suitable for subsequent processing to salable sulfur or sulfuric acid.

Coupled with conventional urea/methanol injection techniques for combustion zone NO_x control, the sodium scrubber can further reduce NO_x emissions up to 90%. The urea injection step reduces NO to N₂ gas and NO₂ gases. Methanol injection will act to oxidize remaining NO or NH₃ slip gases to NO₂. These NO₂ gases will either be reduced to N₂ gas in the sodium sulfite scrubber or be scrubbed forming sodium nitrate in the scrubber solution. The nitrates will ultimately be purged from the system along with the sodium sulfate stripper bottoms or the dilute sulfuric acid stream from the second stage membrane stack. The optional second stage membrane stack is not part of this demonstration.

The SOXAL process is nearly closed-loop; minimal net wastes are generated. The operation is simple and reliable with relatively low operating and capital costs. The process is compact and can be readily retrofit to any sodium scrubber system.

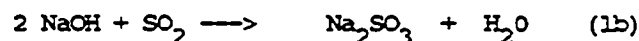
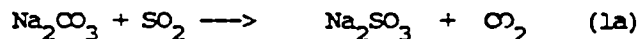
It is applicable to both large utility and smaller industrial boilers using either high or low sulfur coal and offers combined SO_x/NO_x control in a single system.

PROCESS DESCRIPTION

The SOXAL Process (Figure 1) combines sodium based flue gas scrubbing techniques with regeneration of the spent scrubbing solution using AQUATECH Systems bipolar membrane technology. The regenerated solution is recycled to the flue gas scrubber. The concentrated sulfur dioxide stream recovered from the spent scrubbing solution is converted to salable sulfur via Allied-Signal's Catalytic Sulfur Reduction Technology or sulfuric acid using conventional commercial processes.

The flue gas scrubber uses a soluble sodium sulfite to remove greater than 90% of the sulfur dioxide in a staged spray absorber tower. Sodium carbonate or sodium hydroxide replace the small amount of sodium lost in the process. The high solubility of the sodium sulfite allows for the efficient absorption of sulfur dioxide at relatively low liquid to gas ratios without excessive scale formation problems.

The makeup sodium carbonate and recycled scrubbing solution are added directly to the flue gas scrubber where they react with dissolved sulfur dioxide to form sodium sulfite as shown below:



The sodium sulfite formed in these reactions, and in the regeneration of spent sodium bisulfite scrubbing liquor, then reacts with additional dissolved sulfur dioxide to form sodium bisulfite:

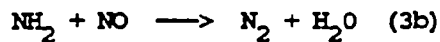
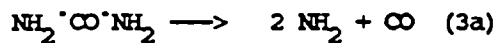


Some of the sodium sulfite is oxidized in the flue gas scrubber to form sodium sulfate. This sulfate species does not react with sulfur dioxide. It is converted in the regeneration system to sodium hydroxide, for recycle to the scrubbing tower, and dilute sulfuric acid, for sale, plant usage or disposal.

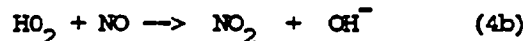
This recovery of sodium sulfate via the second stage membrane stack minimizes the loss of sodium values in the process.

NOx

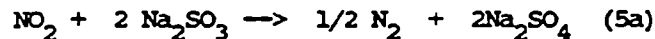
Removal of NOx contaminants by urea/methanol injection into the flue gas is accomplished in a two stage process. First, urea addition reduces approximately 50-70% of the NO contaminants in the flue gas to N₂. This reaction occurs at 1600-1900°F according to the reactions shown in 3a and 3b.



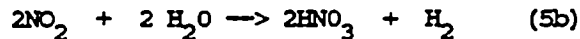
The remaining NO contaminant in the flue gas is oxidized to NO₂ by reaction with methanol. Addition of methanol also reduces ammonia slip, thereby avoiding deposition of salts in downstream ducting and plume visibility problems. This reaction proceeds at 1000-1500 °F as shown in 4a and 4b.



NOx which has been previously converted to NO₂ via commercially available urea/methanol injection in the boiler/economizer sections respectively, will be reduced by the sodium sulfite according to the reaction as shown in 5a:



or scrubbed in the absorber forming sodium nitrate salts as follows:



Note that Na_2SO_3 is oxidized to Na_2SO_4 in reaction (5a). The Na_2SO_4 generated in this fashion is eventually recovered as a solid crystalline product, or processed in the optional secondary AQUATECH Unit.

For this demonstration, the boiler will not be retrofit with the NOx injection facilities. Instead, the NO_2 level will be simulated by injection of NO_2 gas directly into the flue gas slip stream ducting upstream of the absorber. The levels of NO_2 injection will be equivalent to the levels measured commercially at utilities which have been retrofit with the NOx reduction technology as well as a predicted level for the Niagara Mohawk Dunkirk Steam Station No. 4 Boiler.

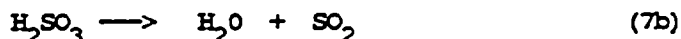
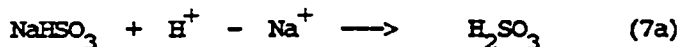
Regeneration of the spent scrubbing liquor is achieved electrolytically using the AQUATECH System's bipolar membrane system. The bipolar membrane separates water molecules into hydroxide and hydroxyl ions. The sodium bisulfite solution is directly regenerated in a two-compartment AQUATECH stack (Figure 2) to form the original sodium sulfite scrubbing solution and gaseous sulfur dioxide.

During regeneration the sodium bisulfite molecules dissociate and the sodium cations migrate across the cation selective membrane towards the cathode. It then combines with hydroxide anions produced in the bipolar membrane to form sodium hydroxide. Most of this sodium hydroxide reacts with the sodium bisulfite to form sodium sulfite. This solution could then be routed to an optional three-compartment AQUATECH stack to pick-up additional sodium values from the sodium sulfate stream after sulfur dioxide recovery:



The bisulfite ion that is not transferred across the cation selective membrane combines with the hydrogen ions from the bipolar membrane to form sulfurous acid. Nearly saturated sulfurous acid solution is continuously recycled around the two-compartment cell stack and adiabatically flashed at

reduced pressure to recover sulfur dioxide gas and water. This concentrated sulfur dioxide stream is a suitable feedstock for producing either sulfur or sulfuric acid using commercially available technologies.



The three-compartment cell stack (Figure 3) can be employed to recover sodium values from sodium chloride, sodium sulfate, formed by sulfite oxidation in the flue gas scrubbing tower and sodium nitrate formed by the removal of NO_2 gases. These sodium values are ultimately collected in the sodium sulfite stripper bottoms stream. This stream can optionally be treated in the second stage membrane stack to form caustic and a dilute mixed acid. The dilute sulfuric acid, nitric acid and hydrochloric acid stream produced in the three-compartment stack can be neutralized by reaction with limestone to form gypsum for disposal or used in-house for ion-exchange regeneration or cleaning of process units.

PREVIOUS DEVELOPMENT WORK

The proposed 2-3 MW Proof-of-Concept program is considered the next logical step in the development of the SOXAL process. Although all components of the SOXAL process have not been demonstrated in an integrated operation, each has been demonstrated in commercial operation or in pilot scale tests.

The two-compartment AQUATECH cell stack technology has been demonstrated using pilot size cell stacks over a one year test period. This 0.5 MW equivalent test program proved the ease of operation, system reliability and membrane durability. Test results showed that the efficiency of the system remained stable with the bisulfite conversion at or near 100% throughout the test.

The three-compartment cell stack technology has been demonstrated in both laboratory and commercial operations for sulfate and fluoride salt conversions. The first AQUATECH three-compartment application has been demonstrated with a mixed potassium fluoride/potassium nitrate salt in a commercial stainless steel pickle liquor regeneration unit at Washington Steel, Washington, Pennsylvania.

Allied-Signal has developed the bipolar membrane over approximately the past fifteen years. The membrane used in any proof-of-concept program will be produced on an existing commercial production line. Continuous membrane refinements are anticipated to provide even more efficient membrane.

PROCESS ECONOMICS

The cost effectiveness of the SOXAL process had been estimated by Stearns-Catalytic under an Electric Power Research Institute (EPRI) contract (SD-3342 Vol.5) in 1986. This initial study found the SOXAL process to be the lowest cost regenerative process. It also found the process to be competitive with the lowest cost throwaway processes.

More recently this study was reevaluated by United Engineering and Constructors. These economics are based on a nominal 300 MW unit burning 2.6 wt% sulfur coal at 65% operating capacity. Operating costs include capital, fixed and variable costs. These economics were not available at the time of this writing, however based on economics generated by Allied-Signal Inc. in connection with the DOE-PEIC program it is believed that the SOXAL process continues to remain competitive.

DEMONSTRATION PROGRAM

The SOXAL Demonstration Program began September 10, 1991 and is anticipated to take approximately 22 months to complete as shown by the schedule (Figure 4).

During the 6 months of scheduled operations period, data will be collected from the SOXAL system to define:

- 1) SO₂ and NO_x removal efficiencies
- 2) Current efficiency for the regeneration unit.
- 3) Sulfate oxidation in the absorber.
- 4) Make-up reagent rates.
- 5) Product quality including concentrations and compositions.
- 6) System integration and control philosophy.
- 7) Membrane stability and performance with respect to foulants.

A conceptual design for a commercial unit as well as estimated costs will be prepared as part of the final report. The program is expected to conclude by July 1993.

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Figure 1
SOXAL[™] Process
General Flow Configuration

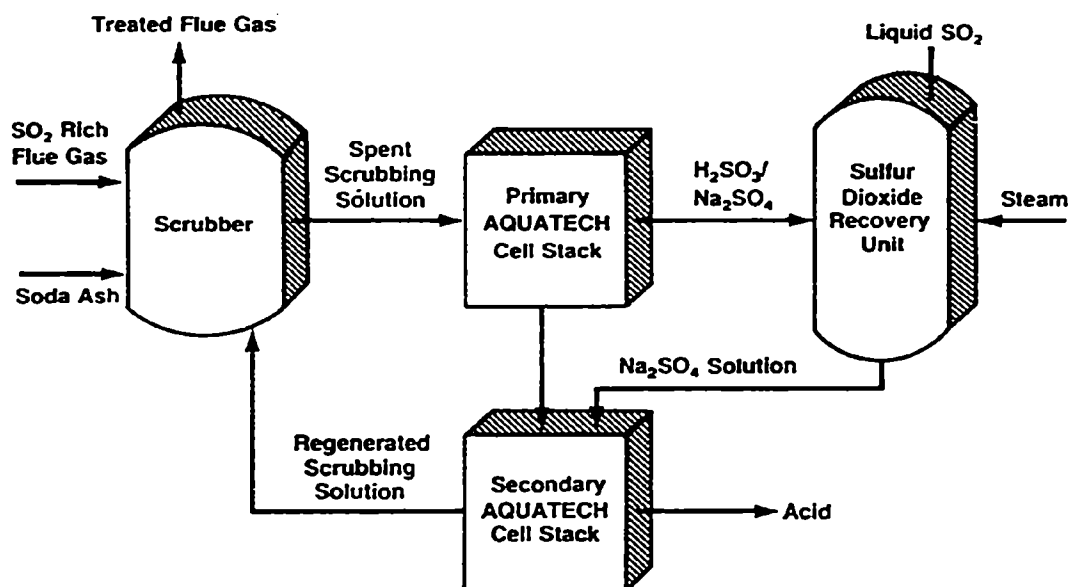


Figure 2
Primary Membrane Stack

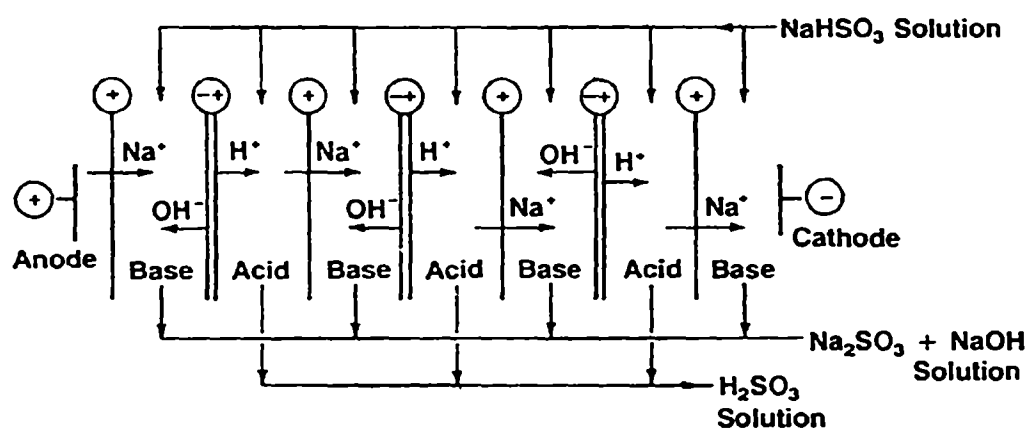


Figure 3
Secondary Membrane Stack

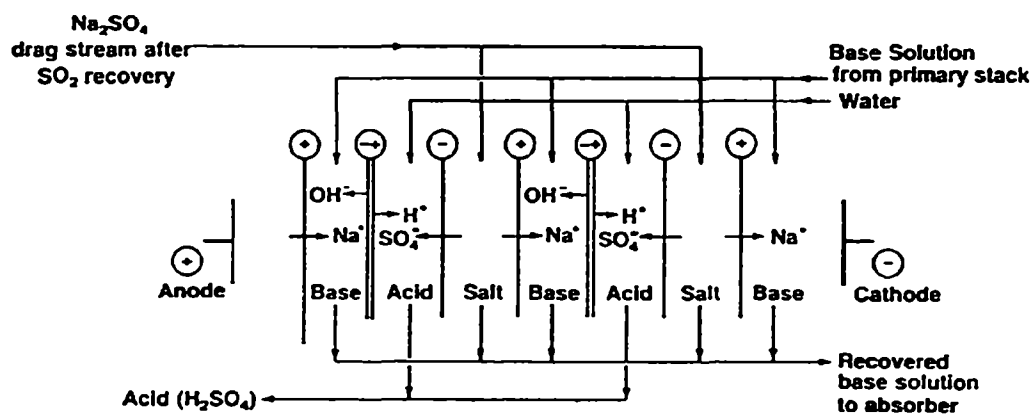
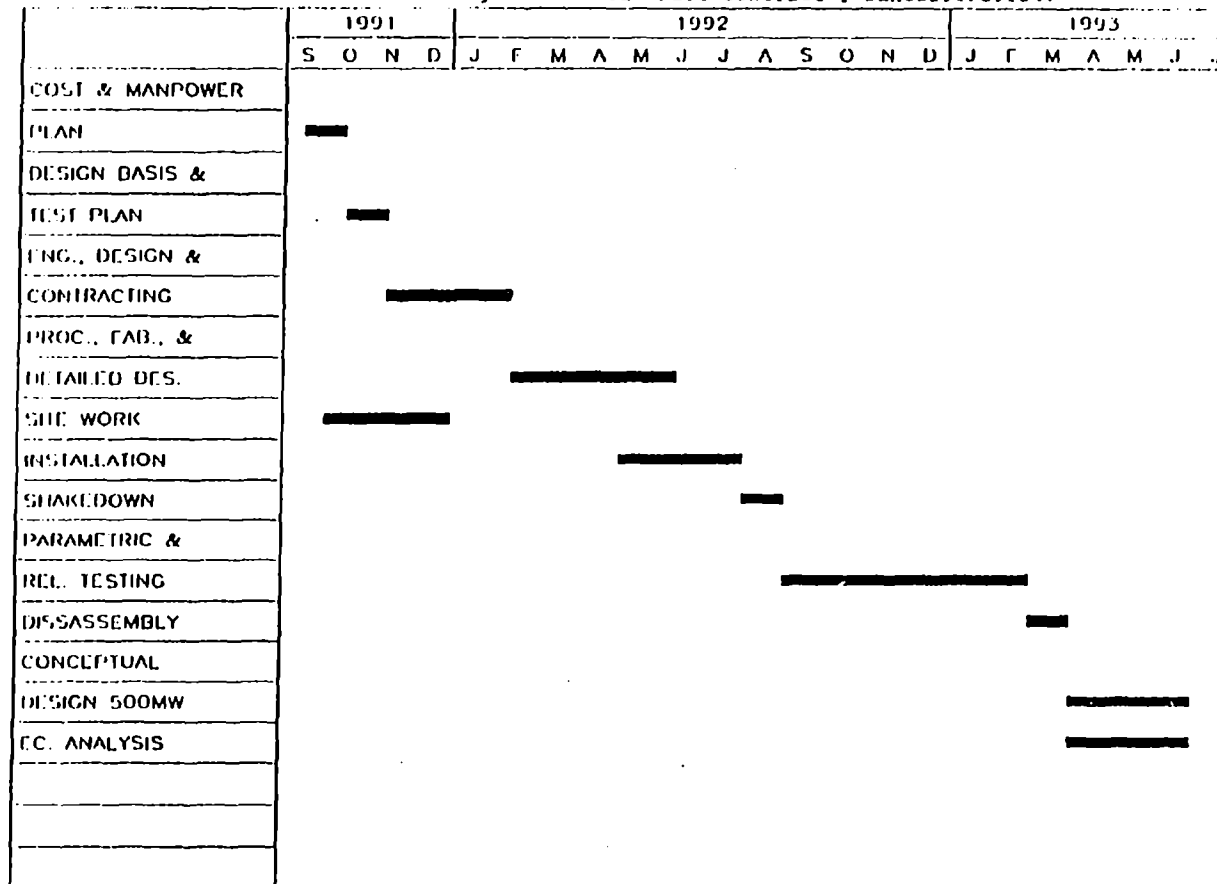


Figure 4

SOXAL Demonstration Program DOE PETC Contract # DEAC2291PC91347



THE HEALY CLEAN COAL PROJECT
AIR QUALITY CONTROL SYSTEM

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ABSTRACT

The Healy Clean Coal Project is a 50 MW nominal new coal fired power plant demonstrating two 350 MMBtu/hr TRW coal combustion systems designed to burn high ash coals while yielding low NO_x emissions. Limestone is introduced into the combustor discharge to create flash calcined material (FCM). The FCM is collected in a fabric filter located downstream of a spray dryer. From the fabric filter, the collected material is slurried and fed into the spray dryer through the atomizer as the active alkali for capture of sulfur dioxide. The integration of the combustion system and the spray dryer/fabric filter with reactivated FCM is expected to result in low NO_x and SO_x emissions. This paper presents the design of the unique air quality control system and the status of the project.

INTRODUCTION

The Healy Clean Coal Project (HCCP) is jointly sponsored by the Alaska Industrial Development and Export Authority (AIDEA) and the U.S. Department of Energy (DOE). The HCCP was selected by DOE in Round III of its Clean Coal Technology Program.

The primary objective of the HCCP is to conduct a cost-shared project that will demonstrate a new power plant design which features innovative integration of an advanced combustor and heat recovery system coupled with both high and low temperature emission control processes. The parties anticipate that, if the demonstration project is successful, the technology could become commercialized during the 1990's and will be capable of (1) achieving significant reductions in the emissions of sulfur dioxide and the oxides of nitrogen from existing facilities to minimize environmental impacts such as transboundary and interstate pollution and/or (2) providing for future energy needs in an environmentally acceptable manner.

The demonstration project is proposed to be built adjacent to the Golden Valley Electric Association (GVEA) existing Healy Unit No. 1 pulverized coal power plant. The site is located near Healy, Alaska. Alaskan bituminous and subbituminous coals will be tested. GVEA will operate and maintain the new power plant facility.

Coal from the adjacent Usibelli Coal Mine (UCM) will be pulverized and burned at the proposed facility to generate high-pressure steam that will be used by the steam turbine generator to produce electricity. Emissions of SO₂ and NO_x from the plant will be controlled using TRW's combustion systems with limestone injection, in conjunction with a boiler supplied by Foster Wheeler. Further SO₂ and particulate removal will be accomplished using Joy Environmental Equipment Company's (Joy) Activated Recycle Spray Absorber System.

The total project activities include design, permitting, procurement, fabrication, construction, start-up, testing, and reporting of results. Construction of the demonstration facility is expected to start in the spring of 1993 and continue for 2.5 years. Following completion of the demonstration test program, the plant is expected to continue to operate and be maintained as a commercial utility electric generation station.

The proposed HCCP is to be a nominal 50 MWe facility consisting of two pulverized coal-fired combustion systems, a boiler, a spray dryer absorber with activation and recycle equipment, a fabric filter, a turbine generator, coal and limestone pulverizing and handling equipment, and associated auxiliary equipment.

The specific objectives of the HCCP demonstration are to: (1) demonstrate the use of Alaskan, low-sulfur bituminous and subbituminous coals of medium to high ash and moisture content; (2) demonstrate the feasibility of large utility boiler repowering capability of the TRW Combustion System; (3) demonstrate large utility boiler retrofit capability of the TRW Combustion System on oil designed boilers with no derating and on pulverized coal and cyclone furnace design boilers with improved performance, and lower NO_x, SO₂, and particulate emissions; (4) demonstrate the enhanced capability of the TRW Combustion System for simultaneous NO_x and SO₂ removal when combined with back-end SO₂

absorption techniques and furnace air staging to maintain emissions at the nominal values of 0.2 lbs of NO_x and 0.01 lbs of particulate matter per MMBtu, and greater than 90% removal of SO₂; (5) demonstrate the energy efficiency of the integrated technology as compared to pulverized coal (PC) and fluidized bed combustor processes; and (6) determine the cost effectiveness of the technology especially in terms of reduced operating costs due to the system's capability to burn low grade/waste coals.

The air pollution control system that will be demonstrated by the project (Figure 1) incorporates the following major components:

- TRW Coal Combustion System
- Foster Wheeler boiler
- Joy Spray Dryer Absorber Fabric Filter System

The integrated air pollution control process that results from the HCCP configuration of these components has been designed to minimize emissions of SO₂, NO_x, and particulates from the facility while firing a broad range of coals.

NO_x emissions are reduced in the coal combustion process by use of the fuel and air-staged combustor system and a boiler that controls fuel and thermal-related conditions which inhibit nitrogen oxide formation. The slagging combustor/boiler system also functions as a limestone calciner and first stage SO₂ removal device in addition to its heat recovery function. Secondary and tertiary SO₂ capture are accomplished by a single spray dryer absorber vessel and a fabric filter respectively. Ash collection in the process is first achieved by the removal of molten slag in the coal combustors followed by flyash particulate removal in the fabric filter system downstream of the spray dry absorber vessel.

This paper describes the unique integrated air pollution control process of the HCCP application. Subsequent sections discuss additional details of the NO_x, SO₂ and particulate control systems. A final section of the paper addresses the current status of the project.

AIR QUALITY CONTROL SYSTEM

The TRW Combustion System will be designed to be installed on the boiler furnace to provide efficient combustion, maintain effective limestone calcination and minimize the formation of NO_x emissions. As shown in Figure 2, the main system components include a precombustor, main combustor, slag recovery section, tertiary air windbox, pulverized coal and limestone feed system, and combustion air system. Figure 3 shows a schematic of the general boiler arrangement and the combustion system installation for the HCCP. In this unique arrangement, the slagging combustors are bottom mounted on the boiler hopper to yield optimum operation and cost benefits.

The coal fired precombustor is used to increase the air inlet temperature to the main combustor for optimum slagging performance. It burns approximately 25-40 percent of the total coal input to the combustor. Combustion is staged to minimize NO_x formation.

The main slagging combustor consists of a water-cooled cylinder which is sloped toward a slag opening. The remaining coal is injected axially into the combustor, rapidly entrained by the swirling precombustor gases and additional air flow, and burned under substoichiometric (fuel-rich) conditions for NO_x control. The ash contained in the burning coal forms drops of molten slag and accumulates on the water-cooled walls as a result of the centrifugal force resulting from the swirling gas flow. The molten slag is driven by aerodynamic and gravity forces through a slot into the bottom of the slag recovery section where it falls into a water-filled tank and is removed by the slag removal system. Approximately 80 percent of the ash in the coal is removed as molten slag.

The hot gas, containing carbon monoxide and hydrogen, is then ducted to the furnace from the slag recovery section through the hot gas exhaust duct. To ensure complete combustion in the furnace, additional air is supplied from the tertiary air windbox to NO_x control ports and to final overfire air ports located in the furnace.

Pulverized limestone, for SO₂ control, is fed into the combustor as shown in Figure 2. While passing into the boiler most of the limestone is decomposed to flash calcined lime by the following reaction:



The mixture of this lime and the ash not removed by the combustors is called Flash Calcined Material (FCM). Some sulfur capture by the entrained CaO also occurs at this time, but the primary SO₂ removal mechanism is through a multiple step process of spray drying the slurried and activated FCM solids (Figure 4).

Once FCM is produced in the furnace via equation (1), it is removed in the fabric filter system. A portion of the material is transported to disposal. Most of the material however, is conveyed to a mixing tank, where it is mixed with water to form a 45% FCM solids slurry. The lime rich FCM material is slaked by agitation of the suspension. A portion of the slurry from the mixing tank passes directly through a screen to the feed tank, where the slurry is continuously agitated. The remainder of the slurry leaving the mixing tank is pumped to a grinding mill, where the suspension is further mechanically activated by abrasive grinding.

By grinding the slurry in a mill, the FCM is activated by a mechanical process whereby the overall surface area of available lime is increased, and coarse lime particle formation is avoided. Thus, the mill enhances the slaking conditions of the FCM, and increases the surface area for optimal SO₂ absorption. FCM slurry leaving the tower mill is transported through the screen to the feed tank.

Feed slurry is pumped from the feed tank to the SDA, where it is atomized via rotary atomization using JOY/Niro dry scrubbing technology. Sulfur dioxide in the flue gas reacts with the FCM slurry as water is simultaneously evaporated. The dry reaction product is removed via the SDA hopper or baghouse catch. Sulfur dioxide is further removed from the flue gas by reacting with the dry FCM on the baghouse filter bags.

The HCCP is an integrated system for the combustion of coal and control of all emissions. The slagging combustor, furnace, and enhanced recycle SDA system all play a part in reducing emissions from the plant. The slagging combustor inhibits NO_x production, generates the FCM for capture of sulfur dioxide, and reduces the potential amount of fly ash by up to eighty percent. The furnace further contributes to the NO_x reduction process and begins the sulfur dioxide removal process. The recycle/reactivation SDA system, which includes the pulse-jet baghouse, completes the collection of particulate and sulfur dioxide.

Removal of any single component in the integrated system results in ramifications on other components. For example, removal of the slagging combustor and replacement with low NO_x burners increases the ash loading out of the furnace by nearly four hundred percent, eliminates the production of FCM which requires the conversion of the recycle/reactivation SDA system to a conventional lime spray dryer system, and possibly increases NO_x emissions. Replacement of the spray dryer with a wet scrubber eliminates the need to generate FCM since all of the particulate would be collected upstream of the wet scrubber in a fabric filter or electrostatic precipitator where there is no way of separating fly ash from FCM.

NO_x Control

Emissions of NO_x are expected to be demonstrated to levels significantly below EPA New Source Performance Standards (NSPS) in the boiler by using slagging combustor technology and known combustion techniques.

The HCCP combustors achieve NO_x control as a combination of the following (two) factors:

1. The combustor functions as a well-stirred reactor under substoichiometric conditions for solid fuel combustion; converting the solid fuel components to a hot, partially oxidized fuel gas in an environment conducive to destroying the complex organic fuel bound nitrogen compounds which could easily be oxidized to NO_x in the presence of excess oxygen.
2. The combustor water cooled enclosure additionally absorbs approximately 10 to 25 percent of the total available heat input to the combustor.

These two conditions together reduce the potential for encountering combustion temperatures in the furnace sufficient for decomposition of molecular nitrogen compounds in the combustion air into forms which can produce thermal NO_x emissions as excess oxygen is made available.

When the exhaust gases leave the combustor, the coal has already been mixed with approximately 80 to 90 percent of the air theoretically necessary to complete combustion. A portion of the remaining 10 to 20 percent is then allowed to mix slowly with the hot fuel gases exiting the combustor and entering the furnace. The hot gases radiate their heat to the furnace walls at rates faster than combustion is allowed to occur so that gas temperatures slowly decay from those at the furnace entrance. After the furnace gases have cooled sufficiently, a second and possibly third stage of furnace combustion air injection is performed as necessary to complete the coal combustion process in an

oxidizing, controlled manner so that combustion gas temperatures are maintained below the thermal NO_x floor where significant NO_x formation begins. This is in contrast with a traditional coal-fired furnace where the pulverized coal is burned in suspension at high excess air rates. Resulting gas temperatures from PC furnaces typically rise significantly above the 2800°F temperature maintained in the slagging combustor and downstream furnace. In the traditional furnace, the pulverized coal is relatively poorly mixed with conventional low NO_x wall burner/suspension firing techniques, and local areas of combustion in the presence of stoichiometric oxygen create hot zones within the flame. These hot, turbulent stoichiometric zones can produce significant NO_x levels in the area of burner throats. This tendency for high, localized NO_x formation is minimized with the slagging combustor through slow, controlled mixing of furnace combustion air with the partially cooled, well-mixed fuel gases discharging from the combustor into the lower furnace NO_x control zone.

The general relationship between low NO_x emissions and combustor stoichiometry resulting from tests at TRW's 50 MMBtu/hr Cleveland demonstration facility are shown in Figure 5. This facility operates with low excess air and no overfire air or NO_x ports in the furnace.

The curve shows that NO_x emissions (while firing bituminous coal) are minimized for the Cleveland combustion process at approximately 30 percent of the current NSPS when the slagging combustor system is operated at a stoichiometry of 0.70 and when all of the final combustion air is added at the combustor exit nozzle at the entrance to the boiler furnace. The HCCP will demonstrate additional NO_x reduction techniques including furnace NO_x ports and furnace over-fire air injection.

NO_x results obtained while firing the HCCP performance coal (Table 1) in the Cleveland slagging combustor system differ from results obtained with other, less volatile fuels. Figure 6 presents NO_x emissions from the facility as a function of main combustor stoichiometry. As can be observed from the figure, very low NO_x emissions are achievable by operating the combustor near or slightly below stoichiometry while firing the HCCP performance coal. These results indicate that NO_x emissions are only mildly dependent on combustor stoichiometry thus providing operating flexibility.

SO₂ Control

Emission levels of SO₂ are controlled to and below NSPS levels using the recycle/reactivation SDA system of Joy Environmental Equipment Company.

The coals, fired in the HCCP combustion system (shown in Table 1), are low sulfur, high moisture, low heating value fuels from a nearby mine. While the project will demonstrate higher SO₂ removal efficiencies, the sulfur content is so low, only a 70% sulfur dioxide removal efficiency is required to satisfy NSPS requirements. Coal 1 is a run-of-mine coal, where care was taken in the mining operation to minimize the amount of overburden and lenses included with the coal. Coal 2 is the performance coal and consists of 50% run-of-mine and 50% waste coal. The waste coal being a lower heating value fuel with significantly more ash. An advantage of the slagging combustor is that it can burn low quality

coals and still meet emissions and performance requirements.

The ash analysis shown in Table 1 indicates that the ash contains a relatively high amount of calcium oxide. As previously discussed, only 20% of the coal ash leaves the boiler as fly ash. This means that only about 20% of the calcium oxide shown in the ash analysis is carried over to the spray dryer.

Tests were performed at the TRW facility in Cleveland and Joy-Niro's facilities in Copenhagen to confirm design conditions for the HCCP. The primary purpose of the tests in Cleveland was to generate FCM that could be used in the Niro test facility. Coal and limestone that are to be used by the HCCP were used for the tests. Preliminary results from the Niro tests show that 70 percent sulfur dioxide removal is attainable at a Ca/S ratio of 1.7, with 90% removal attainable at slightly higher stoichiometries. These tests were accomplished by heating the FCM slurry. Testing is to be performed in the near future to determine the effect of mechanical activation (grinding) of the FCM.

An extensive test program has been proposed to prove various aspects of the sulfur dioxide removal process. It is anticipated that the test program will continue for 2.5 years following startup. The test program will evaluate primary SO₂ removal (removal in the furnace), secondary SO₂ removal (removal in the SDA), and tertiary SO₂ removal (removal in the fabric filter) at various loads. Additional tests will evaluate the following:

- adiabatic humidification of the flue gas in the SDA, with and without limestone injection in the combustor;
- adiabatic humidification of the flue gas in the SDA, combined with dry injection of FCM or flyash downstream of the air heater outlet;
- and dry injection of recycled FCM between the SDA outlet and the fabric filter inlet, with and without adiabatic humidification in the spray dryer.

The test program will attempt to confirm that pilot plant FCM spray drying tests which have been performed at Niro Atomizer's test facility in Copenhagen can be economically scaled up to a commercial sized facility.

Particulate Control

Particulate emissions control on the HCCP is obtained via the slagging combustors and by a pulse-jet baghouse. Each of ten fabric filter compartments will contain 225 six inch diameter fiberglass bags. The effective length of each bag is 20'-0" and the gross air-to-cloth ratio is 2.8:1. The HCCP will demonstrate the effectiveness of a pulse jet baghouse in removing the FCM particulate emissions.

It should be noted that a significant portion of the coal ash never leaves the furnace with the flue gases, since it is estimated that approximately eighty percent of the ash in the coal will leave the slagging combustors as slag.

PROJECT STATUS

The HCCP is currently in the permitting and design phase. A one year meteorological and air quality data collection program has been conducted. Field studies in support of the Environmental Impact Statement and other necessary permits have also been completed. Permit applications to Federal and State agencies are in various stages of development.

In addition to the coal and FCM tests reported, significant engineering studies were prepared including the heat rejection system, final site selection, coal quality, and combustor arrangement. Preliminary station arrangements, piping & instrument diagrams, site plans and other design documents were issued. Procurement of equipment and systems is continuing.

A definitive project cost estimate will be prepared in the first quarter of 1992 for AIDEA and the DOE which will provide the basis for decisions regarding completion of the project.

CONCLUSION

The HCCP features a unique coal combustion and air pollution control process that has the potential to significantly:

- reduce emissions associated with coal fired steam generation systems;
- increase efficiency of the coal combustion process;
- and reduce operational costs and impacts.

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2. Healy Coal Firing at TRW Cleveland Test Facility, Final Report to Alaska Industrial Development and Export Authority, August, 1991.

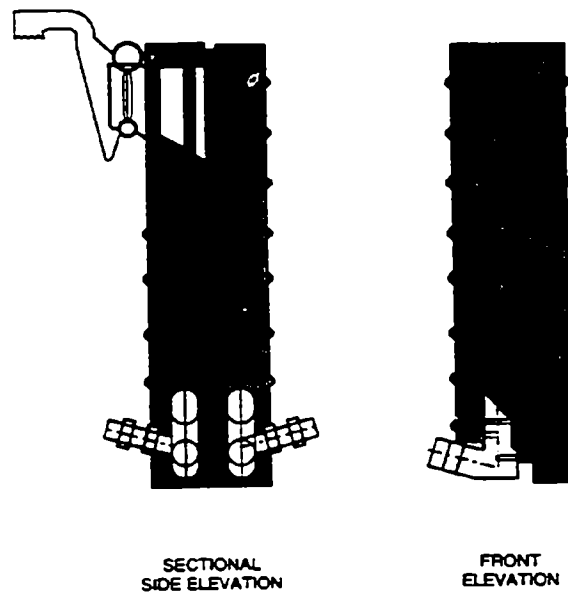


Figure 3. HCCP Combustor Installation.

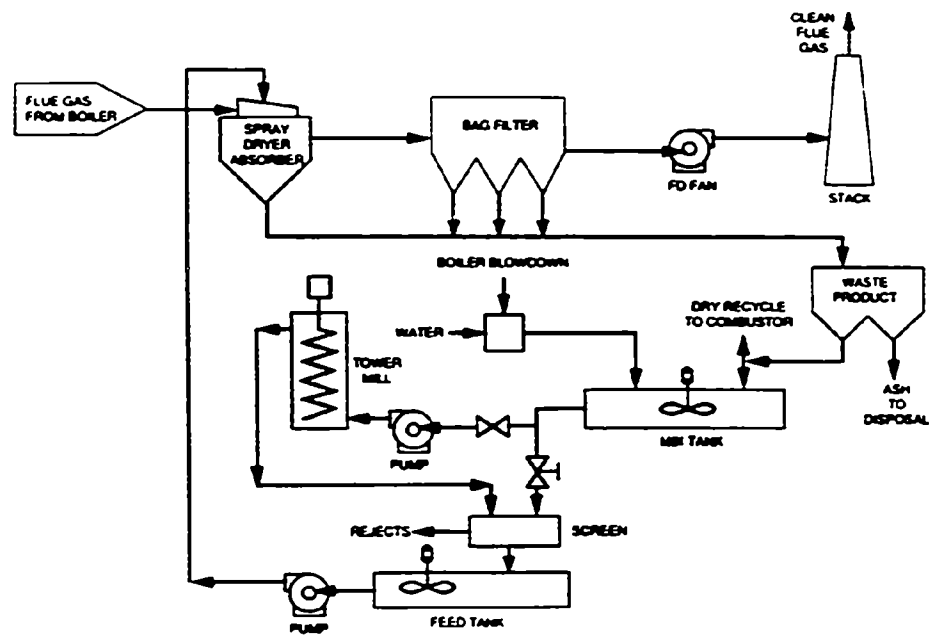


Figure 4. Joy Recycle/Reactivation SDA System.

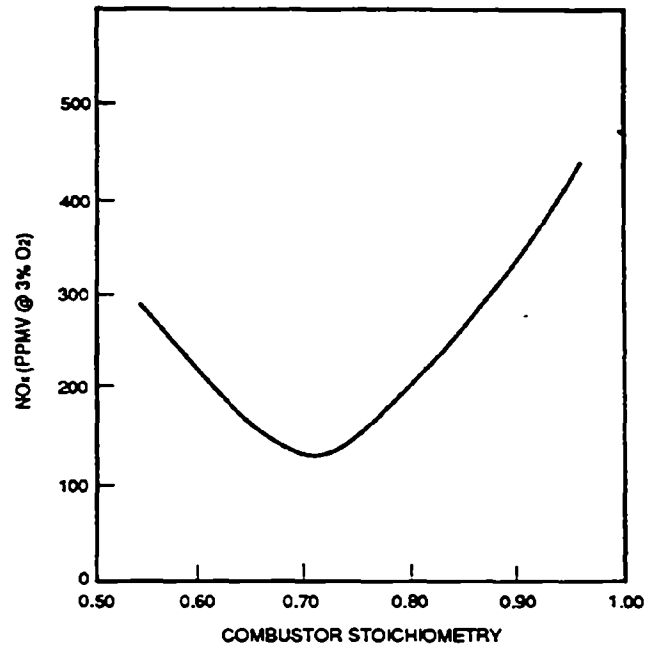


Figure 5. NOx Emissions for Bituminous Coal Versus Combustor Stoichiometry.

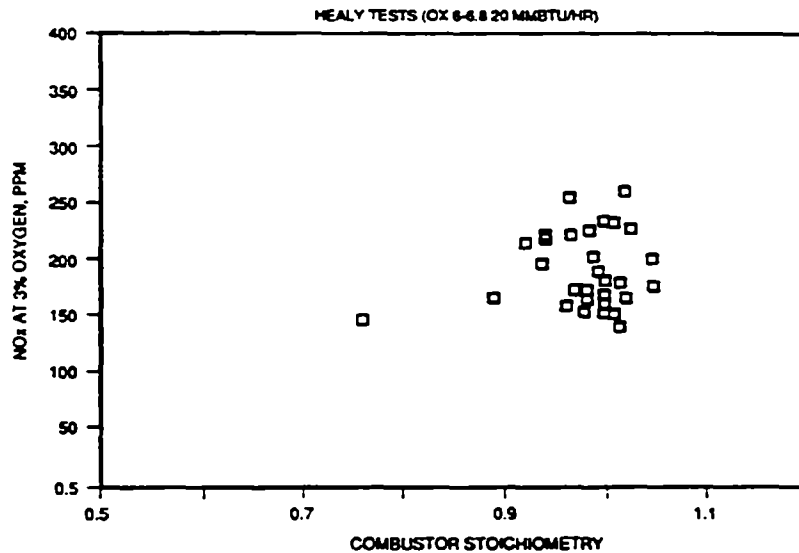


Figure 6. NOx Emissions for HCCP Coal Versus Combustor Stoichiometry.

TABLE 1
COAL AND ASH ANALYSIS

	<u>Coal 1</u>	<u>Coal 2</u>
Proximate Analysis		
Moisture, %	26.35	25.11
Ash, %	8.20	16.60
Volatile, %	34.56	30.78
Fixed Carbon, %	<u>30.89</u>	<u>27.51</u>
Total, %	100.00	100.00
HHV, Btu/lb	7,815	6,960
Ultimate Analysis		
Moisture, %	26.35	25.11
Ash, %	8.20	16.60
Carbon, %	45.55	40.57
Hydrogen, %	3.45	3.07
Nitrogen, %	0.59	0.53
Sulfur, %	0.17	0.15
Oxygen, %	15.66	13.94
Chlorine, %	<u>0.03</u>	<u>0.03</u>
Total	100.00	100.00
Elemental Ash Analysis		
Silicon Dioxide, %	38.61	65.69
Aluminum Oxide, %	16.97	11.09
Titanium Dioxide, %	0.81	0.52
Ferric Oxide, %	7.12	4.90
Calcium Oxide, %	23.75	10.62
Magnesium Oxide, %	3.54	1.87
Potassium Oxide, %	1.02	1.16
Sodium Oxide, %	0.66	0.65
Sulfur Trioxide, %	5.07	2.28
Phosphorus Pentoxide, %	0.48	0.30
Strontium Oxide, %	0.23	0.11
Barium Oxide, %	0.44	0.22
Manganese Oxide, %	0.06	0.04
Undetermined, %	<u>1.24</u>	<u>0.55</u>
Total, %	100.00	100.00

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LIME / LIME STONE SCRUBBING PRODUCING USABLE BY-PRODUCTS

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ABSTRACT

This paper is in two (2) parts. The first part deals with plants manufacturing gypsum, from the sulphur captured in desulphurization plants. It is intended to describe, by using some of these plants as examples, developments made in the past few years and the results that have become available. It outlines the steps in the development of plants, which were followed in retrofitting the FGD plants to the Generating Stations, and our experiences gained.

Between 1983 and 1988, in the Federal Republic of Germany, Generating Station capacity of more than 30,000 MWe were retrofitted with flue gas desulphurization plants. The overall objective was to produce industrial-usable products, from the sulphur captured in these desulphurization processes. The requirements of these desulphurization plants were, in some cases, in excess of what could be achieved by the, then, state-of-the-art technologies. The conditions required over 90% of the desulphurization capacity to be met, using lime/lime stone scrubbing technology. Thyssen, as one of the leaders of lime/lime stone scrubbing, delivered plants for some 8500 MWe of capacity; and desulphurization efficiencies up to, and above, 97% were attained. Also, over a twelve year operating period, boiler availability was 98% to 99%.

The second part of the paper discusses a newly developed process, called the "Bertin Process", a method of producing elemental sulphur from either wet or dry SO_2 lime scrubbing technologies. This process involves two stages. In the first stage, biotransformation of the sulfites or sulfates to H_2S occurs, with recycling of the calcium carbonate to the desulphurization plant. The second stage involves the recovery of elemental sulphur from H_2S , by means of updated REDOX conversion. This paper identifies major components of the system, together with results obtained on a pilot plant in France.

1. INTRODUCTION

Worldwide, various processes have been developed for cleaning the flue gases emitted from fossil fuel power plants. For SO_2 removal, wet processes, generally using limestone as a reagent and producing commercial quality gypsum as a by-product have found general acceptance from a technical and also from an economic stand point. In West Germany during the 80's, wet process flue gas desulfurization systems were installed on approximately 37,000 MWe. The fact that West Germany was behind the USA and Japan in installing this equipment benefitted the installations by virtue of the fact that the designers of these plants gained insight and technical knowledge on the plants installed in the 70's, particularly those in the USA. The experience of these early plants together with the very strong Federal and State Legislation requirements imposed by West German Authorities lead to the emergency of a whole new advanced generation of FGD Designs.

The Thyssen SO_2 flue gas desulfurization (FGD) systems, built recently, in Germany and the USA involve 8500 MWe. To obtain the reliability, efficiency and the gypsum quality required two (2) distinct generations of design. Developments of these designs over more than ten (10) years have formed a basis for a third generation design, which has been installed in West Germany. The enhanced third generation design has been supplied on 1,000 MWe of plants in West Germany. (See Figure 1).

The process is characterized by a combined spray and falling film zone. The absorption sump is equipped with a forced oxidation system for elevated limestone utilization and high gypsum quality. This improved process enables the equipment to meet stricter qualification criteria compared with the requirements of the first and second generation FGD systems as follows:

- Lime Stone Reagent Utilization of 97%+
- Reliability of 99%, no spare absorbers or multiple boilers on a single absorber
- Achieves 95 to 98% SO₂ removal
- Single absorbers of 750 MWe size
- Scaling and Plugging are eliminated
- Includes oxidation and high lime stone utilization - The selection of the pH level in the process insures high level efficiency and high by-product gypsum quality at very economical design criteria.
- Reduce air requirements of forced oxidation result in high quality gypsum as required by German standards with minimum gypsum rejection.
- Low parasitic power of approximately 1.5% of the generator output
- A single central power plant control system providing tight process control and operating stability.

2. IMPORTANT FACTORS INFLUENCING THE FGD PROCESS

The optimum performance of the FGD system is controlled by the following parameters from a chemical view point:

- a) pH of the suspension slurry
- b) The reactivity of the lime stone
- c) Crystallization of the CaSO₄ X 2H₂O gypsum - supersaturation
- d) The composition and solids contents of the suspension
- e) The suspension volume, volumetric size of the reaction vessels, L/G ratio, droplet size/weight distribution, height of the spraying zone.

3. OPERATING EXPERIENCE OF THE THYSSEN FGD LIMESTONE SYSTEM

Wet flue gas desulfurization (FGD) processes are in operation at many power plants around the world. The Thyssen FGD system with lime stone was developed in the early 1980's; since then it has been installed on ten coal fired boilers in the USA and West Germany with a total capacity of approximately 2,500 MW. The earlier generations of design have been successfully modified over the last ten (10) years as a result of on going project improvement programs. These have enhanced the overall process operation and system reliability.

The first application of the Thyssen system was on a 360 MW boiler burning low sulfur (.5%) coal. The end product was unoxidized sludge i.e. calcium sulfite (CaSO₃). Simple dewatering equipment was installed. In comparison, the latest-generation FGD system has shown successful operation on boilers burning up to 2.5% sulfur coal, SO₂ removal efficiencies up to 97%. These criteria have been achieved with lime stone reagent simultaneously producing salable gypsum containing predominantly calcium sulfate (CaSO₄).

The capabilities of the system allows the operator to maximize the overall plant operation with regards to fuel selection and end product quality. If the operator likes to produce FGD gypsum for sale, either for use as a cement additive, soil conditioner or for wallboard manufacturing facilities, the waste disposal cost is drastically reduced. Even at installations where FGD gypsum cannot be sold due to marketing restrictions the oxidized end product (calcium sulfate) is frequently preferred by utilities because of its far better dewatering characteristic compared to the unoxidized sludge (calcium sulfite).

4. RECENT DEVELOPMENTS

Evolution of the Thyssen FGD system has resulted in the development of Very Large Absorber VLA modules (up to 62' diameter). These absorbers are capable of handling the flue gas from approximately a 750 MW boiler (flue gas flow rates up to 2,000,000 ACFM per minute. Thyssen has two (2) such VLA's in operation in West Germany since 1988. Expediency of design as a result of dealing with many retrofit applications, saw the evolution towards large towers to handle the severe space restrictions. Development of the design of the VLA's occurred after extensive field measurements in full scale plants and numerous gas flow studies. For these large absorbers, study of several major design requirements such as, gas liquid contact, nozzle orientation, slurry agitators, were required. These, together with consideration of structural requirements, were incorporated into final designs and have now been demonstrated on operating units.

The state-of-the-art technology not only covers improved materials of construction, such as, alloys and linings, but also mechanical refinements such as the use of hydroclones in combination with belt filters or centrifuges for dewatering, mechanical seals for slurry pumps and different types of reheat systems, etc.. Of course the modern plant also included state-of-art process controls and instrumentation. Many of these design features are included in the plants described in this paper. Details and operating data from the two (2) installations at Rheinisch Westfaelische Elektrizitaets Werke Frimmersdorf Units P & Q are presented later.

5. PROCESS DESCRIPTION

A) Absorber Loop

The untreated flue gas is contacted with recirculating limestone slurry at a pH of 5 to 5.4 in the absorber. A number of spray levels and a Falling Film Contactor (FFC) are used to provide the necessary mass transfer capacity for absorption of the SO₂. The slurry in the absorber loop flows down to the Absorber Recirculation Tank (ART). Fresh limestone slurry is added to the ART based on process demand measured by the incoming SO₂ level and the required outlet emission level. The ART is sized to provide dissolution of limestone as well as desupersaturation of calcium sulfite. The absorber loop operates on a closed loop concept and the bleed to the dewatering system is controlled by density to approximately 15 to 17% by weight.

B) Dewatering

The absorber slurry which contains 15 to 17% by weight of solids, is passed through the dewatering system. Both primary and secondary dewatering stages are required for most plants. Unoxidized sludge (calcium sulphite) has typically been dewatered in a thickener as a first step, although hydroclones may also be used to dewater the unoxidized sludge. For oxidized sludge (gypsum), hydroclones have generally been selected as the primary dewatering device over thickeners because of their lower cost, compact size and superior particle size separation. Vacuum filters have been used for secondary dewatering which produces an end product with a moisture content between 60 and 88% solid for calcium sulfite. If oxidized gypsum sludge is dewatered with a vacuum belt filter an average moisture content of less than 10% is achieved. The dewatered sulfite cake is typically blended with fly ash (and may be lime) to produce a low permeability waste suitable for landfill. The dewater gypsum product can either be used for landfill or sold for various process applications.

6. OPERATING DATA

RHEINISCH WESTFAELISCHE ELEKTRIZITAETS WERKE, FRIMMERSDORF UNITS P & Q

A) General

Frimmersdorf power station is located in North Rhein Westfaelen near Cologne West Germany. Units P & Q are rated at 305 MWe steam generator, the fuel used is ignite. The air pollution control system includes electrostatic precipitators followed by two (2) 50% I.D. fans. From there the raw flue gas at Unit P is ducted to a regenerative reheater (Lungstrom type) before being ducted to the Thyssen FGD scrubber. At unit Q the raw gas is ducted directly to the Thyssen FGD scrubber.

B) FGD Design Basis

FGD system design parameters are summarized as follows:

Flue gas design flow rate 2,350,00 Nm³/h wet (3,814,000 m³/h wet) or 1,460,000 SCFM (2,250,000 ACFM) at 170°C (338°F). The design SO₂ inlet concentration is 5500 mg/Nm³ dry at 6% O₂ or 1925 ppm_{dv}. The maximum SO₂ emission in the stack, is limited by regulation, to less than 400 mg/Nm³ dry at 6% O₂ or 136 ppm_{dv}. This corresponds to an overall removal efficiency of 92.8%. Under these conditions, the individual absorber efficiency was guaranteed at 95% with 100% gas treatment.

C) Reagent Subsystem

The limestone subsystem is rated at 25 tons/hr feed rate of limestone powder to the slurry tank. The limestone slurry is stored in a slurry feed tank prior to pumping to the Absorber Recirculation Tanks (ART's). The sizing of the limestone preparation equipment is based on the maximum inlet SO₂ rate, that is to say the highest design sulfur containing coal at MCR boiler load. The addition of fresh limestone slurry to each ART is regulated to maintain the desired stoichiometric ratio and pH level using the inlet SO₂ mass flow rate signal. pH override signals are incorporated to make sure that the absorber module chemistry operates under the most favorable conditions.

D) Absorber Modules

Each FGD system includes one (1) single VLA absorber module 62 feet in diameter. Each module has its integrated Absorber Recirculation Tank (ART). No spare modules are installed. Uniform gas distribution to the absorber is accomplished with proper ductwork and system layout which eliminates the need for any bypass control dampers. The absorber towers are carbon steel lined with corrosion resistant rubber lining, while stainless steel is used for all slurry recirculation pumps. A wetted Falling Film Contactor (FFC) is installed in the tower to achieve the required 95% SO₂ removal. Silicon carbide slurry spray nozzles are used. The vertical demister consists of two stages, each provided with their own water wash header and nozzles. The lower demister is washed once every hour, while the upper stage demister is washed only once every four (4) hours.

E) Reheater

In the case of Unit P, the raw gas coming from the I.D. fan is cooled from 170°C (338°F) to approximately 110°C (230°F) in the regenerative heater before entering the absorber. The absorber exit gas at approximately 65°C (149°F) is ducted to the regenerative heater and leaves the heater to the stack at approximately 120°C (248°F).

For Unit Q no reheat system was installed. The saturated absorber outlet gas at 65°C (149°F) is directly ducted to the existing cooling tower.

F) Gypsum Dewatering

The produced gypsum slurry in the ART is completely oxidized by the integrated insitue forced oxidation system before leaving the ART. The bleed to the dewatering system is controlled by density. The dewatering system consists of a hydroclone system as pre dewatering device and a vacuum belt filter. Each FGD unit has one dedicated 100% dewatering system and one common is installed as standby.

7. PERFORMANCE DATA FOR FRIMMERSDORF

A) General

This section deals with the test results obtained during the Owner's acceptance test. The following parameters were used in determining the absorber performance:

- SO₂ concentration at absorber inlet, outlet and stack
- Pressure drop across absorber and system
- Absorber gas flow rate
- Absorber droplet carry over
- Gypsum dewatering rate and gypsum quality

Test were conducted at 100% and 80% MCR load. Limestone usage and waste product characteristics and production were evaluated by obtaining and analyzing various samples at different locations in the FGD system. German DIN standards were used for the sampling at SO₂, CO₂, O₂ and particulates.

B) SO₂ Removal Efficiency

SO₂ concentration in the flue gas was measured at the inlet and outlet of the absorber module and in the stack for two cases of gas flow rate (100% and 80%). During the test power production was around 300 MW, the measured average total flow gas at the FGD inlet was 2,150,000 Nm³/hr wet (1,460,000 SCFM). The test therefore were ran at conditions very close to the design basis.

The average SO₂ inlet concentration was around 1650 ppm_{dv}. The individual absorber tower efficiency for Units P & Q were measured at 97% and 98%. Test results at the 80% flow rate and 100% flow rate showed no significant difference in SO₂ removal efficiency between the two rates. During the test the limestone stoichiometric ratio was measured at 1.05 to 1.08. The ART pH ranged between 5.4 and 5.6. CaCO₃ content in the reagent averaged 95% and MgCO₃ content about .2%. The limestone grind during the test were found to be an average of 90% finer than 90 micron.

The excellent SO₂ removal efficiency was demonstrated during every test. The results are predictably consistent with prior data from other installations using the Thyssen FGD systems. Very efficient contact of limestone slurry and the flue gas in the absorber and the enhanced mass transfer contact area provided by the Falling Film Contactor zone (FFC) are the main reasons for the high SO₂ removal rate. Reagent utilization overall was found to be 98% or higher. The high SO₂ removal efficiency was obtained without the use of any additives.

D) Other Performance Parameters

Power consumption, make-up water consumption and pressure drop were also measured. During the test, the power consumption was found to be approximately 5% lower than the guaranteed value. Water consumption was 197.5 gpm. Pressure drop measured across the absorber was 95 mm WC (3.74 in WG) and 120 mm WC (4.72 in. WG) across the regenerative reheater.

E) Gypsum Dewatering

The under flow from the hydrocyclone system was measured at 55 to 65% solids. The moisture content of the vacuum filter cake ranged between 9 and 10% during the test. The purity of the gypsum filter cake was determined at 96-98% gypsum.

1. INTRODUCTION

The Bertin process provides an environmentally safe method for recovery of solid sulfur from flue gas from coal fired boilers or SO_2 producing chemical processes. The process takes place in three (3) distinct stages. In the first stage, the SO_2 is removed from the flue gas, by either wet scrubbing, or by All-Dry scrubbing. The second stage consist of biotransformation of the sulfites or sulfates to H_2S through bacterial action. The transformation occurs in an anaerobic digester. The third stage consist of catalytic transformation of the H_2S into solid sulfur utilizing a modified Redox process.

The environmental benefits of the Bertin System are that the reagent material is recycled from the second stage back to the first stage and also that the sulfur in the SO_2 is recovered as solid sulfur.

2. ABSORPTION OF THE GASEOUS SO_2

The first stage of the process consist of absorption of the SO_2 as SO_3^{2-} . This is achieved in a flue gas desulfurization plant using a reagent. The reagent can be CaCO_3 (calcium carbonate) or sodium bi-carbonate or sodium carbonate. The flue gas desulfurization can be performed with the equipment described in the early part of the paper, in order to meet the SO_2 removal efficiency. For smaller size utility and industrial installations, the wet scrubbing process can be replaced with Proceadair's enhanced All-Dry scrubbing, which is described in a separate paper. This All-Dry system provides the same efficiency as wet scrubbing systems. The SO_2 can also be removed in fluid bed boilers by the addition of lime stone to the feed. In the second two cases the calcium sulfate or calcium sulfite CaSO_4 or CaSO_3 are recovered in the fly ash.

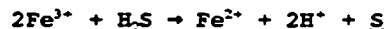
3. BIOTRANSFORMATION OF SULFITES AND SULFATES

The transformation of SO_3^{2-} into H_2S takes place in an aerobic digester. This digester is mechanically agitated. The digester is first fed with an anaerobic sludge from a municipal waste water treatment plant. This sludge contains the sulfur reducing bacteria. The bacteria also need carbon so that the SO_3^{2-} can be transformed into H_2S . The carbon is normally provided in the anaerobic sludge from waste water treatment plants molasses or other sources. The fermentation temperature is about 35°C (95°F) and the pH can vary between 6 and 9. The sulfate concentration in the mixture is maintained at about 50 gr/L. When the scrubber liquor in the first stage is calcium carbonate (CaCO_3) or ammonia carbonate (NH_4), CO_2 , the reagent is regenerated in the digester and recycled to the first stage.

The H_2S that is produced by the action of the bacteria on the sulfates and sulfites is evolved as both gaseous H_2S and also carried dissolved in the water formed in the system. The water, containing the H_2S , is sent to a conventional stripper tower where the H_2S is removed from the water by means of air. The clean water is circulated back to the first stage of the system when a wet scrubbing system is used.

4. OXIDATION OF HYDROGEN SULFITE TO ELEMENTAL SULFA

Oxidation of the hydrogen sulfide to elemental sulfur is achieved by means of oxidizing catalyst dissolved or suspended in liquid media. The modified Redox process used, requires $\text{Fe}^{2+}/\text{Fe}^{3+}$ as catalyst. The H_2S evolved in the digester and the air and H_2S released in the stripping column are passed through a gas liquid tower where the H_2S is absorbed in a solution containing the catalyst. The H_2S is oxidized to water and solid sulfa is precipitated according to the following reaction:



Fe^{2+} iron is simultaneously generated into Fe^{3+} by the excess oxygen present in the gas:

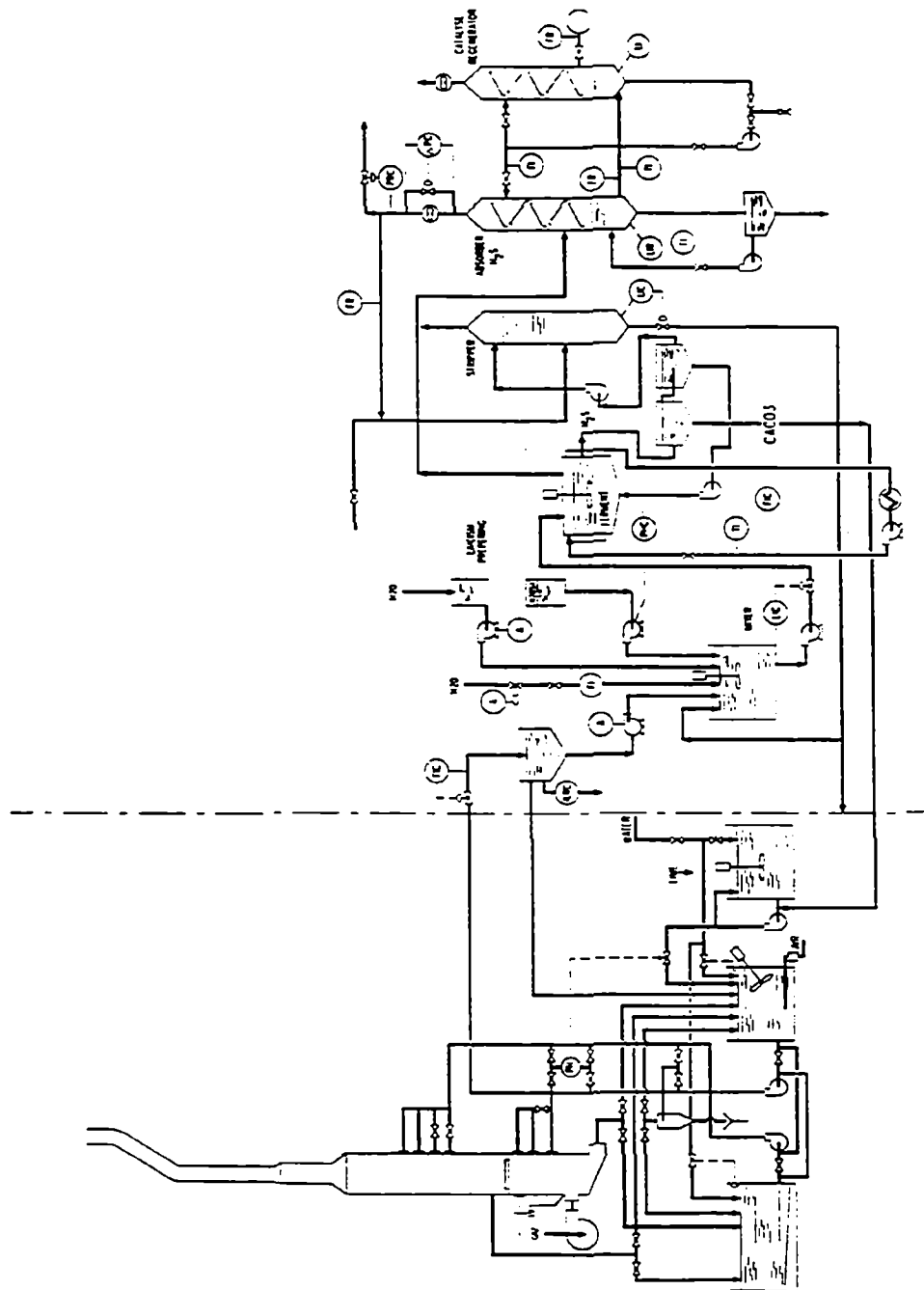


This means that the overall reaction is as follows:



All these reactions occur at ambient pressures and temperature and there is no reagent usage. The absorber towers use inclined trays to avoid plugging problems due to precipitation of the solid sulfur. The sulfur is separated from the liquid by conventional dewatering techniques. The clean catalyst solution is recycled for reuse.

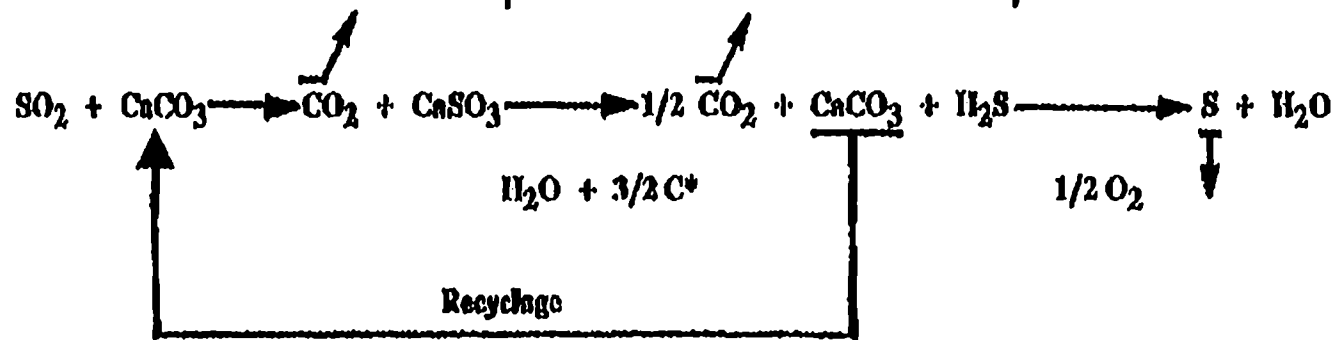
The recovered solid sulfur can further be purified in a sulfur melter to obtain the required purity for acid generation.



Captation de SO_2
(procédé sec ou humide)

Biotransformation
des sulfites ou sulfates en H_2S
par bactéries sulfato-réductrices

Transformation catalytique
de H_2S en soufre solide



PROCEDE BIOSOUTRE (traitement du SO_2)

SCHEMAS CINETIQUES POUR LA DESULFURATION

apport de carbone organique

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Modeling of Furnace Sorbent Injection Processes

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ABSTRACT

One possible approach to increase the cost effectiveness of furnace sorbent injection processes is to enhance SO₂ removal by injecting the sorbent in a slurry form. Various steps involved in SO₂ removal by furnace sorbent slurry injection include evaporation of slurry droplets, sorbent particle heat-up, activation of sorbent by calcination, reduction in active sorbent surface area by sintering, and sulfation of calcined sorbent. An existing model for sulfation and sintering of calcined sorbent, CaO, based upon a simple grain structure was adapted in a user-interactive computer program for simulation of the overall SO₂ removal process. The slurry droplet evaporation, particle heat-up, and sorbent calcination steps were assumed to be instantaneous in the overall model compared to the sulfation step. The effect of sorbent injection on furnace time/temperature profile and particle size reduction was taken into account.

Available dry and slurry sorbent injection data collected at the Ontario Hydro Research Division's Combustion Research Facility were compared with model predictions with good agreement. Injection of sorbent in a slurry form was found to enhance SO₂ capture in two ways:

- reduced sorbent sintering due to cooling of gases, and
- reduction in sorbent particle size during slurrying process.

Both of these factors improve sulfur capture. The model correctly predicted the observed effects of injection temperature and particle size on SO₂ capture for a given sorbent.

MODELING OF FURNACE SORBENT INJECTION PROCESSES

INTRODUCTION

A need for economically feasible SO_2 abatement in older coal-fired utility plants has promoted significant interest in low-cost retrofit flue gas desulfurization processes capable of moderate SO_2 removal. In-furnace injection of limestone in coal-fired boilers is suitable for retrofit applications due to lower capital cost and shorter lead time for installation. Typically, such a process results in up to 45 percent SO_2 removal, with only about 20% calcium utilization. Recent pilot-scale studies at the Ontario Hydro Research Division's Combustion Research Facility (CRF) have indicated that up to 70 percent SO_2 removal could be achieved by injecting the limestone sorbent as an aqueous slurry.¹ The effectiveness of the in-furnace slurry injection process depends on slurry droplet size, injection temperature, and sorbent properties. For successful application of such a concept, it is necessary to understand the mechanisms responsible for the increase in SO_2 removal.

In-furnace injection of limestone and hydrated lime, either in dry or slurry form, involves several steps leading to SO_2 capture which include: evaporation of water in slurry droplets, heat-up of sorbent particles, calcination of sorbent to form highly active CaO , reduction in surface area of active sorbent by sintering, and sulfation of CaO in the presence of excess oxygen to form CaSO_4 . A number of experimental and theoretical studies have been conducted to describe the calcination, sintering, and sulfation steps. A brief analysis of available information on each step is presented describing their contributions to the overall process and relative time scales. A user interactive computer program for the overall SO_2 removal process is described next. Existing dry and slurry sorbent injection data collected at Ontario Hydro CRF are discussed and compared with model predictions.

SLURRY DROPLET EVAPORATION AND PARTICLE HEAT-UP

After injection of a sorbent slurry droplet in a furnace, it is entrained in the flue gas and is exposed to a certain temperature profile depending upon the location of the injection nozzle in furnace, dispersion of droplets, and an existing gas time/temperature profile in the furnace. The time required for evaporation of a droplet can be estimated by determining the rate of heat transfer from the gas to the droplet and the rate of mass transfer from the droplet to the gas phase. The same heat transfer relations also apply in determining the time required by the dried droplets to heat up to the gas

temperature. The dispersion/mixing of droplets in the gas phase can influence the localized temperature and heat transfer rates. However, such information is not usually readily available. Uniform mixing of sorbent droplets/particles in the gas phase may thus be assumed for simplicity. The drying behavior of droplets at moderate temperatures in a spray chamber has been studied extensively.^{2,3} For fine slurry droplets of less than 20 μm diameter, the droplets are entrained rapidly in the gas phase, and the heat and mass transfer coefficients may be approximated by the respective Nusselt and Sherwood numbers of 2.⁴

The heat transferred from gas phase to the droplet is used to evaporate the moisture. Thus, the interrelated simultaneous heat and mass transfer relationships were used to estimate drying times of a 20 μm droplet with an initial moisture content of 80 percent (20 percent solids slurry) and for various furnace injection temperatures. The approximate drying times were found to be 1.8, 1.4, and 1.1 ms for furnace injection temperatures of 1,000, 1,200, and 1,400 $^{\circ}\text{C}$, respectively. The drying time of a droplet at a given temperature is proportional to the square of the droplet diameter.

During slurry droplet evaporation stage, the droplet temperature is held close to its boiling point (i.e. $\sim 100^{\circ}\text{C}$ for atmospheric pressure operation). Upon drying, the dried particle is heated from 100 $^{\circ}\text{C}$ to the gas temperature by heat transfer from the gas phase to the sorbent. In case of dry injection, the sorbent particle is heated from its initial feed temperature. The decomposition of the sorbent to CaO may possibly begin during particle heat-up. However, for the purpose of estimating the particle heat-up time, the sorbent decomposition may be assumed to occur after particle heat-up. For a 10 μm limestone particle, with an initial temperature of 100 $^{\circ}\text{C}$ injected in furnace at 1,200 $^{\circ}\text{C}$, the time required to heat the particle to 1,000, 1,100, 1,150, and 1,190 $^{\circ}\text{C}$ temperature may be estimated to be 0.6, 0.9, 1.1, and 1.8 ms, respectively. (Properties of air and sorbent at a mean gas film temperature were used.) The particle heat-up time is again proportional to the square of the particle diameter.

Furnace Time/Temperature Profile

The heat consumed during water evaporation, sorbent particle heat-up and endothermic calcination of sorbent reduces gas temperature significantly. Since the furnace gas temperature profile dictates the rates of various subprocesses, the furnace temperature drop due to sorbent injection must be taken into account. The amount of sorbent added into the furnace depends upon the Ca:S ratio used and the gas-phase SO_2 concentration. The amount of water used depends upon the weight fraction of solids in slurry. The resulting expression for furnace temperature drop, ΔT , due to limestone sorbent injection is given as:

$$\Delta T = 1.042 \times 10^{-5} C_{\text{SO}_2} (\text{SR}) \left[396.31 + 0.28 T_{\text{inj}} + \left(\frac{1}{w} - 1 \right) (561.0 + 0.545 T_{\text{inj}}) \right] . \quad (1)$$

A similar expression may also be written for hydrated lime sorbent injection:

$$\Delta T = 7.712 \times 10^{-6} C_{\text{SO}_2} (\text{SR}) \left[317.89 + 0.28 T_{\text{inj}} + \left(\frac{1}{w} - 1 \right) (561.0 + 0.545 T_{\text{inj}}) \right] \quad (2)$$

where

ΔT is drop in furnace temperatures, °C

C_{SO_2} is SO_2 concentration in furnace in ppm;

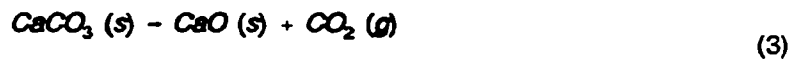
SR is Ca:S stoichiometric ratio;

T_{inj} is furnace temperature at the point of sorbent injection °C; and

w is weight fraction of solids in sorbent feed.

CALCINATION OF SORBENT

Following heat-up of the injected sorbent particles/slurry droplets, the limestone or hydrated lime sorbent is calcined at furnace conditions to produce highly porous and reactive CaO. In-situ calcined CaO has shown to be more reactive than injection of pre-calcined CaO in the furnace.⁵ During calcination, calcium carbonate or calcium hydrate decomposes producing CaO according to the following reactions:



The thermal decomposition of sorbent involves three potential rate controlling steps: (1) heat transfer to the surface and then through the CaO product layer to the reaction interface, (2) mass transfer of CO_2 away from the interface through the product layer, and (3) the chemical reaction. A number of studies have been conducted to determine the controlling step during calcination. Although earlier studies conducted with large particles (1 to 2 cm diameter cylinders) indicated dominance of CO_2 mass transfer and heat transfer,^{6,7} recent data by Borgwardt⁸ and analysis of earlier data by Beruto and Searcy⁹ clearly indicate the chemical kinetics as the controlling mechanism for calcination of small dispersed particles. The studies by Borgwardt⁸ with small particles ranging from 1 to 90 μm show that the rate of decomposition of CaCO_3 at any time is directly proportional to the BET surface area of the remaining unreacted limestone:

$$\frac{d(\text{CaCO}_3)}{dt} = -K_c S_{\text{CaCO}_3} \quad (4)$$

The reaction rate constant, K_c , exhibited an Arrhenius type correlation with temperature. Calcination of hydrate can occur at a much lower temperature than that of carbonate. Thus, at furnace conditions, hydrate may be expected to decompose much more rapidly than carbonates. Data from Bortz and Flament¹⁰ indicate that a hydrate decomposes about 50 times faster than a carbonate. Flow reactor data obtained with 10 μm limestone particles by Borgwardt⁸ indicate that at a temperature of 1,075 °C, 85 to 89 percent of limestone was converted to CaO in a residence time of 0.13 to 0.23 s. At furnace temperatures greater than 1,075 °C, the carbonate decomposition would be even more rapid. Data collected by Mozes et al.¹¹ at the Ontario Hydro CRF indicate essentially complete calcination within the first section of furnace with a residence time of ~ 0.2 s. At the same time, very little sulfation of calcined CaO was observed (<5%) during the same period.

From the overall modeling standpoint, the time scale of the calcination step with respect to sulfation is very important. Because the calcination is much more rapid than the sulfation reaction, the two processes may be considered sequential with the calcination step being independent of sulfation. One important parameter evolved in calcination is the active sorbent surface area. The solid phase decomposition process is not understood well enough to predict the surface area generated. For a given application, the surface area of freshly calcined sorbent must be assigned based upon experimental data. The literature data (e.g., ref. 8) and the modeling studies by Silcox et al.⁵ indicate the carbonate calcine areas of the order of 50 to 60 m^2/g , whereas those of hydrate calcines in the range of 100 m^2/g .

Another important parameter evolved in the calcination stage is the sorbent porous structure and porosity. A nonporous CaCO_3 or Ca(OH)_2 may be expected to produce porous CaO of 54 and 49 percent porosities, respectively. Any porosity inherent in limestone may be expected to increase the porosity of the calcine. Studies by Mozes et al.¹¹ with Beachville limestone with an initial porosity of 17 percent indicated calcine porosities in the range of 25 to 48 percent, significantly less than 54 percent instead of being greater than 54 percent. This could be due to the inherent difficulties associated with calcine sampling without altering its porosity and surface area as noted by Milne et al.¹² The porous structure of the calcine is important in selecting an appropriate model for sulfation reaction. Recent scanning electron microscopy (SEM) analysis of calcined sorbent samples by Milne et al.¹² indicate a sorbent structure composed of small interconnected grains. These studies also did not indicate any significant change in overall sorbent particle dimensions during calcination.

Sintering of Calcine

In a number of experimental studies, the surface area of active CaO has been shown to decrease with time at high enough temperatures.^{5,12-16} The surface area loss is attributed to sintering process. Sintering is the mechanism by which small solid particles coalesce when heated to high enough temperatures below their melting point. Sintering affects the surface area and porosity of the sorbent and reduces its effectiveness for SO₂ capture. Sintering commences immediately after formation of high surface areas during calcination and continues throughout the sorbent's residence time through the sulfation temperature window in the furnace. Thus, surface area reduction by sintering must be taken into account simultaneously with the sulfation process.

A basic two-sphere model was used by German and Munir¹⁷ to develop a correlation for surface area reduction:

$$\left(\frac{S_0 - S}{S_0} \right)^\gamma = K_s t \quad (5)$$

where S is calcine surface area, at time t , S_0 is initial surface area, K_s is the sintering rate coefficient and γ is a constant dependent upon the mechanism of grain migration.

Although this equation can fit sintering data well, it indicates that two calcines of same surface area can have different sintering rates based upon the initial starting surface areas in each case. An empirical approach suggested by Silcox et al.¹⁸ has also been shown to fit data well:

$$\frac{dS}{dt} = -K_s (S - S_{as})^2 \quad (6)$$

where S_{as} is an asymptotic surface area that a calcine can reach after a long period of sintering. The sintering process has been shown to depend upon gas phase CO₂ and H₂O concentrations by Borgwardt.¹⁴ The CO₂ and H₂O concentrations in a given furnace are likely to be in a narrow range, thus the above simple expression may still be adequate in a given case. As shown by Borgwardt⁸ an Arrhenius type correlation can be used to describe variation in K_s with temperature, $K_s = A \exp (B/T)$.

Along with surface area, the sintering process has also been shown to reduce porosity of sorbent material. As explained by Borgwardt,¹⁵ the sintering process may involve an induction period for porosity decline, which has been shown to be about 3 min at 950 °C. Because this order of magnitude of time is much greater than the furnace residence time, the effect of sintering on porosity may be ignored in the furnace injection modeling.

SULFATION OF CALCINED SORBENT

Sulfation of the calcined CaO is a noncatalytic gas-solid reaction and involves several potentially controlling steps: (1) transfer of SO₂ from the bulk gas phase to particle surface, (2) diffusion of SO₂ to the reactive surface within a particle, and (3) reaction between SO₂ and solid CaO. These steps are further complicated by the fact that the reaction product CaSO₄ has a greater molar volume than the CaO sorbent. The product is formed on the reaction surface, and, due to expansion, the product formation will constrict or even completely fill the porous structure of the calcine, thus limiting the sorbent utilization.

To accurately predict the SO₂ removal efficiency and sorbent utilization, the continuous effect of product formation on the porous structure must be adequately taken into account. The product buildup on the reactive surface provides a mass transfer resistance for SO₂ transport to the reactive surface, which is taken into account by defining an effective diffusion coefficient. Various models reported in literature, try to express the sorbent porous structure mathematically, e.g., a single pore model,¹⁹ a random pore model,²⁰ a pore tree model,²¹ or an overlapping grain model.²² A number of modeling and experimental studies have been reported specifically for the CaO and SO₂ reaction.^{5,23-33} The lime deactivation mechanism in most of these models is considered to be the product buildup and slow diffusion of SO₂ through the product layer.

In the SEM analysis of the calcined sorbent its structure appears to be composed of small spherical interconnected grains.¹² The grain structure model may be based upon a simple individual grain structure, as in Silcox et al.,⁵ or an overlapping interconnected grain structure, as discussed by Lindner and Simonsson.²² The complex overlapping grain model involves more model parameters, but has the ability of describing porosity reduction with sintering. The simple grain model cannot realistically simulate porosities lower than 26 percent. However, the initial porosities of calcined sorbent are expected to be greater than 50 percent, and the sintering induced porosity reduction may not be significant during the furnace time scale of 1 to 2 s. The porosity of sulfated sorbent may decrease with a high degree of conversion; however, conversions during furnace injection processes have typically been less than 30 percent. Thus, a simple grain model may be adequate for simulation of in-furnace sorbent injection processes. The reduction of surface area due to sintering can easily be taken into account by increasing the grain size appropriately with time, and the porosity of the sorbent may be assumed to decrease solely because of product formation as dictated by conversion.

Grain Model Formulation

The grain model formulation as described by Hartman and Coughlin²⁸ for the SO₂-lime reaction considers a spherical porous lime particle as composed of solid spherical nonporous CaO grains of uniform size, separated by pores. The reacting SO₂ is first transported from bulk gas phase to the particle surface, which then diffuses through the porous network to a grain reaction surface. As the reaction proceeds, a shell of the CaSO₄ product is formed on the surface of the grain. This product layer provides an additional mass transfer resistance to the diffusing SO₂. The sulfation of individual CaO grains is assumed to follow a shrinking core model. The sulfation reaction is assumed irreversible. The lime particles are assumed to be spherical, with no temperature gradients within a particle. The reacting surface is assumed to be CaO, i.e., the calcination is assumed to be complete in a grain before sulfation commences. The final product is assumed to be CaSO₄ due to an excess of oxygen in the gas phase.

The external mass transfer of SO₂ to particle is expected to be much faster as compared to internal pore diffusion for small particles below 50 µm and thus is not expected to be a rate controlling step.³⁴ The transport of sulfur dioxide within a spherical particle of lime can be described by a diffusion equation:²⁸

$$\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} - \frac{N}{D_{eff}} = 0 \quad , \quad (7)$$

where C is the gas-phase SO₂ concentration at a radial position, R, R is radial distance from center, N is SO₂ consumption rate, and D_{eff} is an effective pore diffusivity of SO₂. The effective diffusivity is given by:

$$D_{eff} = \frac{1}{\frac{1}{D_m} + \frac{1}{D_k}} \quad , \quad (8)$$

where D_m is gas phase molecular diffusivity and D_k is Knudsen pore diffusivity.

The SO₂ reaction rate, N, depends upon both the intrinsic kinetic rate and diffusion of SO₂ in product layer. For a first order reaction kinetics with respect to SO₂ concentration:

$$N = \frac{K_r A C^n}{1 + \frac{K_r}{D_s} r^2 \left(\frac{1}{r} - \frac{1}{r_g'} \right)} \quad , \quad (9)$$

where

- K_r = intrinsic reaction rate coefficient,
- A = surface area per unit volume,
- C = gas phase SO_2 concentration at a radial location R within a lime particle,
- n = reaction order, = 1 for first order
- D_s = diffusivity of SO_2 in the product layer,
- r = radius of reaction interface within spherical grain,
- r'_g = outer radius of partially sulfated grain.

The reaction rate is expressed in terms of a reaction order n . The SO_2 -lime reaction has been studied in a differential reactor by Borgwardt³⁵ with lime particles in the size range of 0.01 to 0.1 cm. These data indicated the reaction order with respect to SO_2 of 1 for particles smaller than 0.05 cm. However, recent experiments by Borgwardt and Bruce²⁵ indicated that for very small particles of 1 μm , the rate of CaSO_4 formation increased with the 0.62 ± 0.07 power of the SO_2 partial pressure. At these small particle sizes, the effect pore diffusion was eliminated. The reactivity of these particles also increased with the square of the BET surface area of the calcine, which may be interpreted as due to dominant diffusion resistance in the product layer. In flow reactor experiments by Coutant et al.³⁶ with 90 μm particles, a reaction order of 0.5 was indicated. Thus, a reaction order of 0.5 to 0.6 with respect to SO_2 concentration seems applicable for particle sizes relevant to furnace injection.

To utilize the grain model formulation as described above, correlations are needed for the intrinsic reaction rate coefficient, K_r , and product layer diffusivity, D_s . The fundamental data obtained with 1 μm particles²⁵ have been used by several investigators to obtain correlations for K_r and D_s . Borgwardt and Bruce found that an Arrhenius type correlation best described the variation of D_s with respect to T .²⁵ The reaction rate coefficient may also be expressed with an Arrhenius type correlation.⁵

The reaction surface area, A , is obtained from the sorbent grain radius, r'_g . This surface area is reduced with time due to sintering process. In the grain model, this may be accounted for by increasing the grain radius, r'_g continuously with time. The sintering rate correlations are used to change r'_g appropriately. The sintering and sulfation processes may thus be considered simultaneously in a grain model.

OVERALL MODEL STRUCTURE

The sorbent calcination, sintering, and sulfation processes are complex and details of these processes are not very well understood. Each of these processes depends upon several important

parameters, e.g., calcine surface area, porosity, and various kinetic correlations. Determination of these parameters experimentally is difficult, and only limited data are available which often provides a combined effect of these processes. Thus, in developing an overall model of this process, emphasis needs to be placed on simplicity and keeping the required model parameters to a necessary minimum.

The overall time scale of the in-furnace processes is about 1 to 2 s. The heat transfer steps of slurry evaporation and particle heat-up are of the order of a few milliseconds. Thus, these steps may be assumed instantaneous with respect to furnace time scale. The dispersion/mixing of sorbent in the gas phase is assumed to be uniform. The change in the furnace time/temperature profile resulting from sorbent injection is assumed to be instantaneous. The sorbent calcination step for carbonates has been shown to be of the order of 0.1 to 0.2 s. For hydrates, this step is much faster. The calcination step provides the surface area and porosity as the input parameters needed for the sulfation model. Although the carbonate decomposition time is significant with respect to overall time scale, this step was considered instantaneous with respect to sulfation in this effort for the following reasons: (1) calcination kinetics is an order of magnitude faster than sulfation kinetics; (2) the present understanding does not provide any estimate of fresh calcine surface area and porosity, the key parameters for sulfation reaction, which still need to be assumed; and (3) calcination and sulfation may be considered sequential processes, with calcination being independent of sulfation.

The fresh calcine surface area and porosity may simply be used as user-supplied input parameters for the overall model, which now primarily would be simultaneous sintering and sulfation model. A sorbent structure composed of individual uniform sorbent grains represents a simple porous structure defined by a single parameter, grain radius. The grain radius is directly related to the calcine surface area. The calcine sorbent porosity is assumed independently as another user-supplied parameter. This simple formulation is also able to incorporate sintering and surface area change by simply increasing the grain radius with time.

Sulfation and Sintering Model

An existing computer code "SO₂EPA" developed by Dr. G. Silcox of the University of Utah, based upon the simple grain structure, was adapted in the overall model in this effort. This program simulates simultaneous sintering and sulfation of calcined CaO under furnace conditions. This code uses finite difference formulation to solve the equation describing SO₂ diffusion and reaction. The reaction order with respect to SO₂ concentration is assumed to be 0.55. Due to the nonlinearity introduced by this reaction order, a Newton-Raphson iteration technique is used to solve the difference equations. Details of this code and solution procedures are given by Silcox et al.⁵

The input parameters to this model include furnace SO_2 concentration, Ca:S ratio for sorbent injection, furnace time/temperature profile as "seen" by injected particles, sorbent particle diameter, initial and asymptotic BET surface area of calcine, initial porosity of calcine, weight fraction of CaCO_3 in raw stone, porosity of product layer, partial pressure of O_2 in furnace gases, and residence time. Additional input parameters related to numerical procedures also need to be specified. The adaptation of the "SO2EPA" code in the present work involved:

- changing the user specified furnace time/temperature profile to take into account heat effects;
- allowing the user to specify an injection temperature in an existing furnace temperature profile; the program recalculates the temperature profile as "seen" by the sorbent;
- modifying the Newton-Raphson iteration procedures to allow faster convergence;
- allowing for particle size change by fragmentation as specified by user;
- allowing all input parameters to be entered interactively; and
- allowing changing various kinetic rate coefficients.

User-Interactive Data Input

A user-interactive computer program 'FSI' was developed in this effort to facilitate simulation of furnace sorbent injection processes.³⁷ This program allows: (1) entering all the data required to run a simulation interactively, (2) saving all the data in a user designated file, (3) reading data from an existing data file, and (4) running the sulfation model using the current data values. The model output can either be saved in a user-specified file, or printed directly on a printer. At startup, all the data values are initialized with default values. All the data input screens are self-explanatory, and additional instructions are available in help files.

The user supplied inputs are divided into five categories: (1) sorbent parameters, (2) furnace time/temperature profile, (3) sorbent injection operating conditions, (4) model simulation parameters, and (5) reaction and diffusion rate coefficients.

MODEL SIMULATIONS

The concept of in-furnace injection of a sorbent in a slurry form for enhanced SO_2 removal has recently been demonstrated in pilot-scale studies at Ontario Hydro CRF.¹ In earlier studies, the effectiveness of dry injection of sorbents was investigated.^{11,38} Thus, these data provide direct

comparison of results of sorbent injection in both dry and slurry form. The data collected in these studies were used for model simulation in present studies.

Experimental Database

The dry sorbent injection data collected at Ontario Hydro CRF include tests conducted with two different limestone sorbents: Beachville limestone and Pt. Anne limestone. The chemical and physical properties of these sorbents relevant to model simulation are given in Table 1. The details of the combustion research facility (experimental conditions and operating procedures) are given in references 1, 11, and 38.

Bulk of the experimental data simulated a furnace quenching rate of 500 °C/s. The sorbents were injected at different locations in the furnace corresponding to injection temperatures in the range of 1,000 to 1,350 °C. The sorbent to sulfur ratios during these tests ranged from 1.5 to 3.0.

The dry sorbent injection SO₂ capture data indicate substantial influence of sorbent injection temperature on SO₂ capture for all sorbents. The different sorbents showed differing reactivities toward SO₂. The sorbents tested differ significantly in the porosities and sorbent particle sizes. The slurry injection data indicated 5 to 30 percent enhancement in SO₂ capture compared to dry sorbent injection under similar conditions. The effect of injection temperature in slurry injection tests was less dramatic than that during dry injection. In both cases, the optimum temperature for sorbent injection was found to be about 1,200 °C.

Model Parameters

Model simulations require a number of sorbent properties and rate coefficients. Sorbent properties include particle diameter, surface area and porosity of fresh calcine, and particle fragmentation estimate if any. The rate coefficients include the two coefficients in the two-parameter Arrhenius correlations for the intrinsic reactivity, product layer diffusivity, and sintering rate (K_{r1} , K_{r2} , D_{s1} , D_{s2} , K_{s1} , and K_{s2} , respectively). During these simulations the surface area of fresh calcine from carbonates was assumed to be 60 m²/g. The inherent sorbent porosities were taken into account in estimating the calcine porosities; thus the porosity of calcine from Beachville limestone was taken as 0.62 and that from Pt. Anne limestone was taken to be 0.7. A number of simulations were conducted with dry injection data to identify a common set of rate coefficient values for the data involving calcium carbonates. The values found to give reasonable fit with data were:

$$K_{r1} = 50.0, D_{s1} = 1.85 \times 10^{-3}, \text{ and } K_{s1} = 25.0.$$

The activation energies were $K_{r2} = -12540$, $D_{s2} = -21200$, and $K_{s2} = -19566$, all in K.

The activation energies were kept constant in all simulations. For slurry injection simulations it was necessary to change one or more rate coefficients to improve fit with observed data. The values used in these simulations are given in Table 2.

Dry Injection Simulation

The simulation results are shown graphically in Figures 1 and 2 to highlight the effect of sorbent injection temperature and Ca:S ratio on SO₂ capture. As seen from these figures, the model predicted the observed trends in the effect of temperature and Ca:S ratio with good agreement in the data and model predictions. For Beachville limestone, the model predictions indicated 1,200 °C as an optimum injection temperature for SO₂ removal as observed experimentally.

During these simulations with Beachville limestone and Pt. Anne limestone the same reaction and diffusion coefficients were used. Thus the differences in the observed SO₂ capture were explained by smaller particle size and high porosity of Pt. Anne limestone sorbent. Additional simulations indicated that decreasing particle size below 3.0 µm did not further increase SO₂ capture significantly; thus the pore diffusion resistances appear to be important only for particles greater than 3.0 µm in diameter.

The model was able to explain the low SO₂ capture for sorbent injections at higher than optimum temperatures for both sorbents. Such sorbent injection leads to rapid sintering and loss in surface area while the temperature is still high enough to prevent sorbent sulfation due to reaction equilibrium considerations. Thus the surface area is reduced without any SO₂ capture resulting in lower overall sorbent reactivity.

Slurry Injection Simulation

These simulation results are shown graphically in Figures 3, 4, and 5 to highlight the effect of injection temperature and Ca:S ratio on SO₂ capture. During the slurry injection experiments, two injection modes were identified depending upon the orientation of the injection nozzles with respect to furnace gas flow.¹ The injection mode presumably influenced the actual furnace temperatures as 'seen' by the injected droplets, and significant differences in SO₂ capture were observed in the two injection modes at a given furnace location. From the modeling standpoint, the difference in the injection modes can only be accounted if the difference in the injection location temperature and the temperature actually experienced by the droplets is known. Since this information could not accurately be obtained, the furnace temperatures reported at the injection location were used in model simulation regardless of the injection mode.

As seen from Figure 3 for Beachville limestone slurry injection, the model appears to simulate the cocurrent injection mode results better than the countercurrent mode results. The model is seen to correctly predict the trend in the observed effect of injection temperature. The location of optimum temperature peak as predicted by model matches closely with cocurrent mode data.

As seen from Figures 3 and 4, the model predicted the SO₂ capture levels at the optimum temperature very well; however, the model underpredicted the SO₂ capture observed at lower temperatures. The observed reactivities at lower temperatures did not drop with temperature as rapidly as the model predicted. The data plotted in Figure 5 show the effect of Ca:S ratio on SO₂ capture at the optimum injection temperature. Good agreement is seen between the model predictions and observed values.

At temperatures higher than the optimum level, the model correctly predicted increased SO₂ captures when compared with the dry injection results. This results from reduced sintering effect at high temperature injections because of substantial cooling of the gas phase. At a Ca:S ratio of 3 the injection of sorbent in the slurry form decreases the gas temperature by an additional 60 to 70 °C, thus preventing rapid sintering without sulfation at high temperatures. As seen from Table 2, simulation of slurry injections data required greater intrinsic reactivity and greater product layer diffusivity values for improving the agreement between model and data. This certainly indicates enhanced reactivity of sorbent by injecting the sorbent in a slurry form beyond that explained by the obvious sintering effect.

The sorbent particle size in slurry injection mode is determined from the slurry droplet size and the solids fraction in slurry. This assumption explained the observed lower SO₂ captures obtained with 17 µm slurry droplets as opposed to 6.0 µm slurry droplets of Pt. Anne limestone sorbent. The effect of particle size results from pore diffusion resistances which were found to be important for dry particle sizes greater than about 3.0 µm. Any further decrease in particle size did not appear to improve SO₂ capture significantly in model simulations. The 3.0 µm dry particle size corresponds to about 5.0 to 6.0 µm slurry droplet size for 40 percent by weight slurry. Thus the simulations concur with the experimental finding of optimum slurry droplet diameter of 6.0 µm.

CONCLUSIONS

The following conclusions may be drawn from the furnace sorbent injection modeling efforts and simulation of experimental data.

- The model simulations of dry sorbent injection pilot plant data indicated very good agreement. The model correctly predicted the effect of injection temperature and

particle size. The lower SO₂ capture observed by injecting sorbent at a higher than optimum temperature was attributed to rapid sintering and surface area loss without any significant SO₂ capture at high temperatures.

- The model successfully simulated observed SO₂ captures during slurry injection at optimum temperatures. The model underpredicted observed SO₂ captures at lower than optimum temperature injections.
- The model indicated reduced sintering effects in slurry sorbent injection as compared to dry sorbent injections. This fact improved performance substantially at higher than optimum temperature injections.
- Slurrying process reduced effective sorbent particle size especially for Beachville limestone which was found to improve SO₂ capture.
- The model predictions were in better agreement with cocurrent slurry injection data than countercurrent slurry injection data. The model, however, correctly predicted the existence of optimum injection temperature as observed.

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Table 1
CHEMICAL AND PHYSICAL PROPERTIES OF SORBENTS

	<u>Beachville Limestone</u>	<u>Pt. Anne Limestone</u>
MgO g/kg	8.0	4.8
CaO g/kg	524.0	535.4
LOI	434.0	
BET area, m ² /g	1.3	2.9
MMD, μm	8.6	3.9
ρ, g/cm ³	2.6	2.3
Porosity %	17.0	55.0

Table 2
RATE COEFFICIENTS USED IN SIMULATIONS

<u>Sorbent</u>	<u>Mode</u>	<u>K_{r1}</u>	<u>D_{s1}</u>	<u>K_{s1}</u>
Beachville limestone	Dry	50	1.85 x 10 ⁻³	25
Pt. Anne limestone	Dry	50	1.85 x 10 ⁻³	25
Beachville limestone	Slurry	100	1.85 x 10 ⁻³	20
Pt. Anne limestone	Slurry	100	3.7 x 10 ⁻³	25

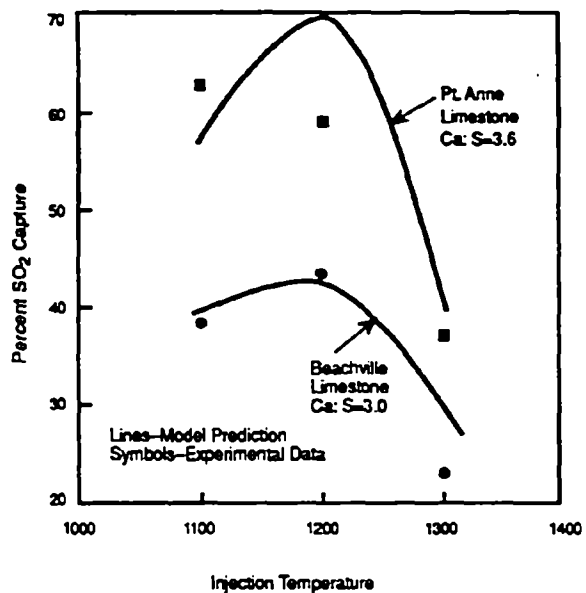


Figure 1. SO_2 Capture as a Function of Injection Temperature—Dry Injection.

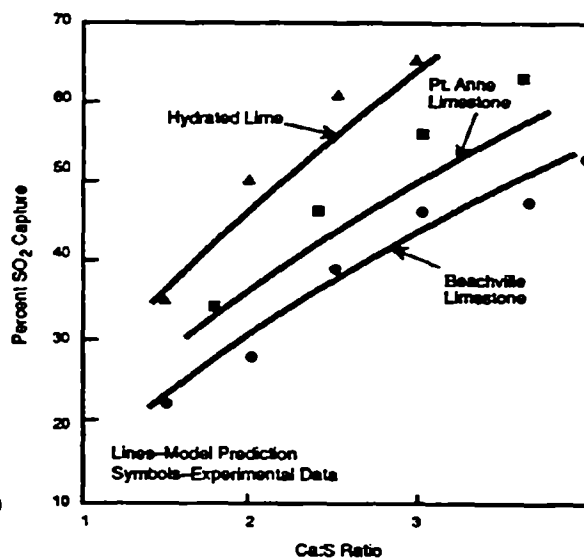


Figure 2. SO_2 Capture as a Function of Ca:S Ratio—Dry Injection.

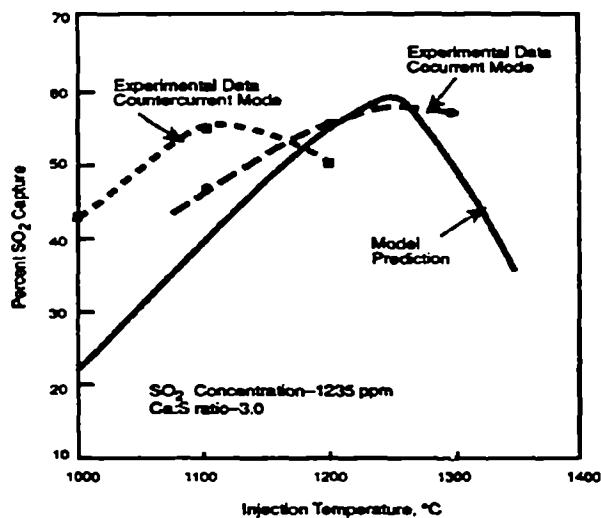


Figure 3. SO_2 Capture as a Function of Injection Temperature—Beachville Limestone Slurry Injection.

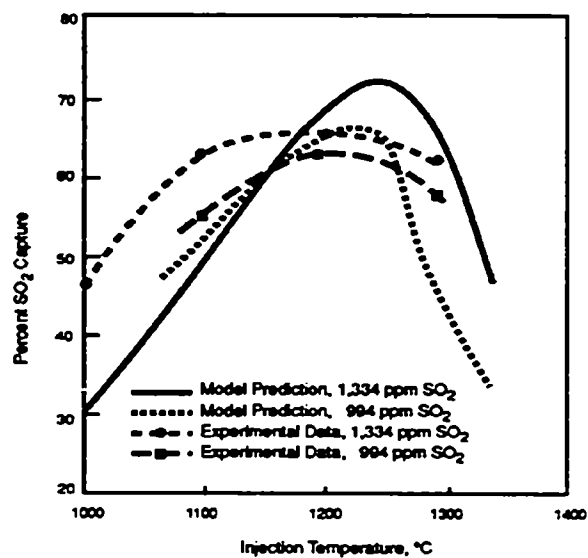


Figure 4. SO₂ Capture as a Function of Injection Temperature-Pt. Anne Limestone Slurry Injection.

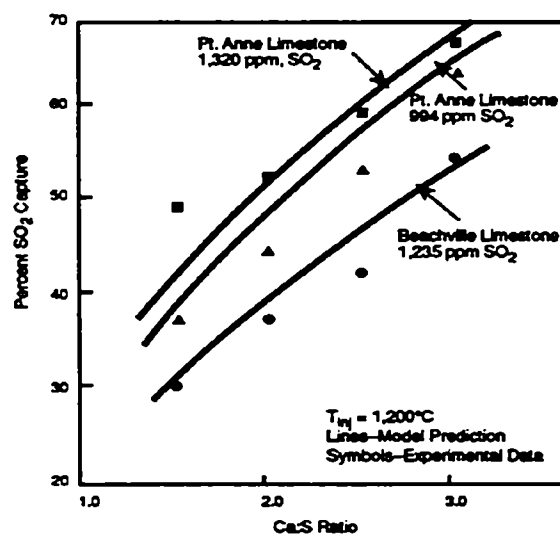


Figure 5. SO₂ Capture as a Function of Ca:S Ratio-Slurry Injection.

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DRY FGD PROCESS USING CALCIUM SORBENTS

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ABSTRACT

This paper describes the Hitachi Simplified FGD (Flue Gas Desulfurization) System. As this is a dry FGD system which does not handle a sorbent as a slurry and is constituted with a few number of auxiliary equipment, compared with semi-dry or wet systems, the system can be operated easily. Furthermore, it has also features such as no waste water and small installation space. There are two basic processes in this system -- DLI (Duct Lime Injection) Type and FLI (Furnace Limestone Injection) Type.

DLI Type is the system in which hydrate lime (Ca(OH)_2) as a sorbent is injected into the duct pneumatically, then flue gas including sorbent is cooled and humidified by water injection in the reactor. Reaction between Ca(OH)_2 and sulfur dioxide (SO_2) is enhanced by this humidification. As sorbent injection in the boiler furnace is not carried out, this system can be applied easily not only coal-fired boiler but also oil-fired boiler whether it is new or retrofitting. While in the FLI Type, limestone (CaCO_3) as a sorbent is injected into the boiler furnace where CaCO_3 is decomposed thermally to produce calcium oxide (CaO) which reacts with SO_2 partially in the furnace. In addition, the reactor is also provided to increase SO_2 removal efficiency by cooling and humidification of flue gas similar to DLI system. FLI system is most applicable to the coal-fired boiler in case the CaCO_3 is more suitable for obtaining than Ca(OH)_2 .

In both DLI and FLI processes, SO_2 removal efficiency was achieved above 70 % and 80 % at Ca/S molar ratio of 2 and 3 respectively.

Hitachi Ltd. and Babcock-Hitachi K.K. have performed various tests for this FGD system, and are proceeding with application to commercial plant. In this paper we also describe sorbent that had larger specific surface area than Ca(OH)_2 by heat treatment of Ca(OH)_2 with certain additives. It was confirmed that its reactivity was higher than that of Ca(OH)_2 .

DRY FGD PROCESS USING CALCIUM SORBENTS

INTRODUCTION

Recently, the problem of environmental pollution due to acid rain has been focused worldwide. One of the major factors of acid rain is its releasing of sulfur oxide, which is generated by combustion of fossil fuels, from thermal power plants. Hitachi Ltd. and Babcock-Hitachi K.K. have been engaged in the development of FGD systems for more than thirty years, and in addition to wet limestone-gypsum systems (1). We have established various FGD systems such as dry activated carbon process, dry absorbents made from fly ash process (2), etc.

As the problem of acid rain has become a global concern, various types of FGD systems are in demand. Recently the FGD system which is a simple system, easy to operate and is low in cost, although SO₂ removal efficiency is not as high as that obtained in wet FGD systems, has been particularly demanded in certain countries due to regional circumstances. In response to these needs, Hitachi Ltd. and Babcock-Hitachi K.K. have developed and established Hitachi Simplified FGD System based on research and development as well as extensive experience so far.

PROCESS DESCRIPTION

There are two basic processes -- DLI (Duct Lime Injection) and FLI (Furnace Limestone Injection) Types. These two processes vary according to the point at which the sorbent is injected into the system. In the DLI type, the sorbent is injected into the flue duct downstream of the Air Preheater, whereas in the FLI Type, the sorbent is injected into the boiler furnace. Selection between the two available processes depends upon the kind of boiler fuel (Coal or Oil) and desulfurization sorbent used (Lime or Limestone). Both processes are provided with a reactor where humidification and SO₂ absorption occur.

Flow diagrams of the two processes are outlined in Figure 1. Key parameters for SO₂ removal are as follows.

- Ca/S molar ratio
- gas temperature (reactor outlet)
- residence time in furnace
- temperature at sorbent injection zone in the furnace

TEST PROCEDURE AND RESULTS FOR DLI AND FLI PROCESS

2,000 Nm³/h Pilot Plant

Flow sheet and photograph of this plant are shown in Figure 2 and 3 respectively.

Flue gas for testing was prepared by injecting SO_2 and fly ash into the flue gas from the boiler. Under the standard condition, SO_2 concentration in the inlet gas was kept at 1800 ppm. After the sorbent was injected pneumatically into the flue gas, it was cooled by humidification in the reactor. The injection nozzle of sorbent was located on the inlet duct of the reactor. Humidification was carried out by injection of fine mists from dual fluid spray nozzles and these mists evaporated completely in the reactor.

Having reacted with SO_2 in the reactor, the sorbent was collected in ESP downstream of the reactor. SO_2 concentration in the inlet and outlet gases were measured by an infrared SO_2 analyzer in order to determine SO_2 removal. The dimensions of the reactor were 0.85 m in diameter and 10 m in height. Inlet gas temperature of the reactor was 150 °C.

Test Furnace

A photograph and outline of the test furnace are shown in Figures 4 and 5 respectively. The furnace was a vertical type having four sorbent injection nozzles, paired on the front and rear wall. Sorbents injection points were located on the zone where the temperature were as high as 1050 °C and 1150 °C, and the sorbent was injected pneumatically into the test furnace.

Reacted sorbent was collected in the bag filter downstream of the furnace. Collected sorbents were injected into the pilot plant reactor for FLI process evaluation. The flow sheet is shown in Figure 6.

Specification of the test furnace were as follows.

- Coal consumption : 4 t/h
- Combustion gas flow rate : 30,000 Nm³/h

Evaluation of DLI Process

In this process, $\text{Ca}(\text{OH})_2$ was injected into the reactor, while water was sprayed separately. The average particle size of fine mist from the dual fluid spray nozzle was approximately 50 μm derived by a laser diffraction technique.

Figure 7 shows the dependence of SO_2 removal on the outlet gas temperature, the relative humidity and injected Ca/S molar ratio. As shown in this figure, SO_2 removal increased as the outlet gas temperature decreased (relative humidity increased) or Ca/S molar ratio increased (3). It was found, however, that the outlet gas temperature should be kept at least 10 °C over the saturated temperature to avoid deposition of the reacted sorbent in the downstream duct or ESP.

Test results indicated that SO_2 removal as high as 70 and 80 % or more was achieved at Ca/S molar ratio of 2 and 3 respectively at an approach-to-saturation temperature of 10 °C.

The effect of SO_2 concentration in the flue gas on the SO_2 removal was also investigated. The result is shown in Figure 8. In the range of 500 - 3000 ppm of SO_2

concentration, the SO₂ removal is considered to be independent of SO₂ concentration.

Evaluation of FLI Process

Evaluation of FLI process was carried out by the result of the furnace and 2000 Nm³/h pilot plant.

In this process, limestone (95 % pass through 325 mesh) was used as an sorbent. Coal fired for this study was a bituminous coal containing 0.57 % of sulfur.

The residence time from the injector to the first gas cooler was approximately 1 second and injection velocity of the sorbent was more than 30 meters per second. SO₂ removal in the test furnace was determined by measuring SO₂ concentration in the flue gas at the outlet with and with-out sorbent injection.

From the previous study (4) on the effect of the temperature of sorbent injection zone in a furnace on SO₂ removal, the optimum injection temperature was found to be 1000 - 1100 °C. From this result, sorbent injection points were determined. The gas condition in the pilot plant was adjusted equal to the outlet gas condition from the test furnace.

The overall SO₂ removal is shown in Figure 9. SO₂ removal in the test furnace was above 30 % at Ca/S ratio of 3, while overall SO₂ removal by injecting collected sorbent in the test furnace into the reactor of the pilot plant was achieved more than 70 % and 80 % at Ca/S molar ratio of 2 and 3 respectively.

During the above tests, no adverse influences due to fouling or slagging in the furnace were observed.

TEST PROCEDURE AND RESULTS FOR HIGHLY REACTIVE SORBENT

Sorbent Preparation

As a next step of our development, we have researched about improvement of SO₂ removal for sorbent. We found that it was possible by additive and heating. Preparation of highly reactive sorbent is as follows.

Sorbent were prepared by slurring Ca(OH)₂ with fly ash and heating them in an autoclave. The heating temperature was varied between 60 - 130 °C. Under the standard condition, 60 g of Ca(OH)₂ was slurried with 40 g of fly ash in 400 ml of distilled water. After being heated for a given period, the slurry was filtered and dried at 110 °C in an oven. The dry sorbents were later used for tests.

When sodium silicate (water glass, which contains approximately 18 % of Na₂O, 37 % SiO₂ and the balance of water) was added to enhance the reactivity of the sorbents, it was first dissolved in distilled water and mixed with Ca(OH)₂ and coal ash. Unless otherwise stated, the procedure for preparation was the same as mentioned above. In this paper, "the amount of sodium silicate added to Ca(OH)₂" was defined as the weight percent of sodium silicate solution including water in it.

Fixed Bed Reactor

The reactivity of sorbents with different surface areas was determined in a fixed bed reactor. The flow sheet is shown in Figure 10. The sorbents were dispersed in alumina sand to avoid channeling and supported on the glass filter in the reactor. The cylindrical pyrex reactor (5 cm in diameter and 15 cm in height) was placed in an oven at temperature controlled between 60 - 90 °C. Simulated flue gas was prepared by mixing N₂, CO₂, O₂, SO₂ and NO gases from gas cylinders. The gas flow rate was 3.0 liters per minute and consisted of 12 % CO₂, 3 % O₂, 300 ppm SO₂, 300 ppm NO and the balance N₂. Steam was added to the gas by evaporating distilled water in an evaporation chamber. Downstream of the reactor, the gas was cooled by ice and the SO₂ concentration in it was measured by an infrared SO₂ analyzer to determine the reactivity of the sorbents.

The amount of sorbent placed in the reactor was adjusted so that the Ca(OH)₂ loading was always 30 milli-grams. The reactivity of the sorbents is expressed as "Ca conversion" which is defined as the molar percent of Ca reacted with SO₂ when the total mole of SO₂ supplied in the reactor is equal to that of Ca in the sorbent.

Evaluation of Highly Reactive Sorbents

The technique to prepare highly-reactive sorbent from Ca(OH)₂ and fly ash is well known (5, 6). In the present study, the effects of slurry heating conditions and additives on the reactivity of sorbents were evaluated.

Before measuring the reactivity of sorbents towards SO₂, the effects of some factors on the specific surface areas of sorbents were investigated. The results are shown in Figures 11 to 13.

Figures 11 and 12 show specific surface area of sorbents as a function of heating time at a given temperature and as a function of heating temperature at a given time respectively. The specific surface area increased according to the slurry heating temperature or heating time.

In order to increase specific surface area of sorbents without increasing slurry heating temperature or time, sodium silicate was added to Ca(OH)₂ and fly ash. Figure 13 indicates the effect of the amount of sodium silicate on the specific surface area of the sorbents. The axis of abscissas in Figure 13 represents the weight percentage of sodium silicate to Ca(OH)₂. The specific surface area increased by adding sodium silicate.

The reactivity of sorbents were studied in a fixed bed reactor. Figure 14 summarizes the relationship between Ca conversion and the specific surface area of sorbents which were prepared at various conditions (slurry heating temperature, time and the amount of sodium silicate added were varied). In these experiments, the temperature and relative humidity in the reactor were kept at 70 °C and 50 % respectively. The data show that the reactivity of sorbents at a given condition is proportional to their surface area.

The above results show that the reactivity of sorbents can be multiplied by addition of fly ash and sodium silicate. In the next step, reactive sorbent with specific surface area of 36.6 m²/g was injected into the reactor of the pilot plant

and its SO₂ removal was compared with that of Ca(OH)₂ (specific surface area : 13 m²/g). This reactive sorbent was prepared by slurring 57 % Ca(OH)₂, 38 % fly ash and 5 % sodium silicate at 125 °C for 3 hours. Figure 15 shows SO₂ removal of the reactive sorbent and Ca(OH)₂ as a function of outlet gas temperature. At the same Ca/S molar ratio, SO₂ removal of the reactive sorbent was much higher than that of Ca(OH)₂. Even at lower Ca/S molar ratio (Ca/S = 1.4), the reactive sorbent performed equal SO₂ removal to that of Ca(OH)₂ at Ca/S molar ratio of 2, resulting in about 30 % decreased sorbent consumption at the same SO₂ removal.

CONCLUSION

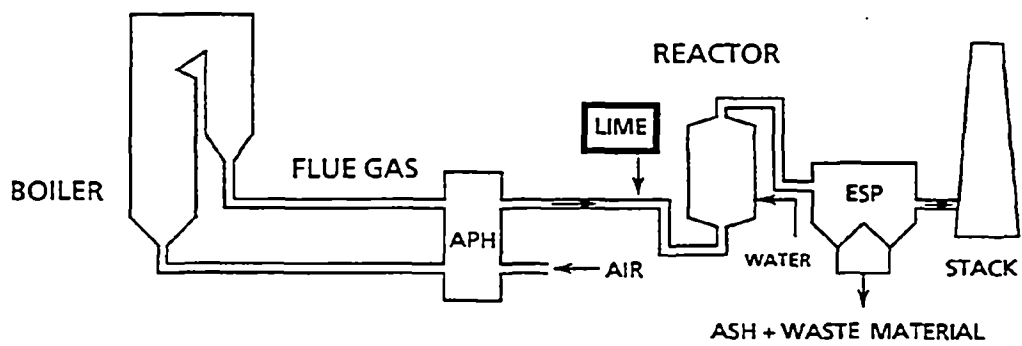
The following conclusions can be drawn from the results of the present study :

1. In both DLI and FLI processes, SO₂ removal was achieved above 70 % and 80 % at Ca/S molar ratios of 2 and 3 respectively.
2. In the range of 500 - 3000 ppm, the SO₂ removal is independent of SO₂ concentration in both processes.
3. SO₂ removal increased in accordance with the lowering of the gas temperature at reactor outlet. However, it should be kept at least 10 °C over the saturated temperature to avoid deposition of the reacted sorbent in the downstream duct or ESP.
4. In view of SO₂ removal and thermal decomposition of limestone, optimum injection temperature in the furnace should be 1000-1100 °C.
5. In the reactor, downstream duct and ESP, scaling was not caused by humidification.
6. The reactivity of sorbents at a given condition is proportional to their surface area.
7. The specific surface area of the sorbents increased by adding sodium silicate as well as by heating slurry longer or at higher temperature.

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DLI - TYPE



FLI - TYPE

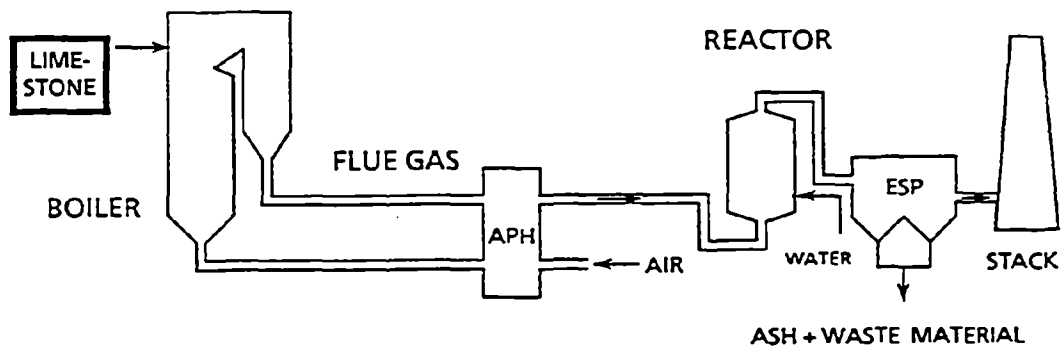


Figure 1. Flow Diagram of the Hitachi Simplified FGD System

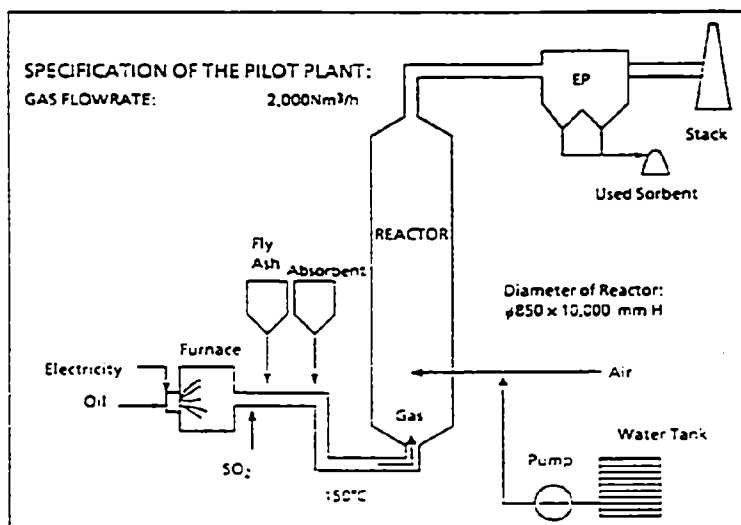


Figure 2. Flow Sheet of 2,000 m³/h Pilot Plant



Figure 3. Photograph of Pilot Plant

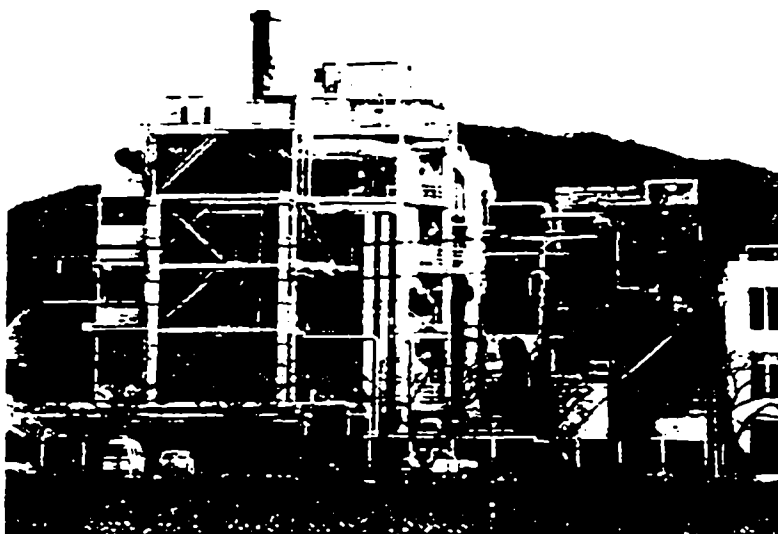


Figure 4. Photograph of Test Furnace

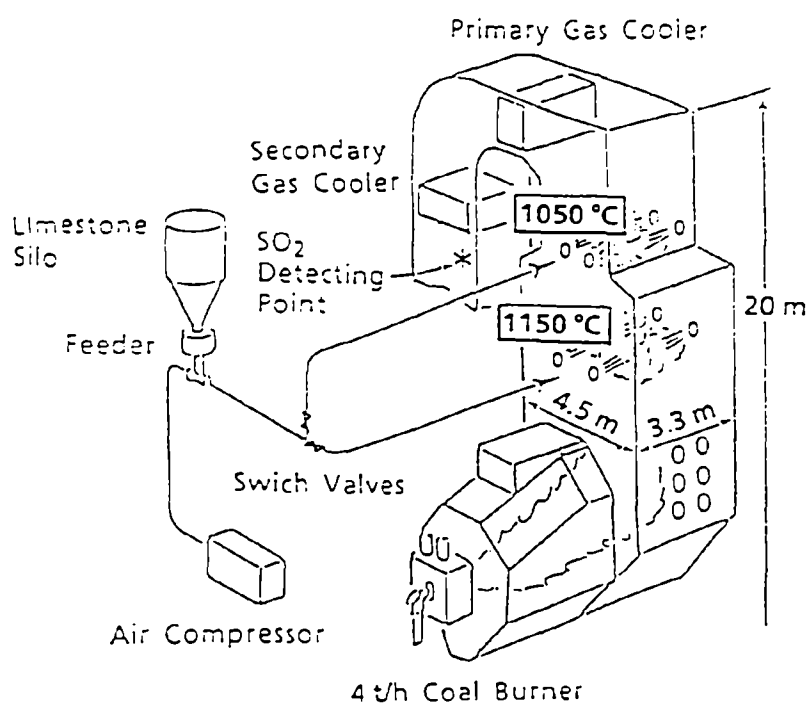


Figure 5. Outline of Test Furnace

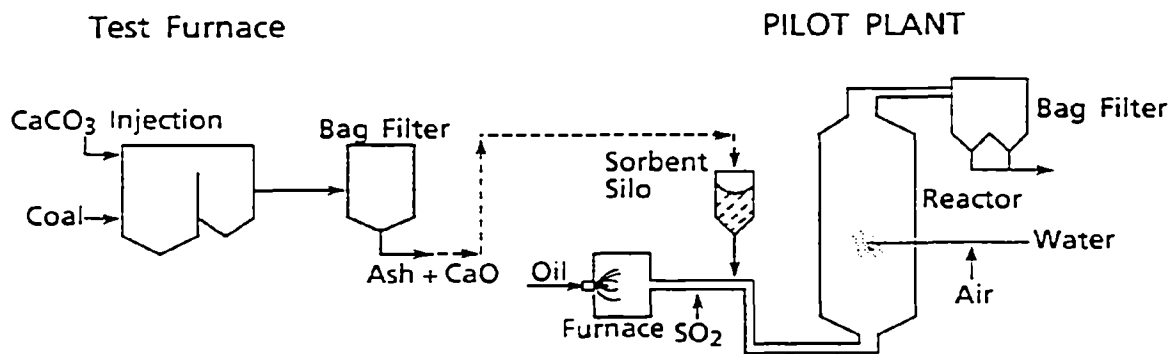


Figure 6. Test Flow Sheet for FLI Process

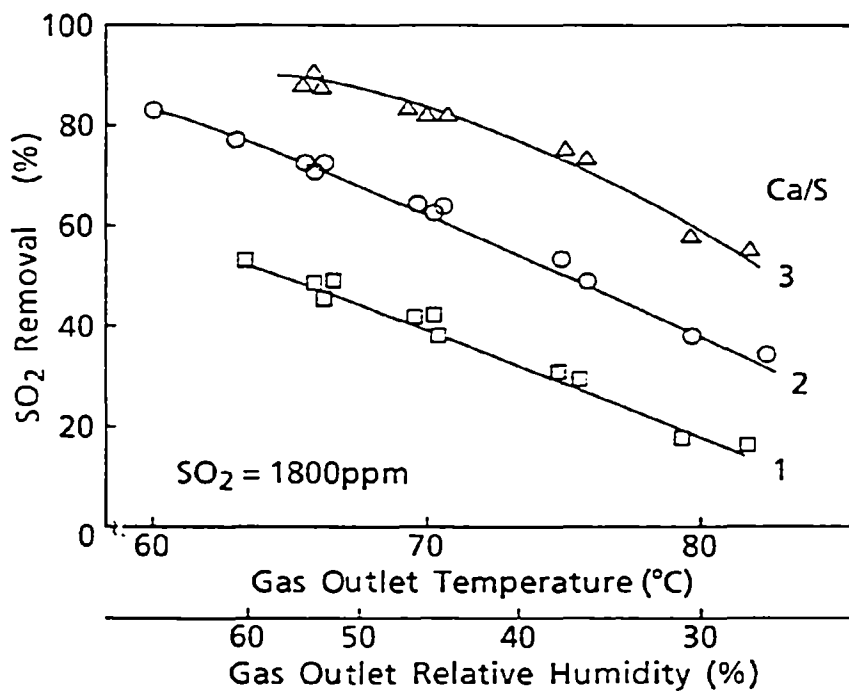


Figure 7. Effect of Reactor Outlet Gas Temperature and Relative Humidity on SO_2 Removal

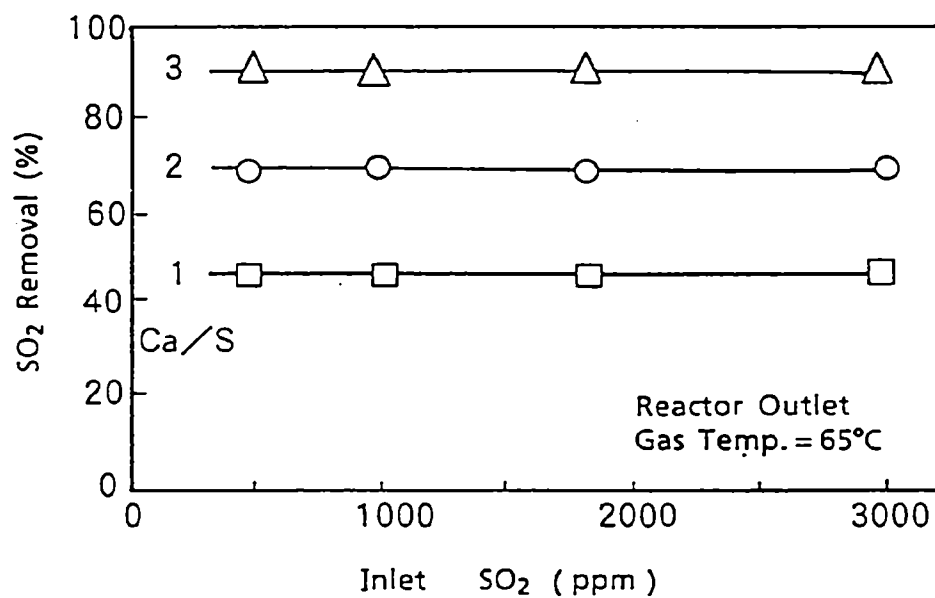


Figure 8. Effect of Reactor Inlet SO₂ Concentration on SO₂ Removal

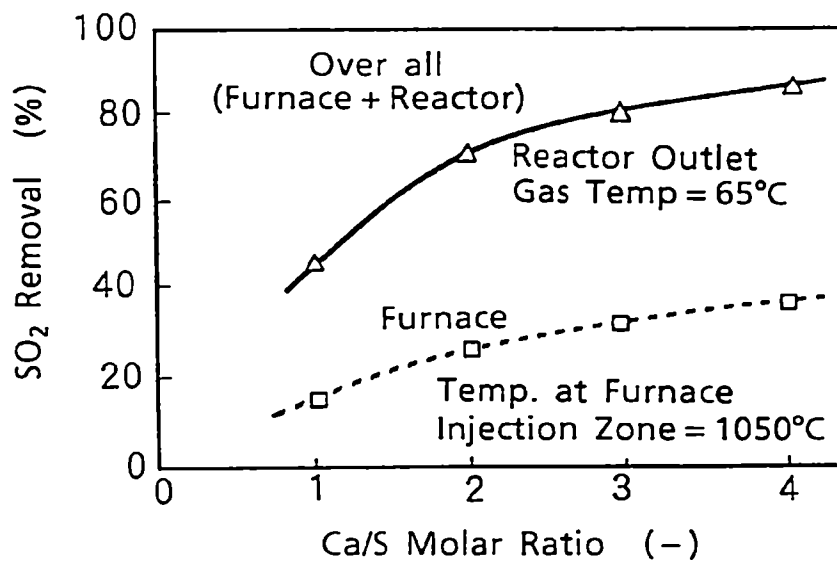


Figure 9. Overall SO₂ Removal in FLI Process and SO₂ Removal in Furnace

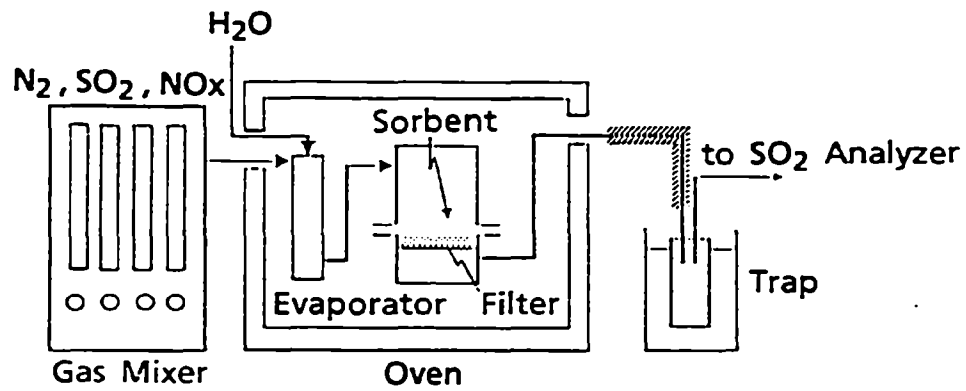


Figure 10. Flow Sheet of Fixed Bed Reactor

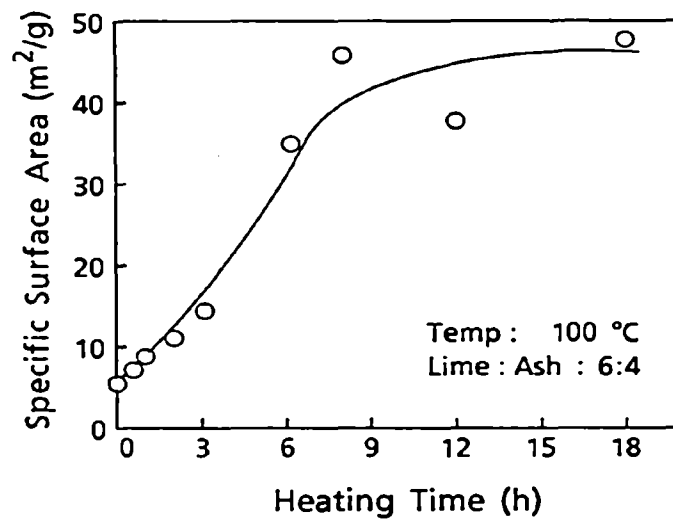


Figure 11. Specific Surface Area of Sorbent as a Function of Heating Time

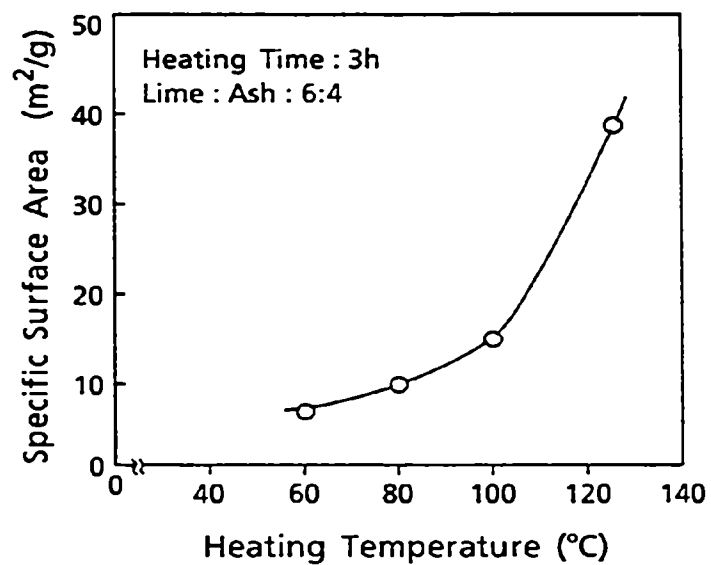


Figure 12. Specific Surface Area of Sorbent as a Function of Heating Temperature

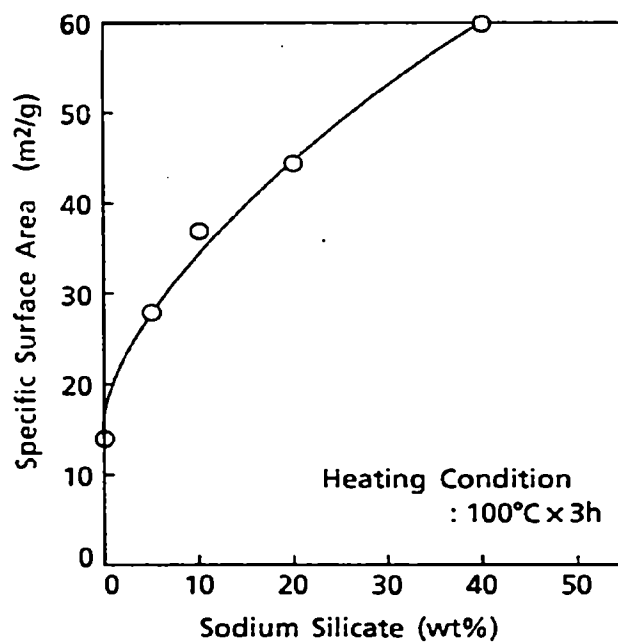


Figure 13. Relationship between Amount of Sodium Silicate and Specific Surface Area

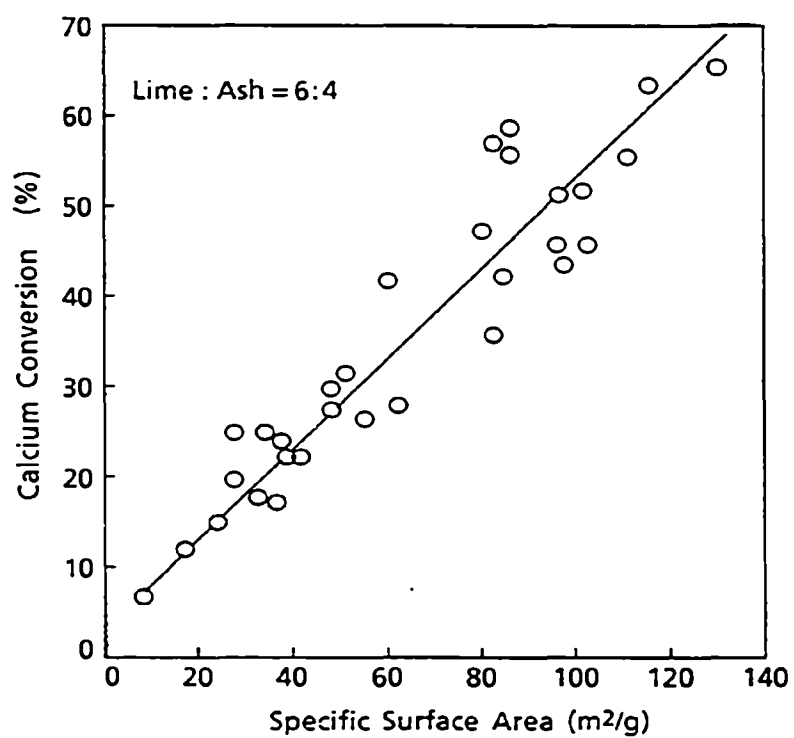


Figure 14. Relationship between Specific Surface Area and Reactivity of Sorbent

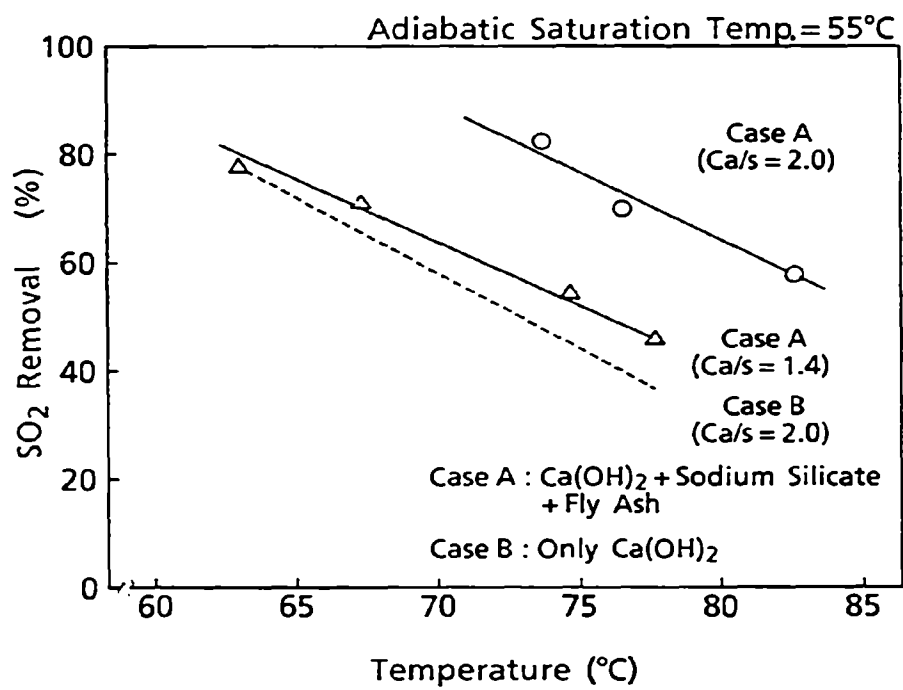


Figure 15. Relationship between Reactor Outlet Gas Temperature and SO₂ Removal

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**CLEAN COAL TECHNOLOGY
OPTIMIZATION MODEL**

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ABSTRACT

Title IV of the Clean Air Act Amendments (CAAA) of 1990 contains provisions for the mitigation of acid rain precipitation through reductions in the annual emission of the acid rain precursors of sulfur dioxide (SO_2) and nitrogen oxide (NO_x). These provisions will affect primarily existing coal-fired power-generating plants by requiring nominal reductions of 5 million and 10 million tons of SO_2 by the years 1995 and 2000, respectively, and 2 million tons of NO_x by the year 2000 relative to the 1980 and 1985-87 reference period.

The 1990 CAAA Title IV provisions are extremely complex in that they establish phased regulatory milestones, unit-level emission allowances and caps, a mechanism for inter-utility trading of emission allowances, and a system of emission allowance credits based on selection of control option and timing of its implementation. The net result of Title IV of the 1990 CAAA is that approximately 147 gigawatts (GW) of generating capacity is eligible to retrofit SO_2 controls by the year 2000.

A number of options are available to bring affected boilers into compliance with Title IV. Market share will be influenced by technology performance and costs. These characteristics can be modeled through a bottom-up technology cost and performance optimization exercise to show their impact on the technology's potential market share. Such a model exists in the form of an integrated data base-model software system. This microcomputer (PC)-based software system consists of a unit (boiler)-level data base (ACIDBASE), a cost and performance engineering model (IAPCS), and a market forecast model (ICEMAN).

INTRODUCTION

Title IV of the Clean Air Act Amendments (CAAA) of 1990 contains provisions for the mitigation of acid rain precipitation through reductions in the annual emission of the acid rain precursors of sulfur dioxide (SO₂) and nitrogen oxide (NO_x). These provisions will affect primarily existing coal-fired power-generating plants by requiring nominal reductions of 5 million and 10 million tons of SO₂ by the years 1995 and 2000, respectively, and 2 million tons of NO_x by the year 2000. These reductions are relative to the 1980 and 1985-87 baseline regulatory period. The resulting emission cap will be held constant, thus requiring additional removals in response to load growth.

The 1990 CAAA Title IV provisions are extremely complex in that they establish phased-in regulatory milestones, unit-level emission allowances and caps, a mechanism for inter-utility trading of emission allowances, and a system of emission allowance credits based on selection of control option and timing of its implementation. The net result of Title IV of the 1990 CAAA is that approximately 147 gigawatts (GW) of generating capacity is eligible to retrofit SO₂ controls by the year 2000.

A number of options are available to bring affected boilers into compliance with Title IV. Market share will be influenced by technology performance and costs. These characteristics can be modeled through a bottom-up technology cost and performance optimization exercise to show their impact on the technology's potential market share. Such a model exists in the form of an integrated data base-model software system designated as the Control Technology Optimization Model. This integrated data base-model set is a microcomputer (PC)-based software system developed specifically for the application of flue gas cleanup (FGC) and clean retrofit and repowering technologies to coal-fired utility boilers.

DESCRIPTION

The integrated PC-based software system (Control Technology Optimization Model) consists of a unit (boiler)-level data base (ACIDBASE), a cost and performance engineering model (IAPCS), and a market forecast model (ICEMAN). Each component in the software system is described in the following subsections in order of progression in the software system.

ACIDBASE

ACIDBASE is a boiler-level data system that contains information for domestic fossil-fuel-generating units for the record years of 1985 to 1987. ACIDBASE provides a separate data file for each individual record year of 1985, 1986, and 1987. These separate record year files are united through internal programming to form a 1985 to 1987 composite derivative data base known as "BASELINE." The BASELINE data base was created to provide information for the 1985 to 1987 reference ("baseline") regulatory period specified in the 1990 CAAA. The BASELINE data system is the "run version" of ACIDBASE that is mated to the rest of the components in the integrated software system.

ACIDBASE originated largely from a number of public domain data bases that exist primarily (but not exclusively) in computerized form. Specifically, information was extracted from Department of Energy (DOE) Environmental Impact Assessment (EIA) Form 767 (Annual Steam Electric Utility Design and Operation Report), the DOE Federal Energy Regulatory Commission (FERC) Form 1 (Annual Report of Public Electric Utilities, Licensees, and Others), DOE EIA Form 412 (Annual Report of Public Electric Utilities), DOE FERC Form 423 (Cost and Quality of Fuels), DOE EIA Form 860 (Annual Electric Generator Report), and DOE Flue Gas Desulfurization Information System (FGDIS). Supplemental information was also obtained from a number of noncomputerized sources: McGraw-Hill's Electric Utility World and the National Coal Association's Steam Electric Plant Factors.

Using the computerized public domain data bases as the primary sources of information, computer tapes of the 1985 through 1987 annual filings for the various data systems were obtained, downloaded, ported into the PC environment, quality checked for data completeness and accuracy, and stored in a PC-based data base management system.

A schematic showing the origination and organization of ACIDBASE is provided in Figure 1. A listing of the data elements contained in ACIDBASE is shown in Figure 2.

INTEGRATED AIR POLLUTION CONTROL SYSTEM

The Integrated Air Pollution Control System (IAPCS) cost engineering and performance model was developed to estimate the costs and predict the performance of SO₂, NO_x, and particulate matter (PM) emission control systems for coal-fired utility boilers. This computerized model includes conventional and emerging technologies that effect pre-, in situ, and post-combustion emission control. The model can accept any combination of the technology "modules" built into the system. Interactions are reflected in a material balance tabulation at the exit of each module. Alterations in material balance are used to account for integrated performance and cost effects. The emission control technologies contained in IAPCS can be selected in either "isolated" (single technology) or "integrated" (multiple technology) configurations. The power of IAPCS lies in its ability to reflect integrated effects of various control configurations. This allows the analyst to identify synergistic interactions and thus optimize performance and cost in terms of integrated cost-effectiveness.

The IAPCS performance and cost-estimating computer model includes both conventional and emerging flue gas cleanup and clean coal technologies (Table 1). The model accepts any combination of these technologies. Output from the model reports reductions in SO₂, NO_x, and PM emissions and associated capital, annual, and cost-effectiveness values (dollars per ton of pollutant removed across the *entire* emission control system).

A unique and important feature of the model is the parameter files. As each module was developed, the important design, cost, and performance parameters (i.e., cost and performance drivers) were included in a parameter file. These parameters are assigned default values that may be changed by the user for a given application. The parameter file is designed to permit the user to modify the important values to reflect those of choice or need.

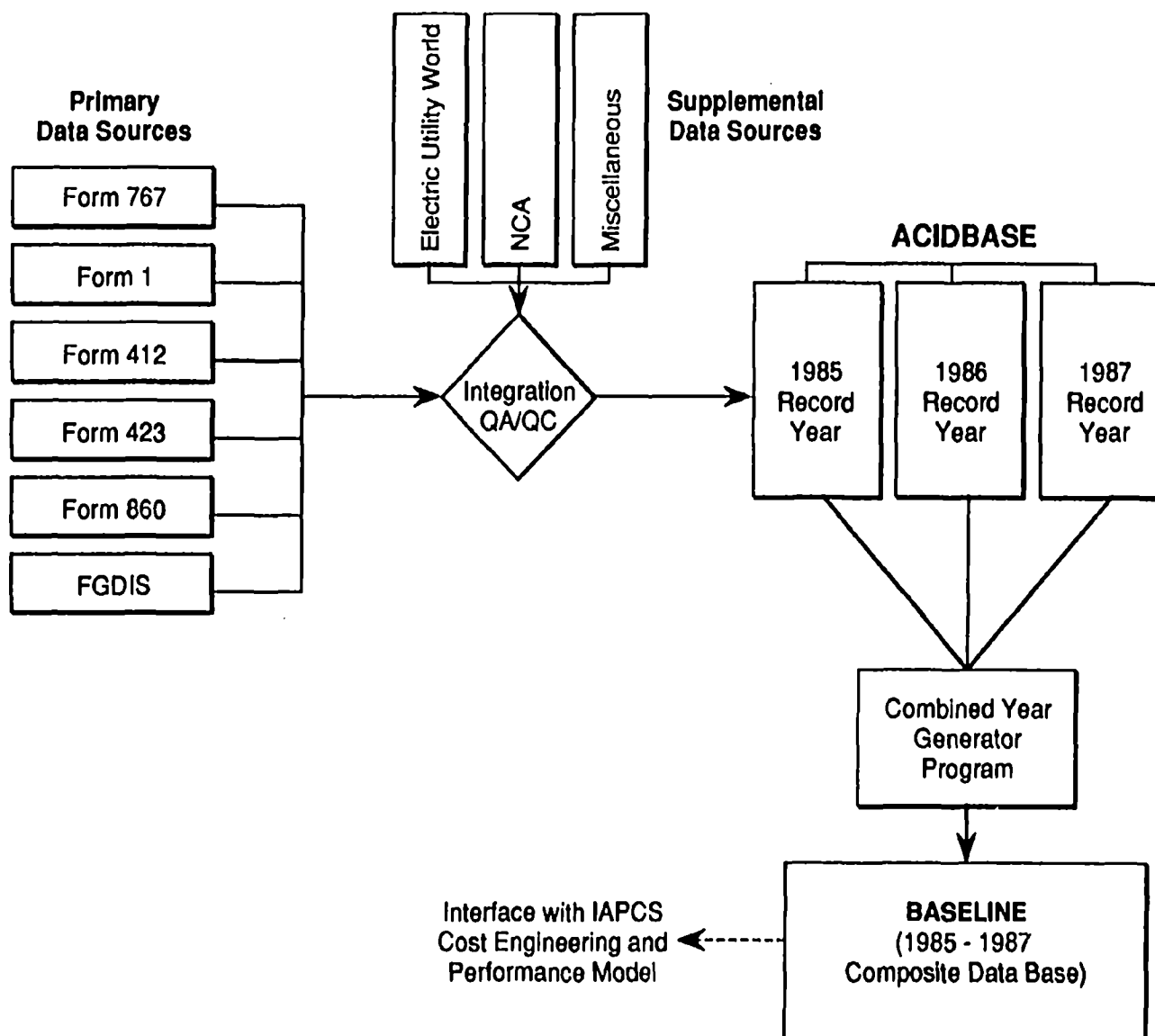


Figure 1. Origination and organization of Acidbase.

Descriptive	Fuel
Oris code	Coal rank
Utility	Heat content
Plant	Sulfur content
State	Pyritic sulfur
Unit No.	Organic sulfur
Boiler No.	Sulfate sulfur
Service date	Ash
Status	Moisture
Geographic regions	Volatile matter
	Fixed carbon
	Chlorine
	Ash alkalinity
	Pyritic sulfur
	Ferrous oxide percent
	Sodium oxide
Boiler	
Nameplate rating	
Net dependable capability	
Summer capability	
Winter capability	
Boiler supplier	
Draft type	
Firing type	
Firing configuration	
Burner type	
Bottom type	
Furnace type	
Furnace depth	
Furnace width	
Furnace height	
Boiler roof-nose	
Boiler bottom-nose	
Furnace plan area	
Boiler special conditions	
Multiple fuel	
Gas availability	
Coal rate	
Coal consumption	
Heat rate	
Capacity factor	
Load profile	
Heat input	
Steam rate	
Steam temperature	
Steam pressure	
Steam cycle	
	Emission Controls
	Gas flow rate
	Gas temperature
	SO ₂ standard
	NO _x standard
	PM standard
	PM collector service date
	PM collection application
	PM type
	PM design
	PM removal
	ESP collection area
	Fabric filter AC ratio
	SO ₂ control service date
	SO ₂ control application
	SO ₂ control type
	SO ₂ control design
	SO ₂ emission rate
	NO _x control application
	NO _x control type
	NO _x control design
	NO _x emission rate
	Acid emissions
	Acid emission rate

Figure 2. Acidbase data elements.

Table 1

IAPCS CONTROL TECHNOLOGY MODULES

<u>Category</u>	<u>Technology</u>	<u>Process</u>
Precombustion	Coal supply options (CSO)	Coal substitution/blending (CS/B) Physical coal cleaning (PCC)
In situ	Low-NO _x combustion (LNC)	Low excess air Overfire air (OFA) Low-NO _x burner (LNB) Low-NO _x concentric firing (LNCFS)
	Limestone injection multistage burner (LMB)	Furnace sorbent injection
	Reburning (NGR)	Natural gas
	Natural gas substitution (NGS)	Natural gas
Postcombustion	Selective catalytic reduction (SCR)	Hot-side
	NOXSO	Coal Natural gas
	Gas conditioning (GC)	SO ₃ Spray humidification
	Dry sorbent injection (DSI)	Nahcolite Trona
	Lime spray drying (LSD)	Spray dryer absorber (SDA) Duct spray drying (DSD)
	Electrostatic precipitator (ESP)	Cold-side
	Fabric filter (FF)	Reverse-air
	Flue gas desulfurization (FGD)	Lime/limestone
Plant	Life extension (LE)	Reboiling Refurbishment
	Demolition and decommissioning (D/D)	Atmospheric FBC (AFBC)
	Repowering	Pressurized FBC (PFBC) Integrated gasification combined cycle (IGCC)

A brief synopsis of IAPCS's capabilities, describing input features, processing, and output reports is summarized below:

- Inputs are provided in either interactive (single-record run) or batch (multiple-record run) modes. The batch mode accesses boiler records through the BASE-LINE data base.
- The model incorporates the basis and format of cost estimation used by the Electric Power Research Institute (EPRI).^{*} The capital cost is built "bottom-up" from calculated process conditions based on user inputs, estimating direct capital costs by process area, which include both direct and indirect costs. The annual cost is also built "bottom-up," estimating fixed and variable operating and maintenance costs and annual carrying charges.
- Several of the files and routines are "system-wide" (i.e., not limited to one particular control technology module). These system-wide features are an important aspect of the model's integrated operation. They include emission calculations, boiler performance, fans, waste disposal, and economic/financial files.
- The model provides the user with the following reports: user input summary, module-specific output, boiler performance, material balance, emission reduction, and costs.
- At the initiation of a run, the user can "optimize" a selected control system. A target emission rate (in lb/10⁶ Btu) may be entered, and the system performance and costs will be run automatically. This optimization routine allows the user to alter the effective efficiency of a chosen control device through bypassing a fraction of the gas stream or by changing the capture efficiency by altering its design and operating parameters.
- The model is designed on a modular basis. This permits a control module in the run stream to pass on its altered conditions to any succeeding module(s) in the downstream flue gas path. These data are then used to generate the design and performance characteristics and cost estimates. The architecture of a modular program is such that it offers the user the greatest flexibility for revising any existing control technology and for adding technologies.

ICEMAN

The IAPCS Cost Effectiveness Maximization Analysis (ICEMAN) model is a market forecast model that selects least-cost technology solutions over time per conditions imposed by the user. A least-cost solution is based on cost-effectiveness of dollars per ton (\$/ton) of pollutant (SO₂/NO_x) removed. Conditions imposed by the user include technology slate, target

^{*} TAG--Technical Assessment Guide, Volume 1: Electricity Supply--1989. EPRI P-6587-L, Volume 1: Rev. 6, Special Report, September 1989.

global (i.e., tons per year) and unit-level (i.e., lb per 10^6 Btu) emission reduction rates, and time horizon (i.e., year or years of analysis extending from 1995 to 2030).

ICEMAN is a postprocessing computer program that is slaved to IAPCS for its input data. Although ICEMAN exists as a separate and independent software system, it cannot function without IAPCS located upstream to provide input data requirements. Moreover, since ICEMAN processes a vast array of records (multiple boiler-multiple technology combinations), IAPCS must be run in a "batch" mode, which requires that the BASELINE data base be situated upstream of IAPCS, providing input data requirements.

ICEMAN accepts output from IAPCS for the boiler population-technology slate case under consideration. The output from IAPCS contains information needed by ICEMAN for processing (cost—capital, annual, and cost-effectiveness and performance—SO₂ and NO_x removed). ICEMAN processes the file to satisfy the global emission target selected by the user. ICEMAN's first pass through the data set selects the most cost-effective technologies across the *entire* boiler population set and sums the corresponding SO₂ (or NO_x) tonnage. The selection process proceeds from the most cost-effective technology-boiler value in the *entire* data set to the least cost-effective value (i.e., lowest numerical \$/ton value to highest numerical \$/ton value). The summed SO₂ (or NO_x) tonnage is dynamically compared with the preselected global emission reduction target. When convergence is achieved (i.e., the summed tonnage satisfies the preselected target), the process stops and results are reported. If convergence is not achieved on the first pass, ICEMAN makes another pass through the data set until convergence is achieved. In simplistic terms, the most cost-effective value not selected in the first pass (in the *entire* data set) is selected and "tested." The test determines if the second pass selection provides more SO₂ (or NO_x) removal than the first pass selection. If yes, the second pass value is retained and the first value is discarded and the new sum value is compared with the preselected target value for convergence. If no, the first pass value is retained and the process continues with the next most cost-effective value in the *entire* data set. This process continues in systematic fashion until convergence is achieved. The process then stops and results are reported.

ICEMAN assigns one technology "solution" to each boiler that is selected in the convergence process. The final result is that each selected boiler is assigned one technology.

ICEMAN also features the ability to forecast over time. This option allows the user to select a time horizon over which emissions are kept constant as a function of a user-provided emission cap. In effect, ICEMAN "holds" selections and makes new selections as the time horizon is changed. For example, this feature allows ICEMAN to prepare market forecasts under conditions of a fixed SO₂ emission cap beyond the year 2000 Phase II regulatory milestone.

SNRB CATALYTIC BAGHOUSE PROCESS DEVELOPMENT AND DEMONSTRATION

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ABSTRACT

The SO_x-NO_x-Rox Box™ (SNRB) process is a Babcock & Wilcox (B&W) patented advanced air pollution control system that provides for significantly reduced SO_x, NO_x, and particulate emissions from coal-fired boilers. The process utilizes a high-temperature catalytic baghouse for the integration of SO_x reduction through the injection of an alkali sorbent such as hydrated lime or sodium bicarbonate, NO_x removal through ammonia injection and selective catalytic reduction, and particulate collection. The advantages of the process include: compact integration of the emission control technologies into a single component, dry sorbent and by-product handling, and improved SCR catalyst life due to lowered SO_x and particulate levels.

The basic SNRB concept has been developed over a period of several years at B&W through a series of pilot-scale research programs initiated in 1979. This successful pilot evaluation of emission control performance of the concept led to selection of the technology for demonstration in the second round of the U.S. Department of Energy (DOE) Innovative Clean Coal Technology Demonstration Program. The current project focuses on the design, installation, and operation of a 5-MW_e equivalent SNRB facility at the Ohio Edison R. E. Burger Plant. Installation of the demonstration facility has been completed and startup activity is underway. The demonstration will be used to generate information for commercialization of the SNRB technology.

INTRODUCTION

B&W's patented SO_x-NO_x-Rox-Box process - also known as SNRB - has been developed to provide boiler operators with a cost-effective way to simultaneously control their emissions of the oxides of sulfur (SO_x) and nitrogen (NO_x), and particulate matter (Rox). Briefly, the process (shown in Figure 1) comprises the injection of both ammonia and dry sorbent upstream of a fabric filter (baghouse). A catalyst for the selective catalytic reduction (SCR) of NO_x is installed inside the filter bags, providing for the destruction of NO_x as the flue gas/ammonia mixture passes over the catalyst. SO_x is absorbed by the sorbent both in the flue gas duct, and as the sorbent resides on the filter bags in the baghouse. Since the SO_x and NO_x removal processes require operation at elevated gas temperatures (550° - 900°F), specially woven high-temperature fabric filter bags are used.

Through the integration of the SO_x, NO_x, and particulate removal processes into a single unit, lower capital cost and space requirements are achieved, and operating procedures are simplified, when compared to a combination of conventional emissions control system comprising separate wet scrubber, SCR, and particulate removal systems.

B&W is currently conducting a multi-phase project funded by the U.S. Department of Energy (DOE) - PETC, the Ohio Coal Development Office (OCDO), and the Electric Power Research Institute (EPRI) under the DOE's Innovative Clean Coal Technology program. The objective of the B&W project is to continue the commercial development of the SNRB concept in a 5-MW_e field demonstration unit at Ohio Edison's R. E. Burger plant located near Shadyside, Ohio. Other members of the project team include Ohio Edison (host utility), Norton Company (catalyst supplier), and Minnesota Mining and Manufacturing - 3M (bag supplier). The minimum emission control targets for the project include the cost-effective reduction of SO_x, NO_x, and particulate emissions in the following manner:

- 70% SO_x removal
- 90% NO_x removal
- Particulate emissions in compliance with the New Source Performance Standards (NSPS) - 0.03 lb/million Btu

Phase I - Design and Permitting - of the program involved the development

of a detailed engineering design for the 5-MW_e SNRB facility, and the preparation of the required environmental and permitting documents. The design activities were supported by the operation of a 1500 ft³/minute SNRB laboratory pilot unit located at B&W's research center in Alliance, Ohio. Installation of the 5-MW_e facility was completed under Phase II - Procurement, Installation, and Startup. Following startup and shakedown activities in late 1991, full operation of the facility will begin in early 1992. A 7-month testing program will follow, wherein detailed operating and performance data will be generated over a wide range of operating conditions. The test work will be conducted as part of Phase III - Demonstration Operation and Restoration - of the program. Phase III will include a detailed engineering and economic analysis of the integration of the technology into an existing boiler plant. This paper is intended to provide a summary of the status of the development of the SNRB technology.

SNRB PROCESS DESCRIPTION

The SNRB process comprises a single process unit - a pulse-jet fabric filter (baghouse) - located upstream of the boiler's combustion air preheater and operating at a temperature 550° - 900°F. One possible arrangement of the SNRB process applied to a utility boiler system is illustrated in Figure 2. A specially woven ceramic fabric is used for the fabrication of the filter bags to permit reliable baghouse operation at these elevated temperatures. Absorption of SO_x is accomplished through the injection of a finely divided dry alkali sorbent into the flue gas stream upstream of the baghouse. The SO_x in the flue gas reacts with the sorbent while the latter is dispersed in the flue gas stream as it flows through the ductwork and baghouse, and while it resides on the filter bags in the form of filter cake. A catalyst for the selective catalytic reduction (SCR) of NO_x is installed inside the filter bags - the clean side of the bags in a pulse-jet baghouse. By injecting ammonia into the flue gas upstream of the baghouse, NO_x is converted to harmless N₂ and H₂O as the gases pass over the catalyst. Particulate matter - fly ash and spent sorbent - is removed as the flue gas passes through the filter bags. Calcium-based sorbents such as calcium hydroxide (hydrated lime) will generally provide the most cost-effective approach for SNRB applications in the eastern United States. These sorbents require baghouse operating temperatures near 850°F for optimal SNRB SO_x removal performance. Typically, flue gas temperatures at the outlet of the economizer are lower than

850°F. Therefore, it may be necessary to remove some economizer heat transfer surface from service to obtain the desired baghouse operating temperature. Detailed analysis of the integration of SNRB with the existing boiler design will be required to optimize overall steam cycle efficiency.

Sodium-based sorbents such as sodium bicarbonate (NaHCO_3) may be the preferred approach for the application of SNRB in the western U.S. where natural deposits of these materials occur. Baghouse operating temperatures in the range of 500° - 800°F will be used for these systems. If maximum NO_x removal performance (90+%) is needed, the lower operating temperature of the SNRB baghouse for sodium applications may result in the need to use a promoted SCR catalyst for NO_x removal in these systems. The higher sorbent costs may be offset by the use of less-expensive bag fabrics at the lower temperatures.

The SO_x - NO_x -Rox Box process has several potential benefits:

- **One Major Component.** Capital cost and space requirements are reduced by performing the SO_x , NO_x , and particulate removal operations in a single piece of equipment.
- **Longer Catalyst Life.** SO_x and particulates are removed from the flue gas stream upstream of the SCR catalyst, minimizing catalyst poisoning, pluggage, and erosion concerns.
- **Dry Materials Handling.** Reagent preparation, handling, and disposal costs are minimized because both the fresh sorbent and waste streams are dry.
- **"Unpromoted Catalyst."** The SCR catalyst used for calcium-based SNRB systems can be an unpromoted zeolite material. This avoids the potential hazardous waste disposal concerns associated with promoted catalysts containing metals such as vanadium.
- **No Flue Gas Reheat Required.** NO_x removal upstream of the boiler air heater eliminates the need for flue gas reheat for optimal NO_x removal performance, as is required in many conventional SCR systems.
- **Increased Boiler Thermal Efficiency.** The SNRB process is one of the few SO_x removal processes offering the potential for a decrease in plant net heat rate due to the removal of SO_3 upstream of the air heater - virtually eliminating acid dew point concerns in the combustion air preheater.

PROCESS DEVELOPMENT WORK AT B&W

Development of the SNRB process began at B&W in 1979 when a series of laboratory screening tests was performed to evaluate the applicability of a variety of materials to the catalytic reduction of NO_x . Materials such as fly ash, transition metals, and a Norton Company zeolite catalyst were evaluated. Development work then proceeded through a series of pilot-scale test programs conducted in baghouses ranging in size from 350 $\text{ft}^3/\text{minute}$ to 3000 $\text{ft}^3/\text{minute}$. It was at this point that 3M's Nextel™ ceramic fiber was identified as a potential material for fabrication of the high temperature bags. Nextel can be used on a continuous basis at temperatures up to 1400°F, with brief temperature excursions up to 2200°F. These in-house development programs eventually led to two OCDO-sponsored testing programs wherein the process concept was further refined, and preliminary performance data was obtained (1).

The successful early pilot test results were used to pursue funding under the DOE Innovative Clean Coal Technology Development Program. In 1989, a proposal was accepted by DOE and OCDO for demonstration of the technology on a larger, intermediate-scale pilot facility. Additional laboratory pilot testing under this program has been completed in support of the design of a 5-MW_e demonstration facility (2,3). Erection of the demonstration facility was completed in September 1990. A preliminary economic analysis based on the laboratory pilot results has been completed to help focus the testing activity in the demonstration facility. The facility will be operated to assess the commercial readiness of the SNRB technology.

LABORATORY PILOT TEST RESULTS

In the early test programs, it was not possible to evaluate a full-size, integrated bag/catalyst arrangement. The bags used in the 3000 $\text{ft}^3/\text{minute}$ baghouse were 4 inches in diameter and 10 feet long, whereas a commercial bag is more likely to be 6-1/4 inches in diameter and 20 feet long. The catalyst was also located in the exhaust plenum of the baghouse, as opposed to being integrated into each filter bag assembly. Since both of these design features could have a significant impact on bag cleanability, the inability to assess these factors was a serious limitation of the early pilot test programs.

Further, the effect on SO_x removal performance of sorbent injection into or upstream of the boiler economizer could not be fully evaluated. In a typical commercial, calcium-based SNRB application, the sorbent will be injected ahead of, or into, the boiler economizer. While passing through the economizer, the flue gases, and hence the sorbent, experience a sharp drop in temperature as heat is extracted. It was anticipated that the time-temperature history of the sorbent could have a significant impact on the SO_x removal process, but the equipment used for the earlier tests did not lend itself to a comprehensive evaluation of these effects. Therefore, while these earlier tests provided encouraging results, it was concluded that additional SNRB laboratory pilot tests were necessary to support the design of the 5-MW_e field demonstration facility.

The primary objective of the most recent series of SNRB laboratory pilot tests was to develop design, operating, and performance specifications for the 5-MW_e field demonstration facility. The major issues addressed included the:

- Performance and operability of commercial-size, integrated bag/catalyst arrangements
- Effect of economizer injection on SO_x removal performance
- SO_x and NO_x removal performance
- Compatibility of the SO_x and NO_x removal processes
- Particulate and NH₃ emissions downstream of the baghouse.

The results of these tests also provided information needed to support a preliminary economic evaluation of the SNRB process.

A schematic of the SNRB laboratory pilot-scale test facility is illustrated in Figure 3. The facility is comprised of a pulverized coal-fired test furnace (5-million Btu/hr thermal input), insulated ductwork, sorbent and ammonia injection systems, a heat exchanger to simulate a utility boiler economizer, a high-temperature SNRB baghouse, and an ID fan. The baghouse contained 12 commercial-size fabric filter bags - 6-1/4 inches in diameter and 20 feet long - yielding an overall collection area of approximately 375 ft². The 1500 ft³ (actual)/minute baghouse was equipped with an on-line pulse-jet cleaning system. The cleaning cycle was initiated by a set-point limiting the differential pressure across the baghouse.

High-temperature, woven, 3M Nextel™ bags were used along with an unpromoted zeolite SCR catalyst from the Norton Company. The catalyst was incorporated into each bag filter assembly.

The heat exchanger used to simulate a utility boiler economizer was a water-cooled, natural convection unit equipped with three independent banks of water-cooled tubes. By varying the number of banks in service, various time-temperature profiles and baghouse inlet temperatures were investigated. The sorbent injection system consisted of a solids feeder, air eductor, and injection nozzle. Sorbent injection was performed at various locations to investigate the effect of residence time at the injection temperature. Two sorbent injection points were located upstream of the simulated economizer. The third was downstream of the economizer, but upstream of the baghouse. Ammonia vapor from a cylinder was diluted with air before being injected into the flue gas upstream of the baghouse.

An Ohio #8 coal containing 2.5 - 4.0% sulfur was fired to produce a flue gas containing 1500 - 2500 ppm SO₂, 600 - 800 ppm NO_x, and 3 - 4% O₂. The coal was selected to be representative of the coal burned at Ohio Edison's R. E. Burger Plant, thereby simulating expected flue gas conditions in the 5-MW_e facility. The desired flue gas operating temperature was obtained by mixing flue gas extracted from two different locations in the water-cooled convection pass of the test furnace. SO₂, NO_x, and O₂ concentrations in the flue gas were continuously monitored at the furnace outlet (before sorbent and NH₃ injection), baghouse inlet, and baghouse outlet. Tests were typically conducted over a 3 to 4-hour period to ensure steady-state test conditions.

Testing was conducted over a range of operating conditions. Major operating parameters varied during the test program included sorbent injection and baghouse operating temperatures, Ca/SO_x and NH₃/NO_x stoichiometries, and sorbent residence times. The laboratory pilot results are briefly summarized in the following three sections.

Particulate Emissions

Woven, seamless bags fabricated of 3M Nextel™ ceramic fibers were used for particulate collection. One of the key objectives of the laboratory pilot tests was to demonstrate, on a continuous basis, particulate emissions in

compliance with the NSPS requirement of 0.03 lb/million Btu. Of particular concern was the cleanability of the fully-integrated bag/catalyst assembly. Figure 4 illustrates the particulate removal results achieved throughout the SNRB laboratory pilot test program. Particulate emissions were determined using both the EPA Method 5 and 17 sampling techniques. As shown in the figure, particulate emissions less than 0.03 lb/million Btu were achieved for the majority of tests. Of equal importance was the fact that the bags could be repeatedly and reliably cleaned using conventional pulse-jet baghouse cleaning technology. The data collected after mid-December were obtained after the fabric filter bags had been removed from the baghouse. It is believed that some of the bags were damaged during their re-installation, leading to the higher particulate emission measured during the subsequent tests. The data points shown in February were obtained during tests with a low-sulfur coal, where inlet dust loadings were much lower than for the Ohio #8 coal tests.

NO_x Removal

The primary NO_x-related objective of the laboratory pilot tests was to determine the design and operating specifications required to achieve at least 90% NO_x removal. Of particular concern were the design of the catalyst and bag/catalyst supports, the required catalyst temperature and ammonia stoichiometry, and the amount of ammonia "slip". The NH₃/NO_x stoichiometry is defined as the molar ratio of injected ammonia to the NO_x in the flue gas, and ammonia slip refers to the amount of unreacted ammonia passing through the SNRB system and exiting the stack. To achieve this objective, the NH₃/NO_x ratio and catalyst temperature were varied over a range of operating conditions to maximize NO_x reduction and minimize NH₃ slip. The catalyst design — shape, formulation, and space velocity (flue gas flow rate divided by catalyst volume) — was also investigated during the tests.

The effect of NH₃/NO_x ratio on NO_x removal is illustrated in Figure 5. At NH₃/NO_x stoichiometries less than 1, the NO_x removal increases from 70% to 90% as NH₃/NO_x stoichiometry increases from 0.8 to 1.0. At NH₃/NO_x stoichiometries greater than 1, NO_x removals level off. In addition, operation at these higher stoichiometry levels also results in higher emissions of unreacted NH₃. These results are also shown in Figure 5. This unreacted ammonia is primarily of concern due to the potential formation of trouble-

some ammonium bisulfate deposits as the flue gases pass through the downstream heat exchanger (air heater). At ammonia stoichiometries greater than 1.1, a sharp increase in NH_3 slip was observed. At stoichiometries lower than 1.1, NH_3 slip was typically less than 20 ppm. The catalyst design and arrangement have been modified for the field demonstration to reduce NH_3 slip.

Several tests were conducted to determine the effect of baghouse operating temperature on NO_x removal performance. The baghouse temperature was varied from 675° - 850°F to determine baghouse operating conditions for optimal NO_x removal performance. As indicated in Figure 6, NO_x removal improved with increasing baghouse temperature up to about 850°F. Operation at temperatures significantly above 850°F is not desirable due to certain irreversible changes in catalyst effectiveness. On the basis of these results, it was concluded that a baghouse temperature of 800° - 850°F was consistent with both the project goal of 90% NO_x removal, and the temperature limits set by the nature of the catalyst.

SO_x Removal

The primary SO_2 -related objective of the SNRB laboratory pilot tests was to determine the design and operating specifications required to achieve at least 70% SO_2 removal with a hydrated lime sorbent. Overall SO_2 removal performance is affected by sorbent characteristics and operating variables such as injection temperature, baghouse temperature, residence time, and calcium/sulfur (Ca/S) stoichiometry. It was of particular interest to evaluate the effect of heat extraction (via the simulated economizer) between the point of sorbent injection and the inlet of the baghouse on SO_2 removal performance. A major portion of the testing was therefore devoted to the relative amounts of SO_2 removal occurring in the ductwork and baghouse. All of the laboratory pilot tests were conducted with a single, commercially-available hydrated lime sorbent. Hence, no information was developed on the potential benefits of using other sorbent materials. Evaluation of alternative sorbents is planned for the field demonstration.

The cost of the SO_2 sorbent is a major contributor to the overall cost of operating a SNRB system. The Ca/S stoichiometry, which is defined as the molar ratio of injected $\text{Ca}(\text{OH})_2$ to SO_2 in the flue gas required to achieve the SO_2 removal goal, is thus an important operating consideration. Tests

were conducted over a wide range of stoichiometric conditions — Ca/S ranged from 1.0 to 4.0 — to determine the impact on SO₂ removal performance. As illustrated in Figure 7, it was found that above a stoichiometry of about 2.5, only slight improvements in SO₂ removal were obtained with increasing stoichiometry. The approach of recycling the spent sorbent to improve sorbent utilization was also investigated, but was found to be ineffective. The reaction of the Ca(OH)₂ and/or its derivatives with CO₂ in the flue gases — which competes with the SO₂ reaction — renders the sorbent ineffective for re-use without intermediate processing.

In order to evaluate SO₂ removal performance over a range of temperatures typical of utility boiler economizers, the sorbent injection temperature was varied from 800° — 1100°F, resulting in baghouse temperatures of 600° — 850°F. Over the range of temperatures tested, SO₂ removal was essentially independent of injection temperature. This suggests that the SO₂ removal performance of commercial SNRB systems will not be adversely affected by variations in economizer temperature within the tested range. However, while the majority of SO₂ removal occurs in the duct, additional removal in the baghouse — as the sorbent resides on the bags in the form of a filter cake — is required in order to meet the minimum goal of 70% SO₂ removal.

The effect of baghouse operating temperature on this incremental baghouse SO₂ removal is also illustrated in Figure 6. As the baghouse operating temperature increases from 730° to 840°F, the total SO₂ removal increases from 60% to 80%. The 70% sulfur removal goal is exceeded at baghouse operating temperatures above about 800°F. It is hypothesized that the incremental baghouse SO₂ removal is due to the fact that at the elevated baghouse temperatures the sorbent continues to dehydrate, thereby generating additional surface area. In the operating range of 600° — 1000°F, the rate of reaction of Ca(OH)₂ with SO₂ is essentially constant. However, SO₂ removal is also a strong function of the available surface area of the sorbent. If significant dehydration continues as the sorbent resides on the filter bags, fresh surface is generated as the water vapor finds its way out of the sorbent particles. This newly-created surface area then becomes available for subsequent reaction with SO₂.

NO_x/SO_x Removal Compatibility

Another important factor addressed by the laboratory pilot tests is the

compatibility of the SO_x and NO_x removal processes. After all, the SNRB process requires that both objectives be accomplished in the same piece of equipment. Figure 6 also illustrates the compatibility of these processes. As previously mentioned, baghouse temperatures in the range of 800° - 850°F are required to meet the NO_x removal performance goal of 90% NO_x removal. The figure illustrates that this same range of baghouse operating temperatures is required to meet the SO₂ removal goal of 70%. This important result means that the two processes can be combined into a single SNRB baghouse without sacrificing the performance of either system.

PRELIMINARY ECONOMIC EVALUATION

The laboratory pilot tests provided a mechanism for assessing the impacts of various design features and operating conditions on the overall performance of the SNRB system. This information was subsequently used to develop design specifications and testing plans for the 5-MW_e SNRB demonstration facility. A preliminary economic assessment of SNRB was also conducted in conjunction with the pilot tests to provide complementary information on the cost impacts of the various potential design, performance, and operating specifications for a commercial SNRB system. The results of this study were subsequently used to prioritize the factors to be investigated in the 5-MW_e facility and to determine what additional testing may be required.

Figure 8 provides a pictorial summary of the major factors contributing to the overall levelized cost (in \$ / ton of SO_x + NO_x removed) of operating a 500-MW_e SNRB system. The case depicted is for a calcium-based SNRB system in a new boiler application. The various costs indicated comprise all of the incremental costs associated with the presence of the SNRB system relative to those of the "base case" boiler system without the SNRB system. For example, the capital cost component identified for the baghouse is actually the incremental cost of the SNRB baghouse relative to the base case particulate collector. Likewise, the cost indicated for waste disposal is the incremental cost of waste disposal for the SNRB system relative to the fly ash disposal costs of the base case. In this regard it should be pointed out that the base case boiler system did not include SO_x or NO_x removal systems.

A detailed discussion of the economic analysis is beyond the scope of this

paper. The purpose of presenting these results is to indicate the type of information used to assess the sensitivity of the overall cost of a SNRB system to the various cost factors. In particular, the figure clearly illustrates the major influence exerted by: 1), the cost of the ceramic filter bags and 2), the cost of the SO₂ sorbent.

The design of the 5-MW_e facility and the associated test plan were therefore tailored to address the sorbent cost issue. In addition, another testing program, utilizing the SNRB laboratory pilot baghouse, has been developed to assess alternative filter bag fabrics.

TECHNOLOGY DEMONSTRATION

The commercial readiness of the SNRB technology is being evaluated through the design, construction, and operation of a 5-MW_e field demonstration facility at Ohio Edison's R. E. Burger plant. A public dedication ceremony was held at the R. E. Burger plant on May 9, 1991, and B&W Construction Company's work on the 5-MW_e facility was completed in September 1991. Operation of the facility will begin in February, 1992, and continue through September. The overall goal of the 5-MW_e tests is to develop the design, operating, and performance information needed by B&W to commercialize the SNRB technology.

The specific objective of the field demonstration tests is to optimize the SO₂, NO_x and particulate removal efficiencies during long-term operation on fully integrated, commercial-size components. A test plan has been developed to facilitate an evaluation of the key operating parameters on SO₂, NO_x and particulate removal performance. Several alternative hydrated lime sorbents, in addition to commercial hydrated lime, will be evaluated for SO₂ removal.

The cost effectiveness of the SNRB technology and the impacts of the process on auxiliary plant equipment and operation will be evaluated. The SNRB demonstration facility will allow evaluation of issues which could not be adequately addressed at the laboratory pilot scale, including:

- Performance of the fully-integrated system on a long-term basis
- Predictive performance curves for commercial applications

- Control philosophy for response to boiler load changes and upsets
- Pressure drop across the SNRB baghouse modules and bag cleaning procedures required to provide reliable, consistent long-term operation
- Catalyst deactivation (catalyst life)
- Operating costs for the system

The findings of the SNRB 5-MW_e field demonstration will be detailed in a final report. The field demonstration will also support a detailed economic and technical feasibility analysis of the technology, development of the design specifications required for a commercial-scale system, and a SNRB process control philosophy.

Features of the 5-MW_e Facility

The SNRB field demonstration facility draws a 5-MW_e (equivalent) flue gas slip stream from Boiler No. 8. The SNRB baghouse consists of six individual modules each containing 42 bag/catalyst assemblies, compared to the single laboratory pilot module which contained 12 similar bag/catalyst assemblies. It is designed to handle about 30,000 ft³/minute of flue gas at a air-to-cloth ratio of 4:1. Other major features include:

- A Bailey Network 90™ system for integrated process control
- Automated ammonia injection system
- Five sorbent injection locations
- A propane-fired heater for control of the sorbent injection temperature
- Baghouse inlet and outlet flue gas heat exchangers to permit flue gas temperatures to be accurately controlled
- Automated, pneumatic sorbent feed and ash disposal systems

A schematic of the 5-MW_e SNRB field demonstration facility is shown in Figure 9. A more detailed description of the facility is provided elsewhere (4).

Filter Fabric Development

Initial economic analysis and pilot investigations identified the critical role the filter bags will play in the technical and economic viability of the SNRB process on a commercial scale. The filter fabric assessment test program is designed to obtain extended term durability data for several alternative high temperature bag fabrics. The test will also include an evaluation of an alternative catalyst design.

The SNRB laboratory pilot baghouse was moved from B&W's Alliance Research Center to the City of Colorado Spring's Martin Drake Plant located in Colorado Springs, Colorado. Erection of the new pilot facility has been completed. The pilot baghouse will be operated continuously over at least a one-year period. Continuous operation will be interrupted periodically to permit removal and examination of selected filter bags for analysis of changes in the bag fabric characteristics over time. Intermediate results from the pilot-scale test will be used to support consideration of a possible extension of the base demonstration facility test plan in which an alternative bag fabric would be evaluated under actual SNRB operating conditions.

The pilot baghouse will draw flue gas from the economizer outlet of the 145-MW_e coal-fired boiler. Inlet flue gas temperatures are expected to range from 650° to 750°F. The baghouse will contain 12 full-scale bags (6-1/4 inches in diameter, 20 feet long). Three alternative bag fabrics, as well as alternative weave patterns, will be evaluated. A standard pulse-jet bag cleaning cycle based on tubesheet pressure drop will be maintained. The test will not involve full simulation of the SNRB process since SO₂ sorbent addition and ammonia injection will not be included. However, significant data on bag fabric durability at elevated temperatures under normal cleaning pulse flexure conditions will be obtained.

Engineering Study

The final phase of the program will include a detailed engineering study by B&W's commercial Environmental Equipment and Energy Services Divisions for the application of SNRB technology to one or more candidate commercial boilers. This study will focus on the boiler plant modifications required for integration of the SNRB technology with conventional boiler design.

Economizer modifications and combustion air preheater design and operating limitations will be specifically addressed.

SUMMARY

At baghouse operating temperatures of 800° - 850°F, the laboratory pilot tests demonstrated that:

- Particulate emissions less than 0.03 lb/million Btu are attainable with the Nextel™ filter bags.
- 90% NO_x removal can be achieved at a NH₃/NO_x stoichiometry of 0.95 - 1.05. NH₃/NO_x stoichiometry is the primary parameter affecting NO_x removal performance. Baghouse operating temperature appears to be of secondary importance.
- 70 to 80% SO₂ removal can be achieved over a Ca(OH)₂/SO₂ stoichiometry range of 2.0 - 2.5. It appears that baghouse operating temperatures of 800° to 850°F are necessary to achieve 70% SO₂ removal.

Future testing will focus on assessment of alternative bag filter fabrics and SO₂ removal performance with alternative sorbents. These two areas appear to present the greatest opportunity for reducing operating and capital costs associated with the SNRB technology.

Construction of the 5-MW_e SNRB demonstration facility has been completed. Shakedown of the process equipment and control systems is underway. Installation of the filter bags and catalyst will be completed in January 1992. Operation of this larger scale facility in 1992 will support continued efforts to commercialize the technology. Potential sites for a commercial demonstration of the technology are being pursued.

ACKNOWLEDGMENTS

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by all of these organizations is also gratefully acknowledged.

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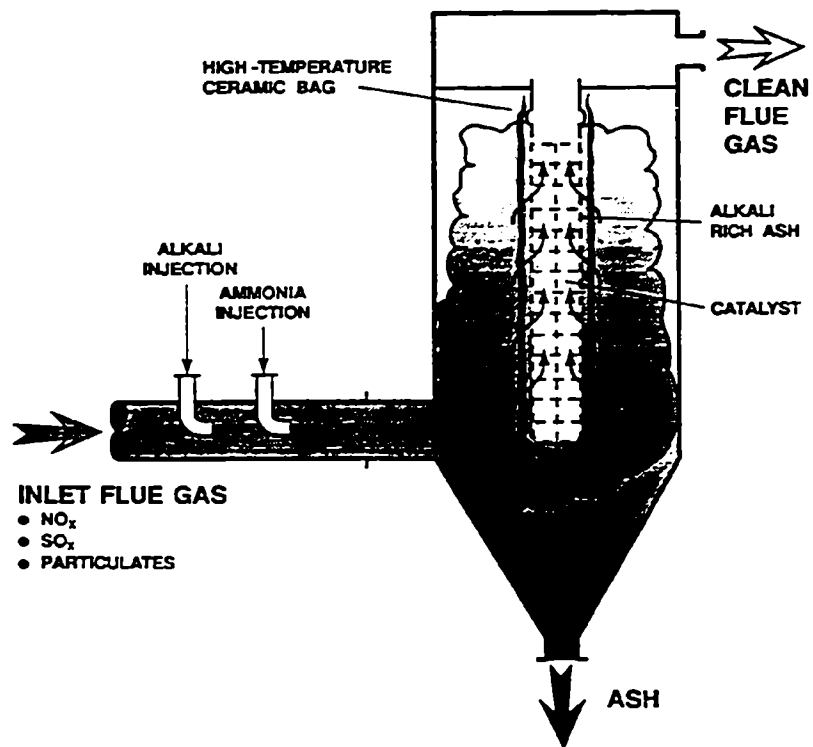


Figure 1. SO_x - NO_x -Rox Box Process

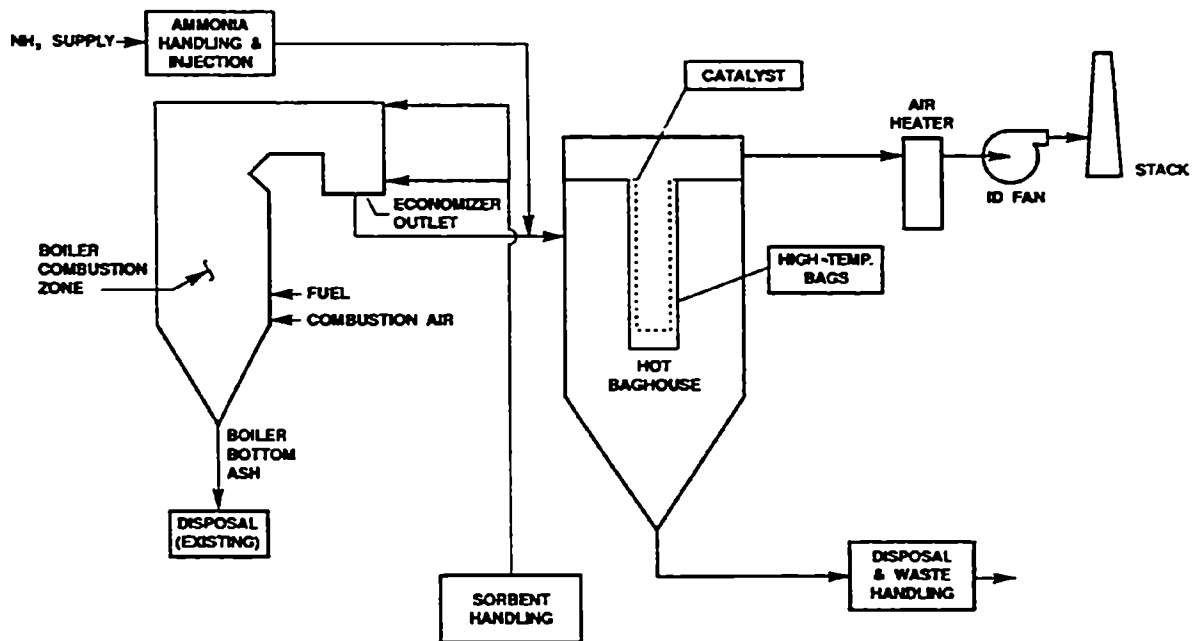


Figure 2. Commercial SNRB Application

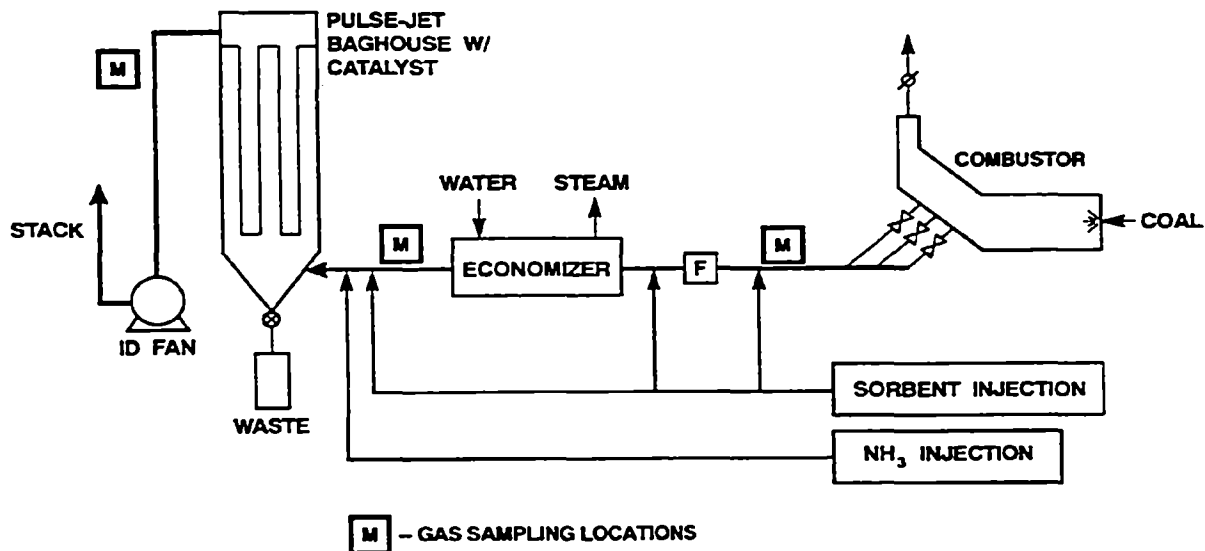


Figure 3. SNRB Laboratory Pilot Facility

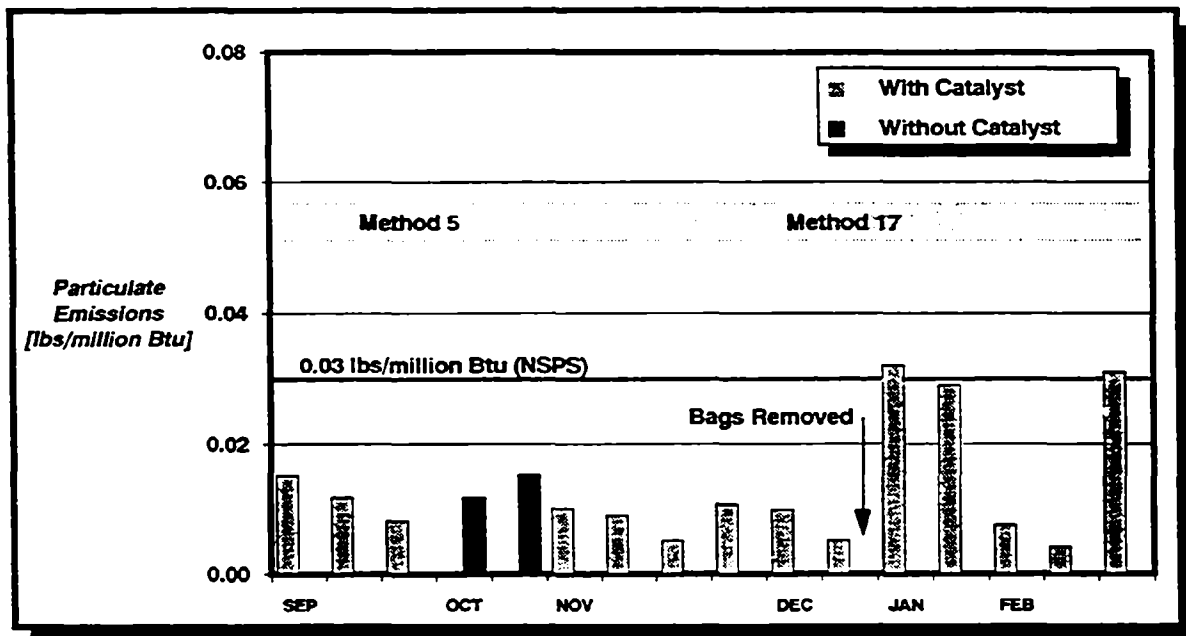


Figure 4. Particulate Emissions Results

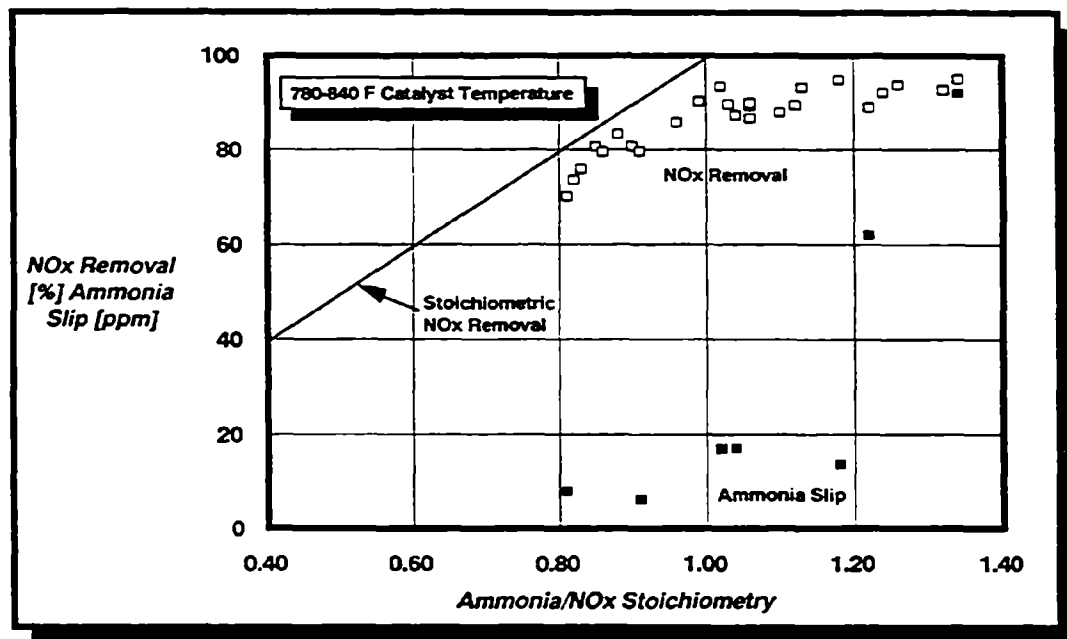


Figure 5. Effect of NH_3/NO_x on NO_x Removal Performance

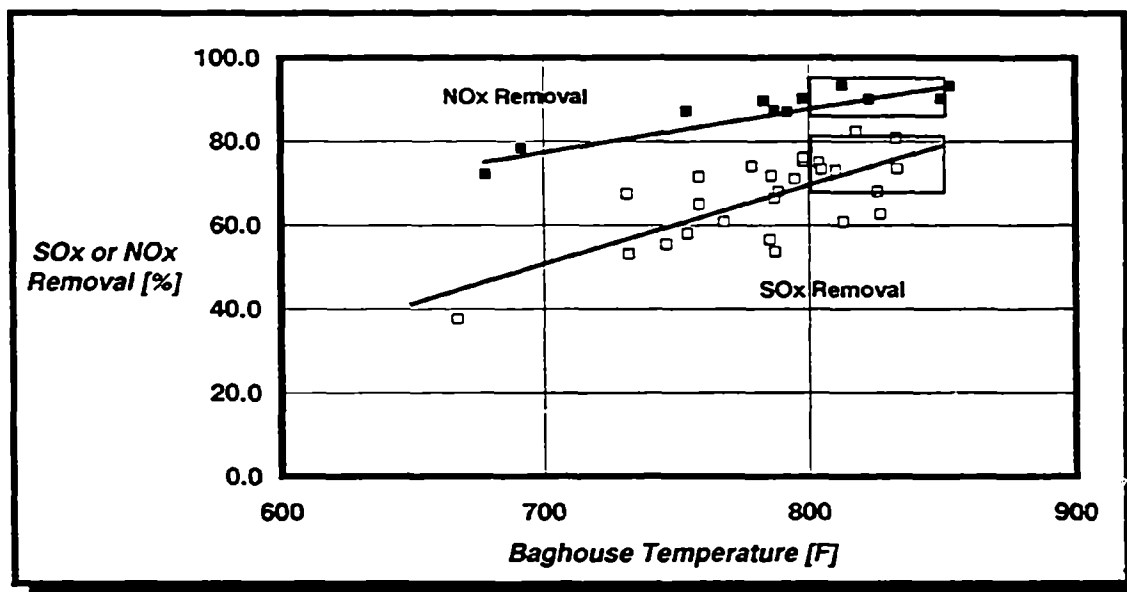


Figure 6. Effect of Baghouse Operating Temperature on SO_x and NO_x Removal Performance

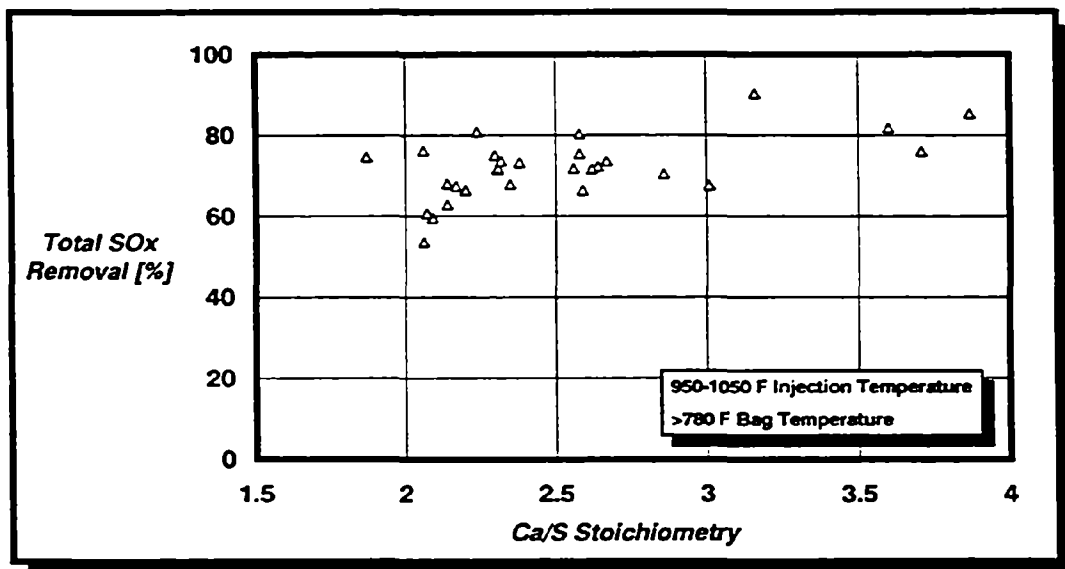


Figure 7. Effect of Ca/S Stoichiometry on SO₂ Removal

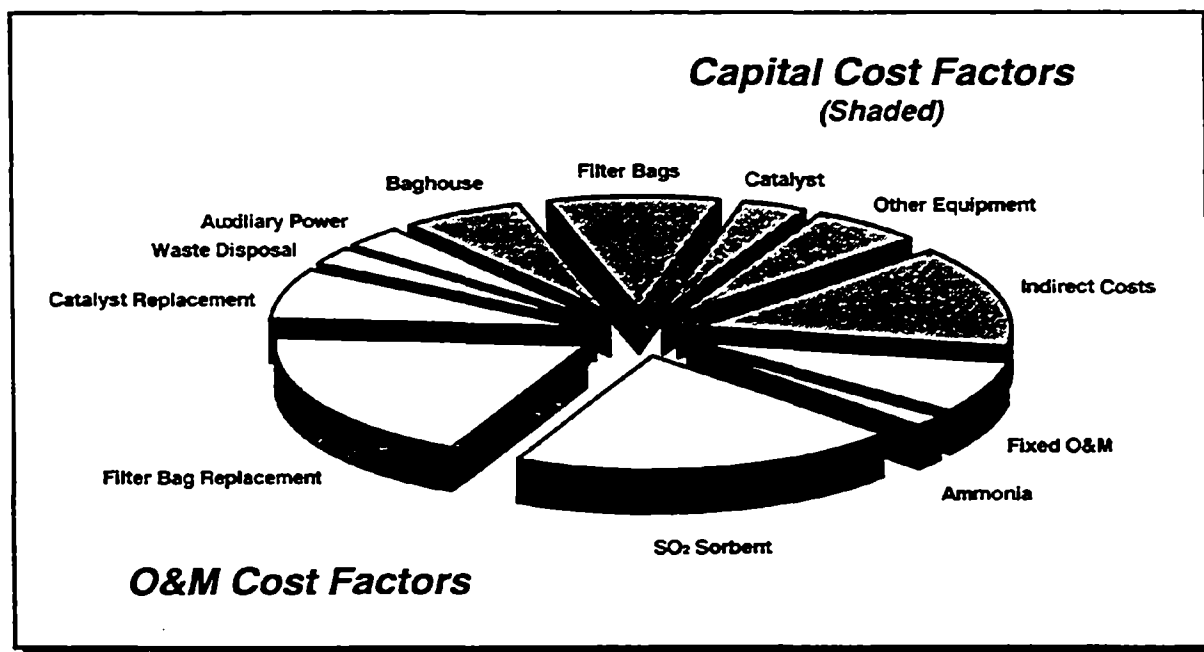


Figure 8. Breakdown of SNRB Levelized Costs

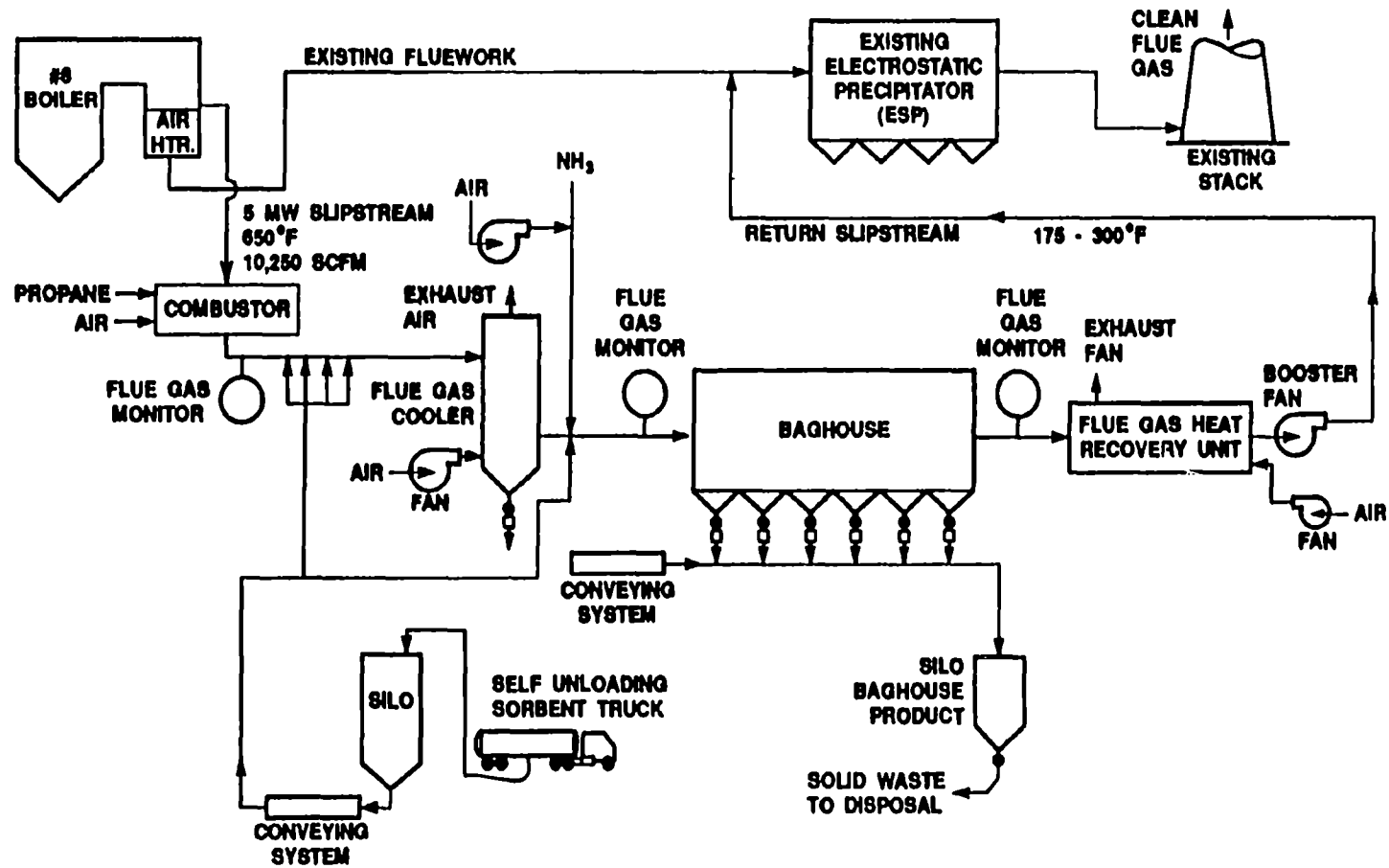


Figure 9. Schematic of the 5-MW_e SNRB Field Demonstration Facility

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**Reaction of Moist Calcium Silicate Reagents with Sulfur
Dioxide in Humidified Flue Gas**

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ABSTRACT

Experimental results are presented for enhancing SO_2 reaction by the addition of moisture to calcium silicate solids. The presence of up to 30-percent initial free moisture increased short-time (<5 s) conversion of calcium silicate solids and of physically mixed $\text{Ca}(\text{OH})_2$ /fly ash solids. The conversion decreased when the initial free moisture increased beyond 30-50 percent. The tendency of solids to agglomerate, as represented by the critical moisture content, was a function of surface area. The critical moisture content was directly equivalent to the pore volume of the solids.

REACTION OF MOIST CALCIUM SILICATE REAGENTS WITH SULFUR DIOXIDE IN HUMIDIFIED FLUE GAS

INTRODUCTION

Dry sorbent duct injection is a viable alternative as a tail-end process for the removal of SO₂ from the gases emitted from coal-fired power plants. Moist solid sorbents are injected into ductwork containing humidified gases from coal fired power plants. The sorbent reacts with the SO₂ in the flue gas and forms calcium sulfite and sulfates. The resulting product is removed from the system by particulate control equipment as a dry solid.

Within the process, gas-solid reaction occurs between the SO₂ in the flue gas and the reagent particles injected into the duct leaving the power plant. Various properties of the sorbent can be examined in order to better understand the reaction according to first principles. One area of focus is to analyze the effect of the initial moisture of the sorbents injected into the duct. Experiments to document the effects of various parameters on the reactivity of the sorbents with the SO₂ were conducted in an isothermal, packed bed reactor to simulate in-duct conditions and bag filter conditions within the ADVACATE process (dry sorbent duct injection). Significant improvements in the operational potential of this process will result from effective understanding of these parameters, and these advances, combined with Federal and State legislation to abate acid rain, could lead to widespread industrial application of this technology. Details of this work can be found in references [1], [2], and [3].

EXPERIMENTAL TECHNIQUES

Sorbent Preparation

The two types of reagents used most often in this study were commercial hydrated lime supplied by Mississippi Lime Company and calcium silicate sorbent prepared by heating a slurry of Clinch River or Meredosia fly ash with Ca(OH)₂. Fly ash and Ca(OH)₂ were slurried for 3-24 h at 90°C, most often at a fly ash loading of 3 g/g

Ca(OH)₂. In some cases, fly ash was ground on a bench-scale attritor prior to slurring with Ca(OH)₂. Also tested were solids produced by physically mixing fly ash and Ca(OH)₂. See Table 1 for information on the fly ashes used.

Table 1
REAGENTS TESTED FOR SO₂ REACTIVITY

Fly Ash Source	Fly ash Type	Slurring		Fly Ash Loading [g/g Ca(OH) ₂]	Sorbent		
		Time [h]	Temperature [°C]		Surface Area [m ² /g]	Pore Volume [cm ³ /g]	Median Pore Size [Å]
Meredosia	U	8	90	3	6.9	0.039	225
Meredosia	G	3	90	3	27.4	0.122	178
Meredosia	G	3	90	2	17.5	0.100	229
Meredosia	G	3	90	1	16.6	0.132	239
Meredosia	G	8	90	3	33.2	0.167	201
Meredosia	G	24	90	3	47.0	0.213	180
Clinch River	G	3	90	3	30.2	0.132	174

U=Unground, G=Ground.

Meredosia U surface area = 1.2 m²/g

Meredosia G surface area = 6.8 m²/g

Clinch River G surface area = 5.6 m²/g

Agglomeration

To study the effects of moisture content on agglomeration of the calcium-based solids, a 5-g sample of the calcium based solids was placed on an 80-mesh sieve (177 µm between wires) and shaken for 10 min. Tests were run on samples with varying amounts of moisture to determine the amount of moisture that caused half the sample to be retained by the 80-mesh sieve. This amount is called the critical moisture (grams of water/grams of wet solids expressed as a percentage).

A standard, 8-in diameter, full-height (2-in depth to cloth), 80-mesh sieve with pan and cover from Brainard-Kilman was used. Water was added dropwise to 5 g of a dry powdered sample in a glass beaker. The water was mixed in manually with a metal chemical spatula. The mixture was spread against the beaker wall and repeatedly chopped in an attempt to distribute the water uniformly and break any clumps. The sample was weighed before water was added and after the water was mixed in to determine the initial moisture content. After the moist sample was weighed,

subsequent steps were performed without delay to minimize evaporation. Each complete test took about 15 min.

The moist sample was spread uniformly over the sieve, the lid placed on, and the assembly placed in a mechanical sieve and the material collected in the pan was weighed. This procedure usually was repeated on 3 or more samples at different moisture content until the critical moisture was bracketed and could be determined by linear interpolation. A fresh sample was used for each test, but all samples came from the same experiment.

Reactor

Experiments for reaction times of 0.5-400 s (most often 0.5-5 s) were performed in the Short-Time Reactor (STR). The system used a fixed-bed reactor centered around a pneumatically actuated sample slider assembly. Moist solids were dispersed on quartz wool and placed in the STR. No conditioning of the solids prior to the contact with SO_2 has been implemented. Exposure to the SO_2 containing process gas was preceded by a thorough dispersion of solids on quartz wool. The amount of excess moisture (free moisture) was determined as weight loss detected by a thermogravimetric analyzer upon heating from room temperature to 100°C .

After reaction with the SO_2 containing gases, the solids were slurried in an aqueous solution of HCl (to dissolve calcium) and H_2O_2 (to oxidize sulfite to sulfate). The flask containing the slurry was sealed and agitated for at least an hour. The resulting solution was filtered and then diluted. Atomic absorption was used to analyze the solution for Ca and ion chromatography was used to determine the sulfate content. Calcium conversion was calculated as the ratio of sulfate to calcium in the solids.

THEORY OF REACTIVITY WITH MOIST SOLIDS

The key variables that affect the gas-solid reaction between SO_2 and $\text{Ca}(\text{OH})_2$ -based sorbents during dry-sorbent injection are the relative humidity and SO_2 concentration of the flue gas and water content and surface structure of the sorbent. Previous spray dryer studies involved the reactivity of sorbent particles suspended in liquid droplets, which as they dried, passed through the liquid, free moisture, and equilibrium stages of reactivity. In the equilibrium stage, the particle is assumed to contain surface water in equilibrium with the relative humidity of the flue gas. While the total reactivity of such a solid has been studied, there have been no efforts to decouple these effects. Mass transfer theory may be applied to the gas-solid reaction system in the presence

of moisture in excess of equilibrium on the surface of a reactive sorbent. The theoretical model below describes the reaction occurring when a wet solid is drying and relates the evaporative drying and the SO₂ capture mechanism.

The model is based on these assumptions:

1. Both water evaporation and SO₂ absorption are controlled by gas phase diffusion.
2. Diffusion occurs in the pores by the Knudsen mechanism.
3. Liquid water is present on the solid predominantly in the pores.

The fluxes of SO₂ and H₂O are given by:

$$\frac{d(\text{SO}_2/\text{area})}{dt} = N_{\text{SO}_2} = -(D_{\text{SO}_2}) \frac{dC_{\text{SO}_2}}{dx} \quad (1)$$

$$\frac{d(\text{H}_2\text{O}/\text{area})}{dt} = N_{\text{H}_2\text{O}} = -(D_{\text{H}_2\text{O}}) \frac{dC_{\text{H}_2\text{O}}}{dx} \quad (2)$$

where:

N_i = molar flux: [mole i/(area-time)]

x = diffusion distance; [length],

C_i = concentration i ; [mole i /volume], and

D_i = Knudsen mass diffusion coefficient [length²/time]

The Knudsen diffusion coefficient is inversely proportional to the square root of the diffusing species. The ratio of the fluxes gives a relationship between the water evaporated from the solid and the SO₂ captured:

$$\frac{\Delta \text{SO}_2}{\Delta \text{H}_2\text{O}} = \frac{D_{\text{SO}_2}(P_{\text{SO}_2})}{D_{\text{H}_2\text{O}}(P_{\text{H}_2\text{O}}^* - P_{\text{H}_2\text{O}})} = \sqrt{\frac{18}{64}} \frac{P_{\text{SO}_2}}{P_{\text{H}_2\text{O}}^* - P_{\text{H}_2\text{O}}} \quad (3)$$

where:

ΔSO_2 = SO₂ captured; [moles/g sorbent]

$\Delta \text{H}_2\text{O}$ = H₂O evaporated; [moles/g sorbent]

P_{SO_2} = SO₂ partial pressure in bulk gas

P_{H_2O} = H₂O partial pressure at gas-liquid interface

$P^*_{H_2O}$ = equilibrium H₂O partial pressure at the gas-liquid interface.

This result assumes that the equilibrium SO₂ partial pressure is zero. The gas/liquid interface is assumed to be at the dry bulb temperature of the gas. The equilibrium H₂O partial pressure is taken as the H₂O vapor pressure at that temperature. The model allows one to predict the conversion of the porous sorbent as a function of the quantity of water evaporated from the sorbent while in contact with SO₂.

In each experiment, the initial water on the reactive sorbent, the relative humidity of the flue gas, and the SO₂ content of the gas are known. Assuming that all of the initial water evaporates during an experiment, the expression is modified to predict the additional Ca utilization of the sorbent based on these parameters:

$$\frac{\Delta SO_2}{Ca} = \sqrt{\frac{18}{64}} \frac{P_{SO_2}}{(P^*_{H_2O} - P_{H_2O})} \left(\frac{\Delta H_2O}{Ca} \right) \quad (4)$$

where Ca = Ca content of the sorbent; [moles/gram sorbent]

This representation does not account for reaction that occurs when the sorbent contains water in equilibrium with the flue gas relative humidity. To account for this effect, data must be taken to obtain the instantaneous conversion for the reaction of the sorbent in equilibrium with the SO₂ containing gas under the same conditions as the sorbent with initial free moisture. We have assumed that the total conversion should be the sum of the expected conversion with equilibrium moisture and the conversion predicted by Eq. (4).

RESULTS

Agglomeration of Moist Solids

The tendency of solids to agglomerate was quantified by measuring the critical moisture by the method described above. Calcium silicate solids were prepared from Mississippi Lime Hydrate and fly ash or silica fume and tested for critical moisture content. Solids with a greater value of critical moisture have a greater capacity for retaining moisture while still being free-flowing.

When critical moisture was expressed as moisture ratio (g water per g of solid), it correlated absolutely with solids pore volume (cm³/g) as shown in Figure 1. Each cm³

of absorbed water at the critical moisture corresponds to one cm³ of particle pore volume. When expressed in terms of critical moisture the relationship is

$$\text{Critical Moisture (\%)} = \frac{100 \cdot [\text{Pore Volume}]}{1.0 + [\text{Pore Volume}]} \quad (5)$$

Agglomeration occurs when the volume of free moisture exceeds the pore volume.

Pore volume and surface area can be related by the cylindrical pore model. Figure 2 shows the relation between the values for calcium silicate sorbents which is given by the equation

$$\text{Pore Volume} = 0.0055 \cdot [\text{Surface Area}] - 0.0055 \quad (6)$$

The slope of this correlation implies a pore radius of 110 Å. Critical moisture increased with increasing surface area of solids. The combination of equations (5) and (6) from Figures 1 and 2 gives the correlation

$$\text{Critical Moisture (\%)} = \frac{0.55 \cdot [\text{Surface Area}]}{1.0 + 0.0055 \cdot [\text{Surface Area}]} \quad (7)$$

A linear best fit of the data in Figure 3 gives

$$\text{Critical Moisture (\%)} = 0.425 \cdot [\text{Surface Area}] + 1.3 \quad (8)$$

To test the effect of fly ash loading on critical moisture, solids were prepared from slurries of ground Clinch River fly ash (7.5 m²/g) with calcium sulfite hemihydrate, gypsum, and varying fractions of Ca(OH)₂ present. The fly ash loading was varied from 0.25 to 4 g/g Ca(OH)₂. Extremes of no Ca(OH)₂ and no fly ash were represented by dry mixtures of ash, hemihydrate and gypsum (1:0.75:0.25) and by Ca(OH)₂ alone. Figure 4 shows the effect of Ca(OH)₂ fraction on both the critical moisture and surface area of solids prepared by slurrying at 90°C for 8 h. Both properties peak in the solids with a fly ash loading of 1.0. With greater amounts of Ca(OH)₂, excess unreacted Ca(OH)₂ may dilute the properties of the solid product. Lesser amounts of Ca(OH)₂ may starve the slurry solution for alkalinity. Also shown in Figure 4 are data for solids prepared without hemihydrate or gypsum present. For a given fly ash loading, the presence of hemihydrate and gypsum in the slurry results in solids with greater critical moisture and surface area.

Reactivity Results

Reactivity of solid sorbents with SO₂ was measured as a function of the initial moisture content of the solids. The experiments in the Short Time Reactor were performed with three types of solids:

1. Unreacted mixtures of Mississippi lime hydrate and Meredosia fly ash
2. Calcium silicate prepared from unground Clinch River ash
3. Calcium silicate prepared from Meredosia ash with various levels of grinding.

Physical mixtures of 6 mg Ca(OH)₂ and 20 mg unground Meredosia fly ash were exposed to 2000 ppm SO₂ in the STR operated at an 11°C (20°F) approach to saturation (approximately 60 percent relative humidity [RH]). Baseline experiments were performed with dry Ca(OH)₂ only and then with the dry mixture. Following baseline tests, solid mixtures were used with 3.9, 12.4, and 18.3 percent initial free moisture. Figure 5 gives the conversion of calcium as a function of contact time for dry Ca(OH)₂ and for the mixtures. Higher conversions were measured for solids with increased level of initial free moisture than for dry Ca(OH)₂. For a given contact time, the conversion generally increased with increased initial free moisture. The effect of initial free moisture was more pronounced at longer contact times (60 and 400 s). For example, the conversion at 5 s contact time was 2.8 and 4.7 percent and at 400 s contact time was 7.3 and 36 percent for dry Mississippi Ca(OH)₂ and a mixture of dry Mississippi Ca(OH)₂ and moist Meredosia fly ash with 18.3 percent initial free moisture, respectively.

In a different series of experiments, calcium silicate solids (30.2 m²/g) were prepared by slurring 3 g ground Clinch River Fly Ash/g Ca(OH)₂ at 90°C for 3 hours. Baseline reactivity experiments were conducted with equilibrium moisture. Considerably higher conversion was measured for solids produced by slurring Ca(OH)₂ and ground fly ash than previously measured for dry Ca(OH)₂ alone. For example, with 5 s contact time, the conversion of dry fly ash/Ca(OH)₂ sorbent was 7.4 percent, compared to 2.8 percent for dry Mississippi Ca(OH)₂. Solids were then prepared by re-wetting calcium silicate solids (30.2 m²/g surface area) to yield 3 levels of initial free moisture: 8.5, 12 and 40 percent. The results are shown in Figure 6, giving the conversion of calcium as a function of contact time with 2000 ppm SO₂ at approximately 60 percent

RH. For each initial moisture tested, the conversion increased with contact time. Except for 0.3 s contact time, the conversion increased with initial free moisture.

The comparison of conversion measured for all three types of solids is shown in Figure 7. With the 5 s contact time, calcium silicate solids consistently yielded higher conversion than physically mixed fly ash/ $\text{Ca}(\text{OH})_2$ solids. The physically mixed fly/ash $\text{Ca}(\text{OH})_2$ was tested with up to approximately 20 percent initial free moisture. Calcium silicate solids were tested with up to approximately 60 percent initial free moisture. Attempts to produce a physically mixed $\text{Ca}(\text{OH})_2$ and fly ash with initial free moisture above 20 percent were unsuccessful. Figure 7 gives calcium conversion with 5 s contact time in the STR at 2000 ppm SO_2 and approximately 60 percent RH. The 5 s conversion of calcium silicate solids leveled off at 30-40 percent initial free moisture. Increasing the amount of an initial free moisture above 40 percent resulted in decreased conversion with SO_2 . With short contact time (0.5-1 s) of calcium silicate solids with SO_2 , the effect of an increased amount of initial free moisture was weak, and the maximum conversion of calcium was only about 5 percent. Significantly increased conversion as a result of increased levels of initial free moisture took place for 3 and 5 s contact time, as evident from Figure 8.

Reactivity of four calcium silicate solids with surface area varying from 6.9 to 47.0 m^2/g and with an initial free moisture content of up to 60 percent is presented in Figure 7. Figure 9 shows the general effect of contact time and initial moisture on the reactivity of the calcium silicate solids with the SO_2 . As contact time increases, Ca conversion increases. As the initial moisture increases for a given contact time, Ca conversion generally increases until a maximum initial moisture is reached beyond which conversion dramatically decreases. Maximum conversion with SO_2 was measured for each solid. The maximum conversion increased with increasing solids surface area. For 6.9, 27.4, 33.2, and 47.0 m^2/g solids, the corresponding maximum conversion with SO_2 was 12.3, 15.2, 17.5, and 22.2 percent, respectively. The initial free moisture content for which the maximum conversion for given solids was measured (optimum moisture content) varied with specific surface area as shown in Figure 10. Increasing the amount of initial free moisture above the optimum caused conversion to decrease.

A possible explanation for the maximum conversion is the agglomeration of the solids at greater moisture content. Figure 10 also shows the critical moisture content of the solids estimated by Eq. (8). The critical moisture content has the same trend as the optimum moisture content giving maximum conversion. However, the critical moisture content is less than half of the optimum moisture content.

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The theory models the trend of the Ca conversion well up to the critical moisture content of each sorbent. Above the critical moisture content the solids may form large agglomerates. These agglomerates may not dry completely in the short-time experiment and the assumptions of the theory would not apply.

Analysis of data presented in Figure 7 indicates that SO₂ conversion of solids containing initial free moisture is a weak function of solids surface area below optimum moisture content of 6.9 m²/g solids (30 percent initial free moisture). However, increasing the surface area of solids provides for higher optimum moisture content with resulting higher conversion of solids with SO₂.

CONCLUSIONS

Initial free moisture increases short-time (<5 s) conversion of calcium silicate solids and of physically mixed Ca(OH)₂/fly ash solids.

Agglomeration of calcium silicate solids due to moisture is a function of their surface area. The critical moisture content at which agglomeration occurs is directly proportional to solids pore volume. The presence of calcium sulfite hemihydrate and gypsum in a slurry of ground low calcium fly ash results in solids with increased critical moisture and surface area.

ACKNOWLEDGMENTS

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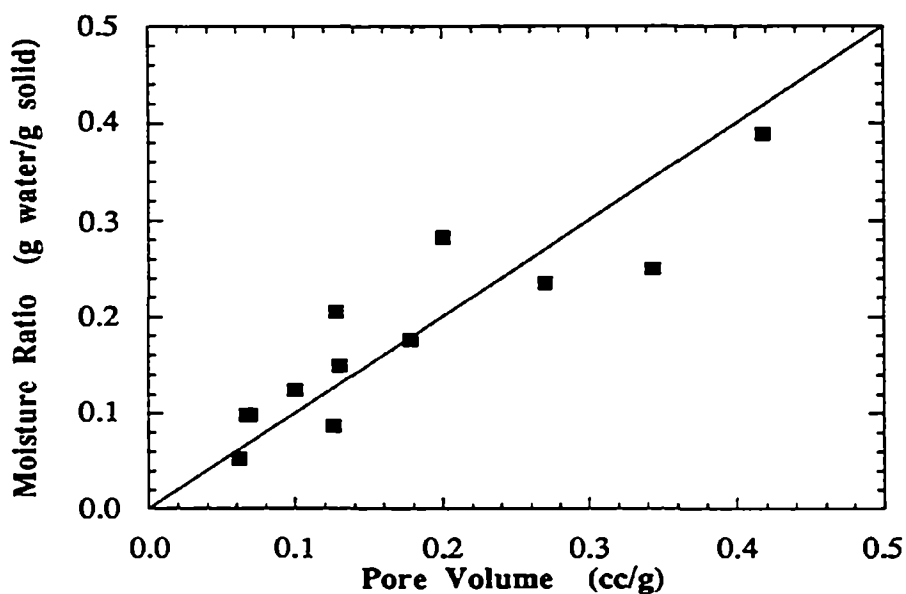


FIGURE 1: Correlation of critical moisture with pore volume for calcium silicate solids.

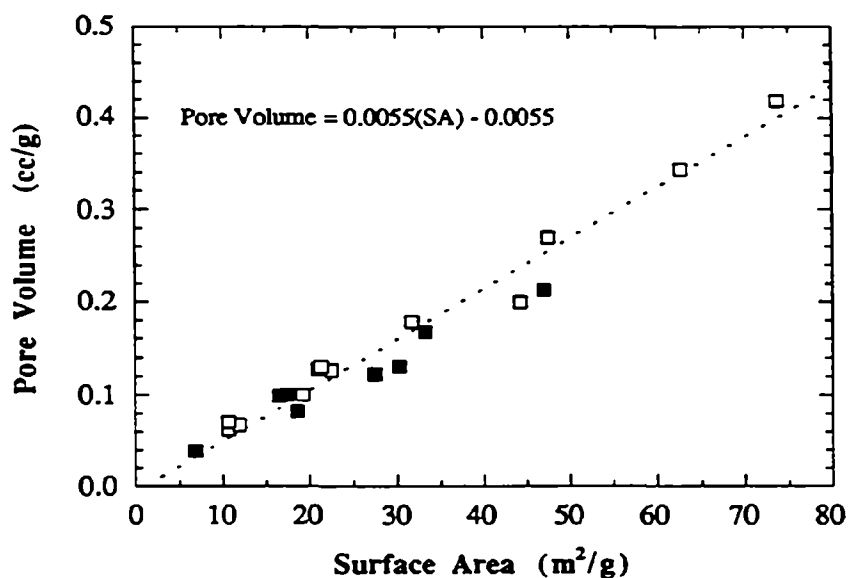


FIGURE 2: Correlation of particle pore volume with specific surface area (solid symbols represent data for sorbents in Table 1; open symbols are for additional samples represented in Figure 1; dotted lines and equation are a least-squares fit of the data).

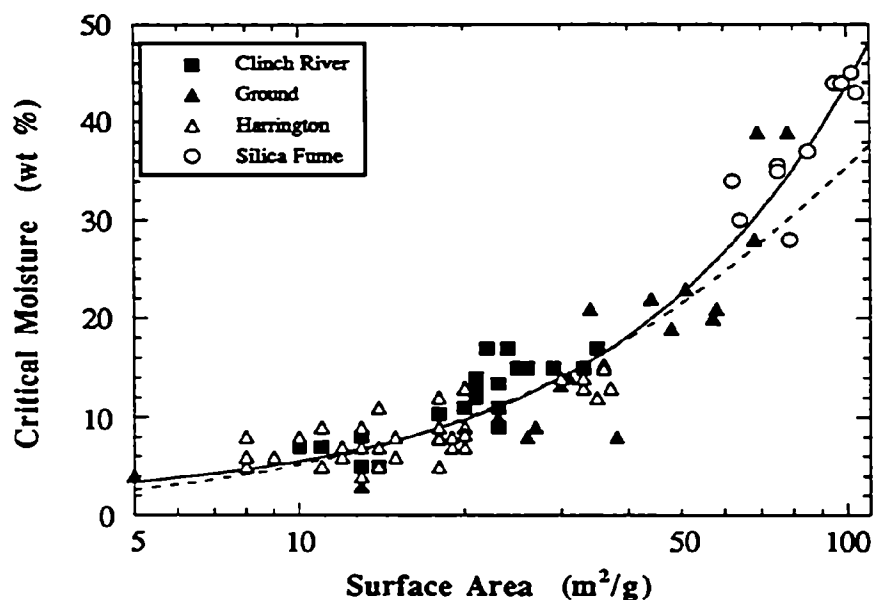


FIGURE 3: Correlation of critical moisture with surface area. Slurry times range from 15 min to 24 h. Dotted line represents the correlation predicted by Eq. (7); the solid line is a least squares fit of the data given by Eq. (8).

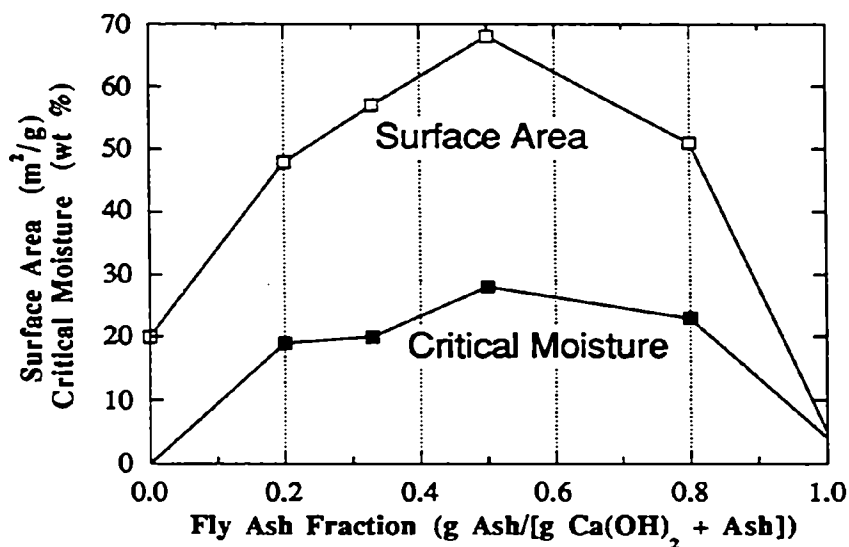


FIGURE 4: Effect of Ca(OH)_2 fraction on the surface area and critical moisture content of solids prepared by slurring for 8 h ground Clinch River fly ash, calcium sulfite hemihydrate and gypsum, weight ratio 4:3:1 (respectively) held constant each time.

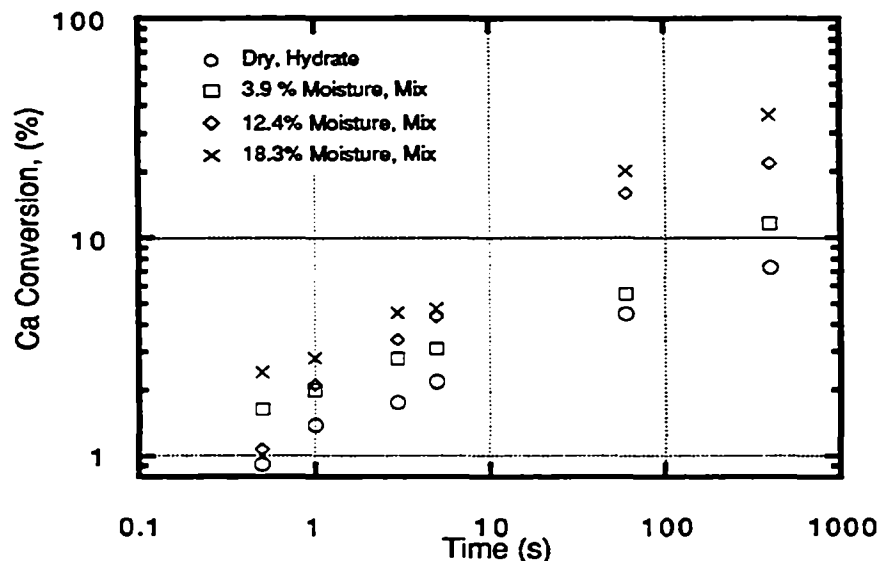


FIGURE 5: Effect of initial free moisture on the reactivity of $\text{Ca}(\text{OH})_2$ physically mixed with moist Meredosia fly ash (STR, 2000 ppm SO_2 , 60% relative humidity).

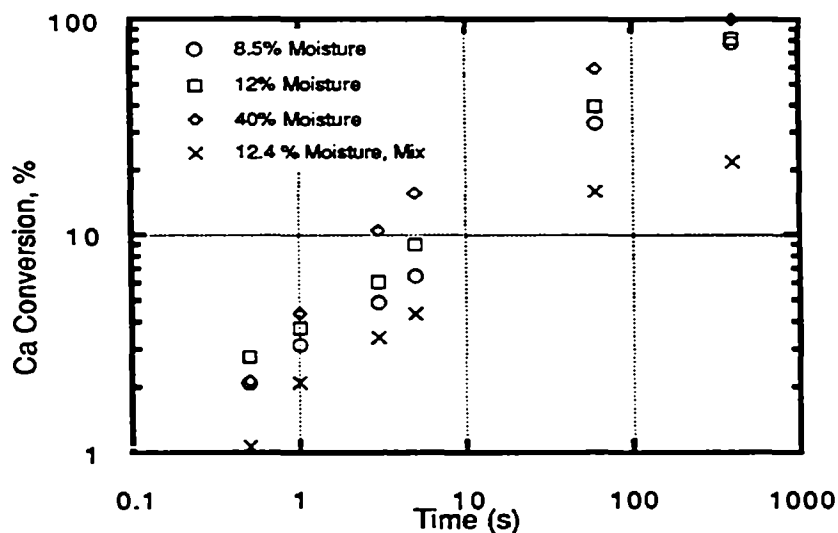


FIGURE 6: Effect of initial moisture on the reactivity of $30.2 \text{ m}^2/\text{g}$ surface area calcium silicate solids prepared from Clinch River fly ash. Reactivity comparison for physically mixed and chemically reacted fly ash/ $\text{Ca}(\text{OH})_2$. (STR, 2000 ppm SO_2 , 60% relative humidity, 11°C approach to saturation) Mix is a mixture obtained by physically mixing Meredosia fly ash with Mississippi hydrated lime.

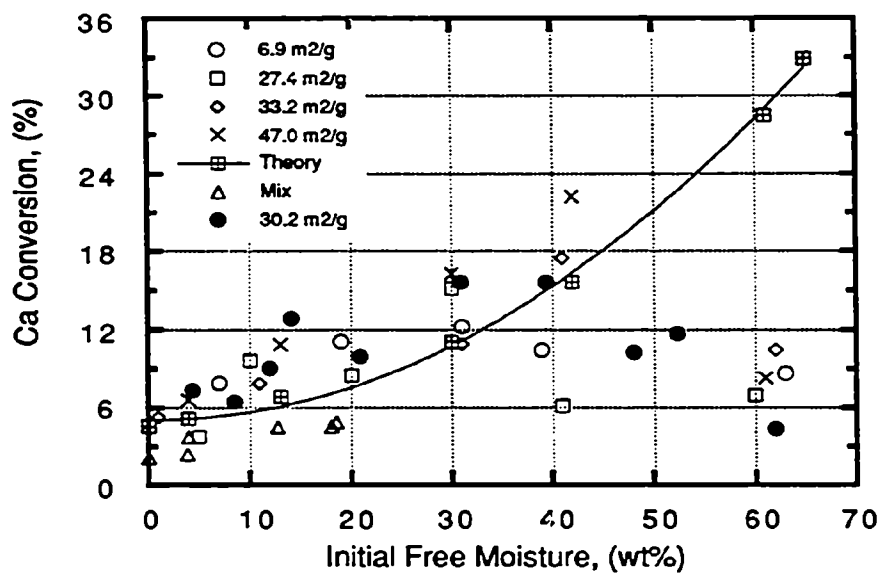


FIGURE 7: Effect of solids surface area, initial free moisture, and sorbent type on the reactivity of moist solids and comparison with Additive theory. (STR, 2000 ppm SO₂, 60% relative humidity, 5 sec contact time)

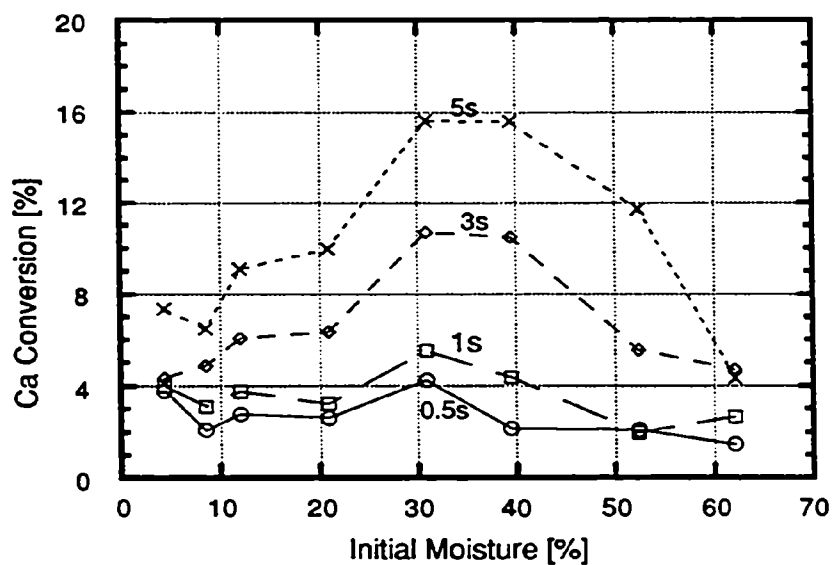


FIGURE 8: Effect of contact time on the reactivity of Clinch River calcium silicate solids, surface area 30.2 m²/g. (STR, 2000 ppm SO₂, 60% relative humidity)

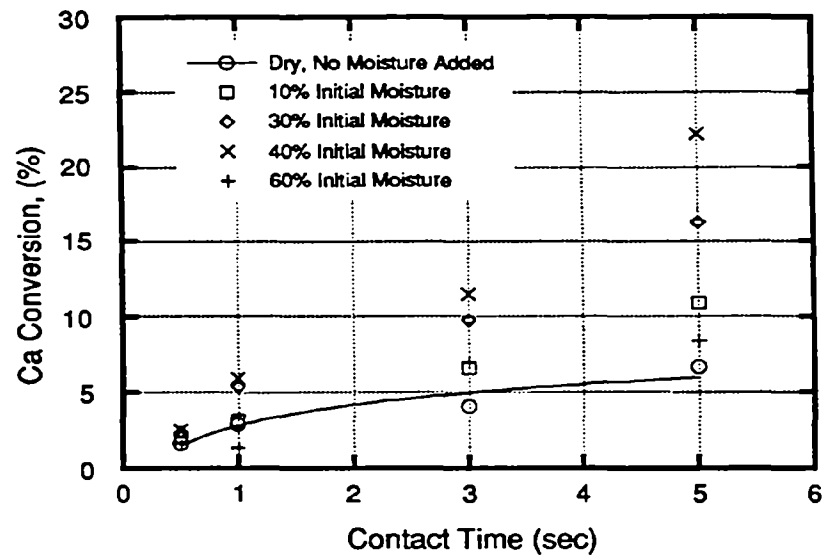


FIGURE 9: Effect of initial free moisture on the reactivity with SO_2 of $47.0 \text{ m}^2/\text{g}$ sorbent (ground Meredosia fly ash/ $\text{Ca}(\text{OH})_2$; loading 3 g/g; 60% relative humidity, 2000 ppm SO_2).

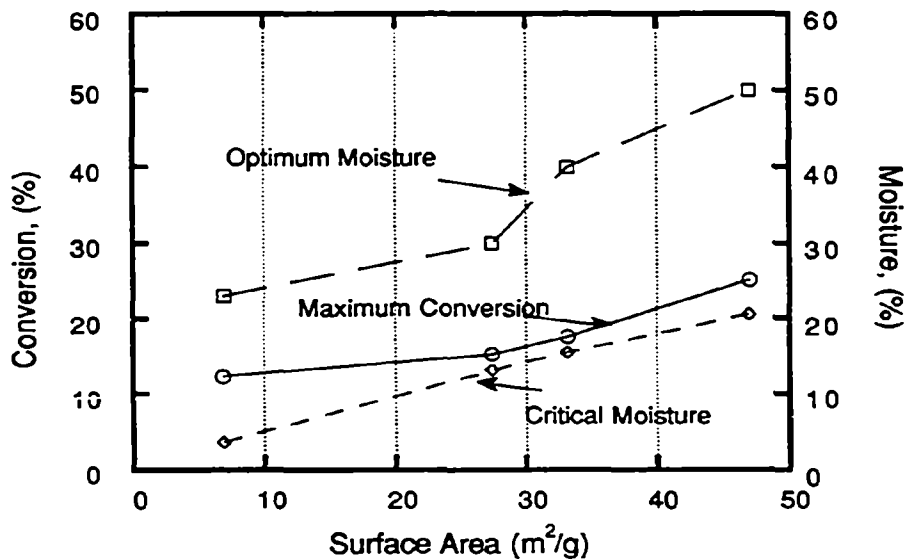


FIGURE 10: Effect of surface area on optimum moisture and maximum conversion. (STR, 2000 ppm SO_2 , 60% relative humidity, 5 sec contact time)

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**Commercial Application of Dry FGD using High Surface
Area Hydrated Lime**

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ABSTRACT

Details are provided of the performance and economics of first-of-its-kind advanced technology for production and use of high surface area hydrated lime (HSH) presently employed by 40 west European industrial emission sources mainly in Germany, including coal fired boilers, for removal of SO₂, HCl and other flue gas pollutants. A description is also given of practical engineering experience in retrofitting and commissioning of dry sorption by HSH in bituminous coal service. Recent technological advancements discussed include commercial operations using HSH bolstered with carbonaceous additive to achieve simultaneous removal of toxic organics and trace metals along with acid gas components. An assessment is made of the applicability of the technology for retrofit installations in medium/high sulfur coal service in the U.S.A. A cost benefit evaluation compares dry scrubbing with HSH against semi-dry (spray dryer) scrubbing using quicklime.

INTRODUCTION

As an outgrowth of the massive national SO₂ emission reduction program that began in Germany in 1983, dry sorption technology utilizing unique, high surface area hydrated lime (HSH) has gained extensive, large-scale utilization in an array of industrial and municipal services. A commercial HSH production facility in that country supplies an array of boilers, incinerators and other sources, providing tailored reagent for cost effective control of acid gas and toxic emissions, typically without need for an excessive, impractical increase in flue gas humidity.

PROGRESS IN LIME SORBENT DEVELOPMENT FOR DRY REMOVAL

Dry sorption is a simple process for flue gas cleaning characterized by low investment and is therefore especially attractive for many retrofit applications. The disadvantage of generally higher reagent consumption in dry operation is further compensated by use of novel improved reagents or mixes of such reagents designed for advantageous use in the specific application. To sorb diverse acid waste gas components such as hydrogen fluoride, hydrogen chloride and sulfur dioxide, lime hydrates with high surface area (HSH) have been developed (1) and these materials are now in commercial use (2). Alternatively, regular hydrated lime is mixed during hydration with components such as sugar to enhance reagent effectiveness for increased efficiency of SO₂ removal (3). An additional important development is the use of lime hydrate, particularly HSH, intermixed with pulverized lignite coke (a carbonaceous additive) to gain simultaneous removal of acid gas components, trace quantities of mercury, cadmium, etc. (4), as well as chlorinated organics: PCDD (dioxin) and PCDF (furan).

Improved lime reagents such as HSH have the following advantages over normal hydrated lime:

- A smaller quantity of reagent is required.
- Higher pollutant removal rates are achieved.
- The quantity of wastes to be disposed is less.

Obviously such improvements must not be negated by excessive reagent cost. High reagent cost for such improved reagent supply may be tolerable as long as dry sorption is competitive with other processes as in SO₂ removal applications for utility boilers. A notable example of improved lime sorbent is the present, first, commercial-scale production of HSH (tradename-WUELFRA-sorp) and its use by more than forty (40) industrial and municipal emission sources in western Europe, primarily Germany.

COMMERCIAL HSH PRODUCTION IN EUROPE

A commercial scale unit, previously described in detail in the U.S. (2), began operation two years ago at a rate of six metric tons per hour (40,000 tons per year). This sorbent is produced in an alcohol hydration process protected by US and other patents and primarily characterized by manufacture of a product with warranted BET surface area of greater than 35 m²/g. This value is twice that of regular lime hydrate, slaked with water, which has a BET value of approximately 17 m²/g. Compared with conventional hydrate, HSH is superior because of very small

grain size ranging between 2.0 and 2.5 micrometers. Furthermore, HSH has very high flowability and, injected with carrier air, is readily distributed throughout the waste gas to be cleaned, even at carrier air rates well below 1 m³ per kilogram HSH. The disadvantage of HSH is low bulk density, approximately 300 grams per liter (18 lb/ft³), which is 25% less than the 400 grams per liter (24 lb/ft³) density of normal lime hydrate, and greater storage volume is needed per weight unit of lime stored.

The commercial HSH production in Germany has a CaO content of more than 73.0% with a fixed alcohol content of approximately 1%. In addition to HSH as is, mixtures of it with up to 20% pulverized lignite coke, (designated WUELFRASorp C-20), have been available. There is presently a marked increase in demand for such tailored lime/coke mixture calling for supply with a coke content of only 5-8%.

The present FOB-factory selling price of HSH manufactured in Europe is approximately 40% above the price of normal hydrate. However, diverse HSH consumers readily compensate for this premium price by benefit of savings and improvements such as decreased sorbent consumption, smaller waste disposal quantity and, above all, assured compliance with mandated emission limits. Ongoing improvements in economics of the manufacturing process are expected to lower the FOB-factory price to a level of only 20-25% above the selling price of normal hydrate. It is likely that this reduced level of price premium will also be applicable in HSH supply from future U.S. facilities for manufacture of HSH. The anticipated substantial decrease in manufacturing costs can be achieved in new production plants by process modifications to the effluent return to the continuous lime hydration reactors 1 and 2, shown as item A in Figure 1. This is significant in lime hydration because in the presence of alcohol the reactivity of water with calcium oxide is depressed to a degree that varies with the amount of alcohol present. The contemplated design changes allow control of process water reactivity leading to higher production rates as well as more complete hydration reaction. This in turn will allow elimination of the batch vacuum operation illustrated by item B of Figure 1. These significant improvements are the direct result of the learning curve that has been made available through sustained operation of commercial facilities for HSH production.

OVERVIEW OF COMMERCIAL SUPPLY OF HSH PRODUCT

HSH is consumed in a wide range of European industries and municipal services, the nine most important of which are shown in Table 1. They are listed in the order

of decreasing consumption, i.e. special waste incinerators (hazardous waste incinerators) consume the largest portion and the glass industry the smallest amount of the total present production of 10,000 annual metric tons. The supply to utilities for flue gas SO₂ removal currently ranks sixth. As is to be expected, the production facility is only operating at 25% of capacity since WUELFRASorp and WUELFRASorp C are new products for flue gas cleaning which continue to be systematically introduced to candidate consumers via testing programs through which the demand is being expanded so as to gain a more substantial market.

COMMERCIAL APPLICATION OF HSH PRINCIPALLY FOR HCl REMOVAL FROM WASTE GAS STREAMS

The degree of removal of HCl by dry sorption is proportional to the magnitude of the surface area of the hydrate solids used. Application of HSH for this service is therefore especially effective. Moreover, the rate of removal is independent of the reaction temperature over a wide range of temperatures.

Single-Stage Operation

The flow sheet of a relevant single-stage flue gas cleaning facility serving a hazardous waste incinerator is shown in Figure 2 and the performance results are given in Table 2. The HSH is injected at a rate of 200 kilograms per hour at 180°C (356°F). The fabric filter collecting the gasborne solid waste is operating at the same temperature. It is of critical importance to this reagent user that, despite high and widely varying HCl and SO₂ concentration in the raw gas, the legally required emission limits be maintained in a manner reflected by Table 2. The system operates with very high reliability removing more than 99% of HCl.

Two-Stage Gas Cleaning

In a recent new use of HSH at a municipal waste incinerator served by two-step gas cleaning, a small portion of the HSH is injected at 250°C (482°F), upstream of flue gas cooling using a heat exchanger. Downstream of gas cooling, HSH intermixed with 8% pulverized lignite coke is injected in combination at 150°C (302°F). The performance results are as shown in Table 3. HCl removal is in excess of 99% and PCDD (dioxin) and PCDF (furan) are lowered by 98%. Especially significant in this example is the very low consumption of HSH, 15 kilograms per ton of municipal waste, as contrasted with estimated consumption of 35-40 kilograms per ton of waste for alternative normal hydrate. Moreover, the specified emission limit of less than 10 mg HCl per normal cubic meter, newly applicable on March 1, 1994, cannot be achieved with normal lime hydrate.

COMMERCIAL APPLICATION OF HSH PRINCIPALLY FOR SO₂ REMOVAL

A survey of the recent U.S. literature on the subject (8 through 16) emphasizes that removal of SO₂ from utility boiler flue gas is influenced by the temperature and the partial pressure of water vapor. If additional humidification is used, the location at which the water is injected in relation to the point of hydrate injection is important. Also, additives such as sodium hydroxide, if used in the humidification water, improve SO₂ removal.

European commercial performance experience for three SO₂ removal applications using HSH is as follows:

SO₂ Removal Without Humidification

In 1987 the first dry sorption application for HSH began operation using a supply of reagent from early pilot plant manufacturing facilities and providing dry SO₂ removal for two 7.5 mW(t) anthracite coal fired boilers at 170-185°C (338-365°F) flue gas temperature. At that time the required flue gas retention time for SO₂ capture was not known and therefore, a reactor vessel (5) was installed after the HSH injection point. A simple vertical cylindrical design was provided as per schematic Figure 3, with rotating wall scrapers to eliminate build-up on the inner walls. Numerical performance data are shown in Table 4 under Case 1. Although this type industrial fuel, unique to Germany, has very low fuel hydrogen content, the supply in this case was high in surface moisture. Therefore, flue gas humidification was not necessary to gain targeted SO₂ removal. The system was tested over a wide range of Ca/S molar ratios, comparing HSH with normal hydrate. In this plant SO₂ removal greater than 50% must be achieved, which, per Figure 4, is possible with HSH use at a Ca/S ratio of approximately 1.7. Using normal hydrate the Ca/S ratio to achieve this removal rate would, as per Figure 4, be greater than 3.7.

Reduced Temperature Service When Firing Anthracite

In commercial systems serving two 35 mW(t) anthracite coal fired boilers, as well as a similar system for a 70 mW(t) unit in Poland presently under construction, HSH along with humidification water is added as per Figure 3 via a venturi jet feeder upstream of a reactor vessel (5). The German systems operate at an SO₂ removal efficiency of more than 50% to meet the mandated emission limit. This is possible in this commercial operation by using HSH at a Ca/S molar ratio of 1.8 with an operating temperature of approximately 95°C (203°F). See the performance description in Table 4 for Case 2 in this anthracite coal application with very low raw gas water content. Note that even after humidification accompanied by a

reduction in the gas temperature to 95°C (203°F) the water vapor content is very much less than it would be for a bituminous coal application. The operator of this system has found that lowering the temperature by further water addition to less than 90°C (194°F) to achieve further humidification cooling allows removal efficiency of more than 65% at the same Ca/S ratio of 1.8. This level of humidification corresponds to an absolute humidity of less than 0.03 lb water vapor per lb of dry gas, substantially less than unhumidified flue gas from bituminous coal fired boilers, indicating that HSH will typically provide comparable or better performance than this in US applications without need for use of flue gas humidification means. Additionally, the plant operator has found that the rotating scrapers in the reactor vessel need not be operated continuously.

High Sulfur Service .

As illustrated in Figure 5, HSH is used for high (90+%) efficiency desulfurization of 250°C (482°F) flue gas of 6,000 mg/Nm³ (2,160 ppm) SO₂ strength issuing from a tunnel kiln used to cure tar bonded magnesite bricks. This application is thus directly comparable in flue gas SO₂ level to U.S. high-sulfur coal fired boiler service. In the first of two HSH injection steps a small quantity of the reagent is added to the raw flue gas prior to humidification to adsorb the small amount of SO₃ present. After humidification cooling of the gas to a temperature of 68 to 80°C (154 to 176°F) the balance of HSH is injected to achieve SO₂ removal in a 2m diameter by 8m high reactor vessel of special design. Provision is also made for partial recycle to the lower part of the reactor of reaction product solids from the downstream flue gas dedusting step. As indicated by a family of curves entered in Figure 4, SO₂ removal efficiency is extremely sensitive to flue gas temperature in the reactor. Note that at 68°C (154°F) and a Ca/S molar ratio of 3.0, 90% SO₂ removal is achieved, whereas above 75°C (167°F) the SO₂ removal is less than 70%. The flue gas wet bulb temperature is approximately 54°C (129°F) and thus, 90% removal operation via HSH at 68°C (154°F) requires 14°C (25°F) approach to the wet bulb. The guaranteed stack SO₂ emission level of 500 mg/Nm³ (180 ppm) is readily maintained at a stoichiometric ratio of 2.8. Severe peaks in raw gas SO₂ strength are generated during periodic charging of the tunnel kiln, but the gas cleaning system has been able to meet these conditions without difficulty. Further, while very substantial gas residence time is provided by the reactor vessel, it has been determined that only 2 to 3 seconds gas residence time is needed to gain performance achieved. Waste residue collected in the fabric filter (Figure 5) is amorphous calcium sulfite, which converts to calcium sulfate after extended storage or under conditions of increased temperature.

Optimized Point of Entry of Humidifying Water When Required in SO₂ Service

Pilot test work has verified that the location of the flue gas humidification step is of substantial importance in optimizing gas cleaning operation. Using a pilot plant system as per Figure 6 with a flue gas flow rate of 350 normal cubic meters per hour the location of water injection in relation to feed of normal lime or HSH was tested using a synthetic gas containing 3,600 mg SO₂ per normal cubic meter (1,300 ppm). Testing was focused only on gas cleaning performance of the reactor proper with a flue gas retention time of 3 seconds and without taking into account removal in the downstream fabric filter. The effect of changing the water injection location is shown in Figure 7 data, wherein 35 kg/h water addition corresponds to a water vapor content of 10.5%. Best results are obtained by adding one half of the H₂O at each of locations 1 and 2 in Figure 6. If only half of the water is added at either location 1 or 2, significantly higher removals are achieved when the water addition is made downstream of the hydrate feed. This leads to the conclusion, also given in diverse publications (6, 12, and 13), that for optimum performance the lime hydrate must be finely dispersed in the gas before humidifying water is added.

CONTEMPLATED FUTURE USE OF HSH IN INTEGRATED GAS CLEANING SERVICE (7)

A tailored, enhanced, dry alkaline reagent such as HSH intermixed with lignite coke lends itself advantageously to simultaneous removal of acid gases along with chlorinated organics and/or trace heavy metals as may be appropriate for air toxics emission reduction. One such application is cleaning of flue gas from municipal solid waste incineration, which, effective March 1, 1994, must be upgraded in Germany to meet emission limits as follows:

- HCl: 10 mg/Nm³ (6 ppm)
- SO₂: 50 mg/Nm³ (18 ppm)
- Dioxin and furan: 0.1 ng/Nm³, toxic equivalent (TE)

Since these new emissions limits are not typically achievable in the commonly used spray dryer type gas cleaning systems, large-scale tests have been conducted over extended periods to show the benefit and adequacy of system performance augmentation by HSH. Results summarized in Table 5 indicate that a two stage process as per Figure 8, with a spray dryer followed by dry injection of HSH, meets the new emission limits while at the same time actually providing a reduction in the overall amount of lime used. As indicated in Table 5, the customary spray dryer system alone, without meeting the emission limits, consumed lime reagent in the amount of 250 to 305 kilograms per hour of lime hydrate. With

HSH injection incorporated as a second contact stage upstream of the dry collector, only an overall total of 220 kilograms per hour of hydrate (milk of lime hydrate plus HSH) were needed. HSH with 20% pulverized lignite coke was used in these tests. The TE (toxic equivalent) reduction of chlorinated organics from 6.3 nanograms per normal cubic meter in the feed gas to the extremely low value of 0.015 nanogram per normal cubic meter in the clean gas indicates an unnecessarily large amount of coke use. Therefore, in further testing, the lignite coke addition will be reduced to the level of 8-10%.

HIGH TEMPERATURE SORPTION

In a manner that parallels current major field developmental activity in the US (10) aimed at economical, dry primary SO₂ capture via sorbent injection at the boiler economizer, extensive pilot plant tests with good results have been performed in Germany at 450°C (842°F). It has been verified that SO₂ removal is directly proportional to hydrate surface area. Moreover, flue gas humidification is not necessary because SO₂ is converted to the form, calcium sulfate, in this mode. Apparently the crystal (chemically bonded) water of the lime hydrate plays a contributing role in major enhancement of SO₂ sorption at such elevated temperature. Commercial installations of this type have not yet been carried out.

Sub-scale tests have been performed in the U.S. at an SO₂ strength of 2,600 ppm (7,200 mg/Nm³) and Ca/S of 2 leading to late 1991, proof of concept system demonstration under US Department of Energy and Electric Power Research Institute funding (10) using German-manufactured HSH. With injection at 1000°F (538°C) of HSH having a surface area greater than 35m²/g, SO₂ removal of 60 to 65% can be achieved without flue gas humidification. In conjunction with a modest degree of flue gas humidification downstream of the air preheater for the purpose of improving ESP particulate removal (11) a further improvement in SO₂ removal is accomplished.

USE OF HSH FOR RETROFITTING IN U.S. MEDIUM/HIGH SULFUR COAL SERVICE

Based on German commercial experience described herein, including high-sulfur service, it can be seen that the high surface area of HSH permits its use in highly diverse ways:

- In conjunction with duct injection at between 135 and 185°C (275 and 365°F) it affords means to achieve 65% SO₂ removal, i.e. more than the array of other dry injection technologies, with flue gas humidification limited to that required to cool to 90°C (194°F) with a

very substantial 50°C (70+°F) approach to wet bulb.

- It is expected to provide 65% SO₂ removal solely by economizer injection without flue gas humidification. This removal will be augmented through a limited amount of flue gas humidification downstream of the air preheater for the purpose of improving ESP particulate removal efficiency.
- Further, as an alternative to lime spray dryer use, it may be employed downstream of the air preheater in conjunction with flue gas humidification to achieve 85-90% SO₂ removal.

These single-stage design alternatives for U.S. bituminous coal service with 2.6% sulfur level (approx. 1,700 ppm: 4,700 mg/Nm³), the reference coal for EPRI FGD cost program data (17), are displayed in Table 6.

Optimum use of HSH for high removal efficiency in such high-sulfur coal service may call for multi-staging, e.g. economizer injection at low Ca/S ratio augmented by moderate humidification and residence time downstream of the air preheater. Table 7 offers a trial comparison at the 300 mWe capacity level of such HSH system design for 85-90% SO₂ removal (Case 5) against cost program data for wet FGD, lime spray drying and an array of dry injection technologies previously evaluated by EPRI (17).

Favorable economics of such optimal HSH use, projected from commercial operation and testing in Germany, is the result of the unique match of its physical and chemical properties with the diverse sorption regimes at the boiler exit. Moreover, without great investment in gas cleaning equipment, HSH effectively and advantageously utilizes available residence time and water vapor concentrations.

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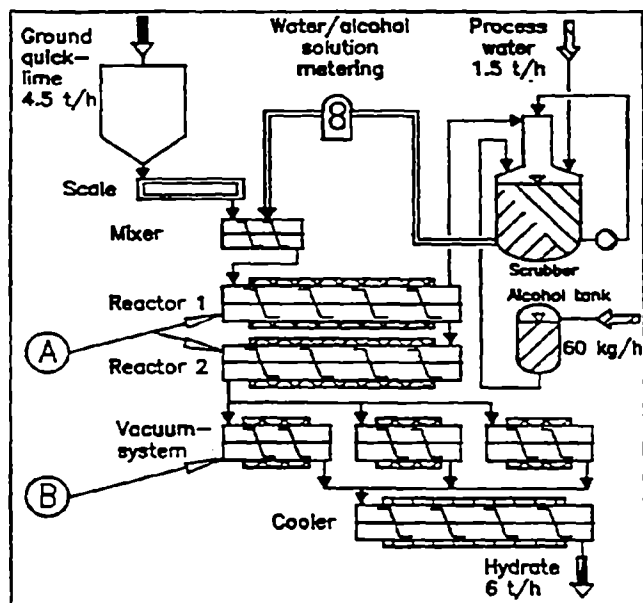


Figure 1. Flowsheet of HSH (WUELFRASorp®) production

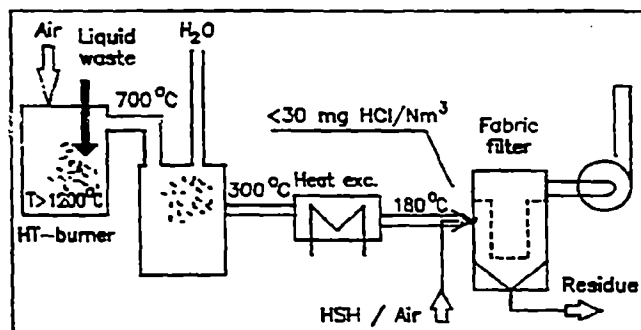


Figure 2. SWI with dry sorption only

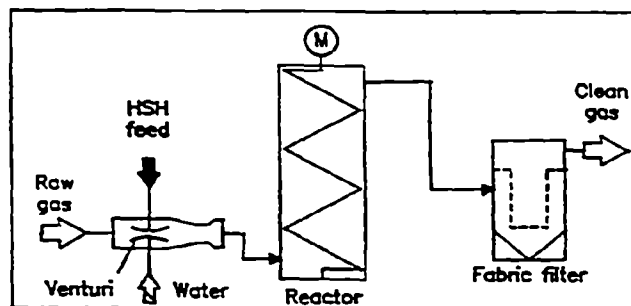


Figure 3. Coal-fired power plant with dry sorption system

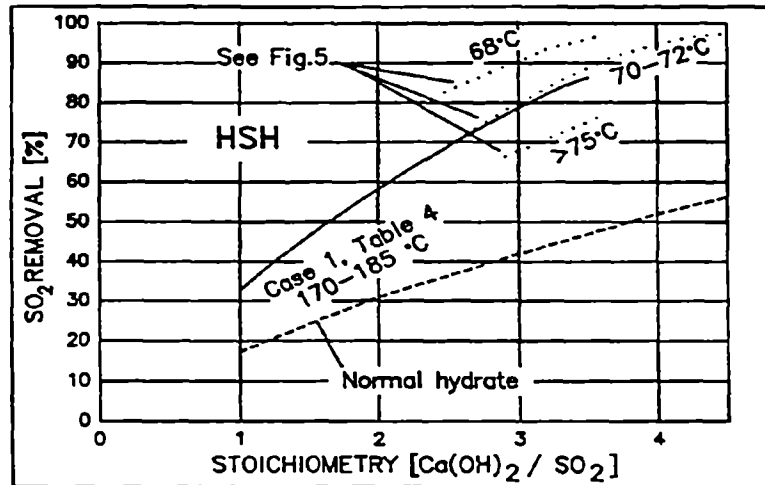


Figure 4. SO_2 Dry-Sorption in Power Plant (Case 1; Tab. 4) and Behind a Refractories-Tunnel-Kiln (Fig. 5)

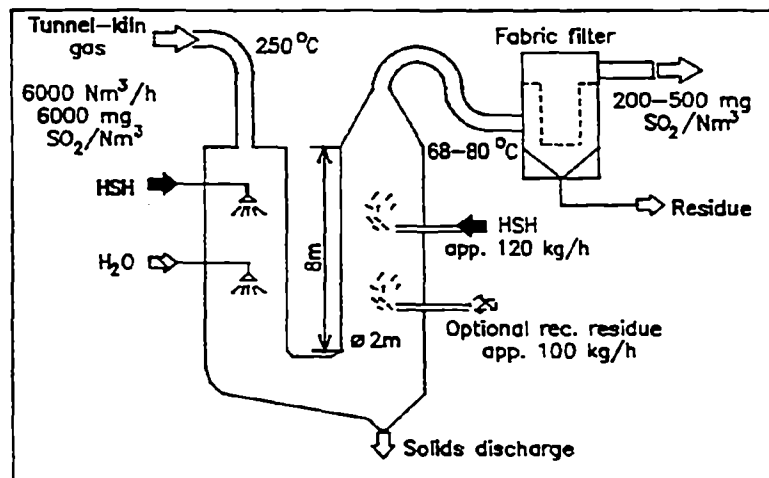


Figure 5. Reactor for low temperature SO_2 removal with HSH

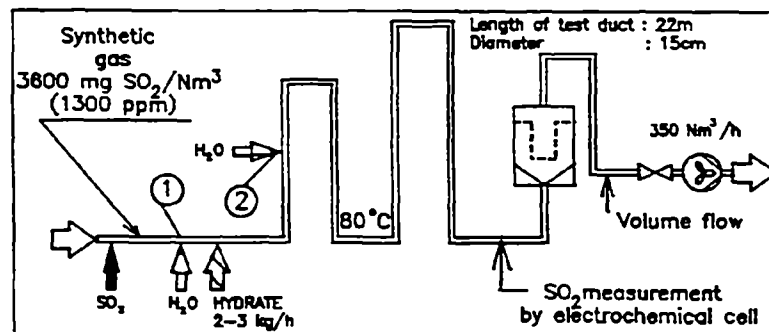


Figure 6. Schematic of pilot system

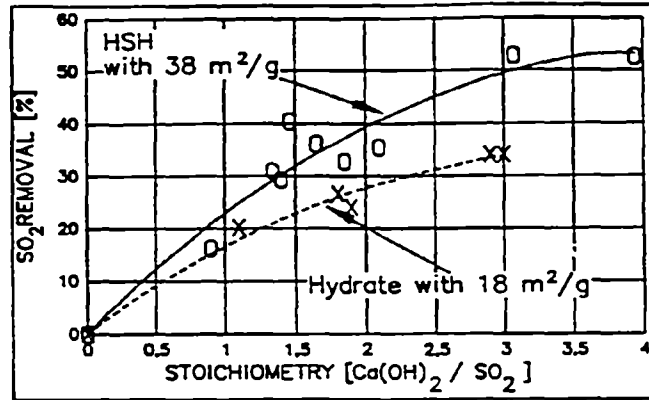


Figure 7b. Test Conditions as in Fig. 7a
Comparison of Hydrates

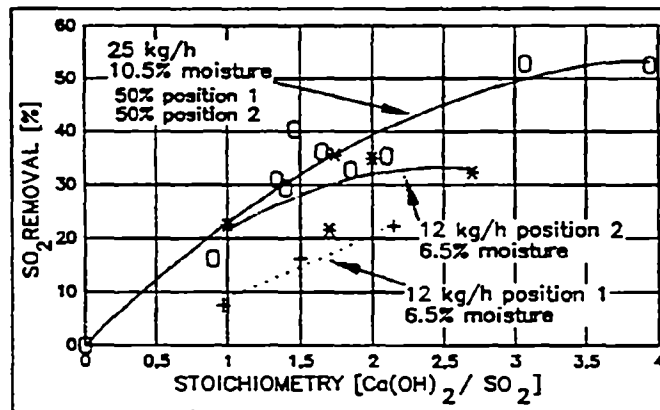


Figure 7a. SO_2 -Removal, 80 C
Position of H_2O Injection

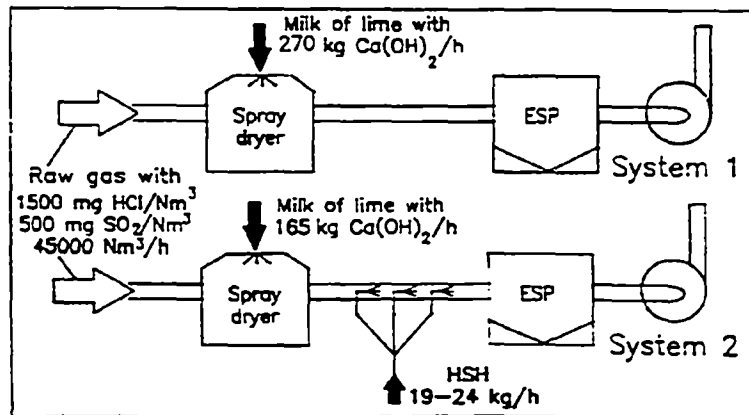


Figure 8. Scheme of a MWI working with spray dryer only (System 1)
and with the combination spray dryer/dry sorption (System 2)

Table 1
RANGE OF COMMERCIAL APPLICATION OF HSH
IN CLEANING OF WASTE GASES

<u>Rank</u>	<u>Service</u>	<u>Pollutants</u>	<u>With/Without Coke Additive</u>
1	SWI (special waste incinerator)	HCl/SO ₂ /PCDD/PCDF/Hg	Without/ With
2	MWI (municipal waste incinerator)	HCl/SO ₂ /PCDD/PCDF/Hg	Without/ With
3	Aluminum industry (Recycling)	HCl/PCDD/PCDF	Without/ With
4	Ceramic industry/ refractories	SO ₂	Without
5	Industrial furnace	SO ₃ /SO ₂ /HCl	Without
6	Power plant	SO ₂	Without
7	Burning of sewage sludge	HCl	Without
8	Thermal treatment of contaminated soil	SO ₂ /Hg	Without/ With
9	Glass industry	SO ₂	Without

Note: Total amount of reagent product sold is app. 10,000 metric t/year.

Table 2

SPECIAL WASTE INCINERATION WITH DRY SORPTION

FUEL FIRED: 1.6 m³/h HIGHLY CHLORINATED, ORGANIC-LIQUID COMPOUNDS
 VOLUME OF GAS: App. 12,000 Nm³/h
 DOSING RATE, NORMAL HSH: App. 200 kg/h
 WATER VAPOR (MOISTURE): App. 25%

	HCl Concentration (mg/Nm ³)	SO ₂ Concentration (mg/Nm ³)
Raw gas	4,000 to 10,000	50 to 3,000
Clean gas	< 30	< 60

Removal Efficiency (%)	
HCl	SO ₂
99.2 - 99.7	86 - 97

Stoichiometric Ratio (to Acid Compounds)
App. 3.0

Table 3

MUNICIPAL WASTE INCINERATION WITH DRY SORPTION

Capacity	:	3 x 5 t waste/h
Volume of gas	:	3 x 26,000 Nm ³
Temperature before air cooler	:	App. 250°C (482°F)
HSH dosing rate before cooler	:	15 kg/h
Temperature after cooler	:	App. 150°C (302°F)
Lignite-coke-containing HSH dosing rate after cooler	:	60 kg/h
Raw gas pollutants	:	App. 1,000 mg HCl/Nm ³
(Preliminary information)	:	n.d. SO ₂ * App. 56-82 ng TE/Nm ³ PCDD/-DF
Clean gas pollutants	:	App. 10 mg HCl/Nm ³ n.d. SO ₂ App. 1 ng TE/Nm ³
Removal efficiency	:	99% HCl n.d. SO ₂ App. 98.2-98.8% PCDD/-DF
Stoichiometric ratio, molar, (Ca/HCl) : or	:	2.6 App. 15 kg HSH/t waste

* n.d. = not determined

Table 4

COAL-FIRED POWER PLANTS WITH DRY SORPTION SYSTEMS

		Case 1: <u>2 x 7.5 mW(t) Units</u>	Case 2: <u>2 x 35 mW(t) Units</u>
Flue gas volume	Nm ³ /h	Each 10,400	Each 22,000
Temperature after heat exchanger	°C	170-185 (338-365°F)	135-140 (275-284°F)
Flue gas water vapor content without water injection	%	App. 6*	App. 2*
Water for humidi- fication	m ³ /h	None	1.2
Water vapor content after water injection	%	Unchanged	App. 6.5
Temperature after water injection	°C	Unchanged	App. 95 (203°F)
Pollutant concen- tration in raw gas	mg/Nm ³	SO ₂ :1,350 (486 ppm)	SO ₂ :1,800 (648 ppm) HCl: 400 (252 ppm)
Pollutant concen- tration in clean gas	mg/Nm ³	See Figure 4	SO ₂ : 800 (288 ppm)
SO ₂ removal efficiency	%	See Figure 4	56**
Stoichiometric ratio		See Figure 4	App 1.8

* Unique fueling with anthracite coal (low coal hydrogen content)

** As per system operation to achieve 50% SO₂ removal. With humidification cooling of gas below 90°C (194°F), > 65% SO₂ removal is obtained.

Table 5

COMPARISON OF POLLUTANT CONCENTRATIONS WITH SYSTEM 1 (SPRAY DRYER)
AND SYSTEM 2 (COMBINATION SPRAY DRYER/DRY SORPTION)

	<u>HCl (mg/Nm³)</u>		<u>SO₂ (mg/Nm³)</u>		<u>TE (ng/Nm³)</u>		<u>Total Consumption of Milk of Lime + HSH (kg/h)</u>
	<u>Raw</u>	<u>Clean</u>	<u>Raw</u>	<u>Clean</u>	<u>Raw</u>	<u>Clean</u>	
<u>System 1</u> (Spray Dryer)							
Entire test period	1,160	29	387	100	n.d.	n.d.	250
Single day	1,363	29	353	96	n.d.	n.d.	305
<hr/>							
<u>System 2</u> (Spray Dryer w/ Downstream HSH/ 20% Coke Inj.)							
Entire test period	1,093	6	250	42	n.d.	n.d.	220
Single day	1,416	8	195	43	6.3	0.015	220

Note: Limit values to be met by existing system according to 17. BImSchV by March 1, 1994 are:

HCl < 10 mg/Nm³

SO₂ < 50 mg/Nm³

PCDD and PCDF (as TE, toxic equivalent, factored) < 0.1 ng/Nm³

n.d. = not determined

Table 6

SINGLE STAGE APPLICATION MEANS FOR HSH IN
2.6% SULFUR BITUMINOUS COAL SERVICE

	<u>Duct Injection, Medium Efficiency</u>	<u>Economizer Injection, Medium Efficiency</u>	<u>Duct Injection, High Efficiency</u>
Injection temperature, °C	135-185 (275-365°F)	538 (1000°F)	135-185 (275-365°F)
Operating temperature, °C	App. 90 (194°F)	Below injection temperature	68-72 (154-162°F)
Ca/S ratio	1.8	2.0	App. 3.0
Humidification	Cool to to 90°C (194°F)**	None. Used to augment ESP per- formance.	Yes
Approach to gas wet bulb, °C	50 (70+°F)	No humidification	14-17 (25-31°F)
SO ₂ removal efficiency, %	60	65	85-90
Major capital equipment	None	None	< 3 seconds gas residence time*

* Estimated flue gas residence time after HSH injection and gas humidification

** Possibly a higher operating temperature will be adequate in bituminous coal service in the U.S. due to high water vapor content of raw flue gas.

Table 7

300 MWE CAPITAL REQUIREMENT AND TOTAL LEVELIZED COST (30 YEARS)
FOR MODERATELY DIFFICULT, HIGH (2.6%) SULFUR RETROFIT FOR SO₂ REMOVAL

<u>Case</u>	<u>SO₂ Removal (%)</u>	<u>Capital Cost (\$/kW)</u>	<u>Total Control Cost (\$/ton SO₂)</u>
1. Wet FGD	90	150-280	350-600
2. Spray Dryer (Semi-Dry)	90	140-210	360-540
3. Dry Injection Technologies (U.S.)	40-60	70-120	420-750
4. Dry Injection Technologies (FRG; HSH)	App. 60	75	550
5. Multi-stage (FRG; HSH) (Preliminary Estimate)	85-90	<120	<400

Note: Costs are expressed in constant 1990 dollars.

**INITIAL OPERATING EXPERIENCE
OF THE SNOX PROCESS**

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ABSTRACT

The SNOX Process catalytically removes greater than 95% of the SO_2 and the NO_x from utility coal-fired boiler flue gases and, with integration of recovered heat, has significantly lower O&M costs than conventional technologies. Two SNOX Process units have recently been commissioned in Europe - a 30 MW plant in Gela, Italy and a 305 MW plant in Vodskov, Denmark. Also, a 35 MW demonstration unit will startup in the United States late this year.

The SNOX Process is a highly efficient pollution control technology which produces a salable concentrated sulfuric acid byproduct and no waste streams, liquid or solid. With integration into the furnace block, the SNOX Process can supply heated combustion air which more than compensates for the energy requirements of the air pollution control equipment. Ammonia is the only reagent required.

This paper describes the SNOX Process and presents the startup experiences and initial operating data for two SNOX applications in Europe. The soon-to-be commissioned U.S. demonstration of the process is also discussed.

INTRODUCTION

The current global emphasis on environmental protection and pollution abatement has fostered the development of several new technologies and processes focused on pollution control in the power production industry. Many of these new technologies and processes represent significant improvements over those currently employed. These improvements are in the areas of increased pollutant removal efficiencies, reduced reagent requirements, reduced waste streams, and reduced operating costs. The U.S. Department of Energy (DOE), through its Clean Coal Technology Program (CCTP), is presently providing funds for the development and demonstration of the most promising of these new processes. One such process is a catalytic de-NO_x/de-SO_x process developed in Denmark by Haldor Topsøe A/S and offered under license in North America by Asea Brown Boveri (ABB) Environmental Systems.

This highly efficient technology, known as the SNOX Process, has successfully been demonstrated at a 6,200 SCFM (10,000 Nm³/h) pilot scale facility in Skærbæk, Denmark for over 20,000 hours. The exceptional performance of this pilot facility fostered predictions of the successful application of this process to the utility power production market and has provided the design data necessary for the full-scale units which have come on-line this year. One of these units treats a 30 MW equivalent of flue gas from a petroleum coke-fired furnace in Gela, Italy. The Gela SNOX Plant was commissioned in April. The performance of this unit has exceeded its design targets for sulfur dioxide (SO₂), nitrogen oxide (NO_x) and particulate removal. The sulfuric acid produced by this unit is used for fertilizer production in an adjacent plant.

In August of this year a much larger SNOX installation went on-line in Vodskov, Denmark to treat the flue gas from a 300 MW coal-fired power plant. While operating data from this unit is just becoming available, initial indications are that the SNOX Process has again exceeded its design performance targets. This Plant represents the final step in introducing the SNOX Process to the utility power generation market.

Late this year the SNOX Process will be demonstrated in the United States as part of the DOE CCTP on high sulfur Ohio coal at the Niles Plant of the Ohio Edison Company. This SNOX facility will treat a 35 MW equivalent flue gas slipstream and target 95% SO₂ removal, 90% NO_x removal, and less than 0.0004 gr/SCF (1 mg/Nm³) of particulate emissions. Operating data from this plant will be available in early 1992.

THE SNOX PROCESS

The SNOX Process consists of five key areas; particulate collection, NO_x reduction, SO₂ oxidation, sulfuric acid (H₂SO₄) condensation and acid conditioning. The integration of these individual steps is shown in Figure 1 which is a process flow schematic for a typical full-scale application of the SNOX Process.

To briefly discuss Figure 1, flue gas leaving the air preheater is treated in a particulate control device and passed through the cold side of a gas/gas heat exchanger (GGH) which raises the gas temperature to above 700°F (370°C). An ammonia and air mixture is then added to the gas prior to the selective catalytic reactor (SCR) where nitrogen oxides are reduced to free nitrogen and water. The flue gas leaves the SCR, its temperature is adjusted slightly, and enters the SO₂ converter which oxidizes SO₂ to sulfur trioxide (SO₃). The SO₃ laden gas is passed through the hot side of the GGH where it is cooled as the incoming flue gas is heated. The processed flue gas then enters a falling film condenser (the WSA-Condenser) where it is further cooled with ambient air to below the sulfuric acid dewpoint. Acid condenses out of the gas phase on borosilicate glass tubes and is subsequently collected, cooled, and stored. Cooling air leaves the WSA-Condenser at over 390°F (200°C) and is used for furnace combustion air after collecting more heat through the air preheater.

Particulate Collection

The degree of particulate collection upstream of the SO₂ Converter has a significant effect on the operating costs of this process. This correlation is due to the inherent characteristic of the SO₂ oxidation catalyst to collect and retain greater than 95% of all particulate matter entrained in the flue gas. The collection of this particulate matter, over time, increases the pressure drop across the SO₂ Converter. The initial pressure drop can, however, be restored through on-line catalyst screening (described later). Higher dust loads therefore require more frequent catalyst screening which provides an incentive to utilize a high efficiency particulate collector upstream of the SNOX Process area. A target dust level of

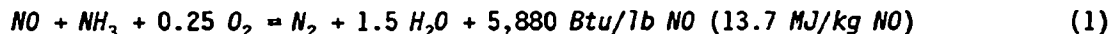
0.0004 gr/SCF (1 mg/Nm³) leaving the collector is used for design. A fabric filter with GoreTex® membrane bags has been demonstrated to achieve this very low emission level. As a consequence of both the high efficiency dust collector and the dust retention characteristics of the SO₂ Converter, particulate emissions from the system are significantly less than 0.0004 gr/SCF (1 mg/Nm³) which is far below any current regulations or standards.

It should be noted that while a high efficiency particulate collector has benefits related to system operating costs, the economics do not require it exclusively. The SNOX plant currently operating in Italy, for instance, uses an electrostatic precipitator (ESP) and is expected to require SO₂ Converter catalyst screening at two week intervals. For comparison, the Niles Demonstration Project with a fabric filter and GoreTex® bags is expected to require screening only once every year.

Nitrogen Oxide Reduction

After the particulate matter is collected and the temperature of the flue gas is increased to over 700°F (370°C) through the GGH, an ammonia (NH₃) and air mixture is introduced to the gas stream via a nozzle grid located upstream of the SCR. A slipstream of hot air from the WSA-Condenser is used to evaporate and dilute a metered mass of ammonia. The resultant mixture is agitated with a static mixer and supplied to the nozzle grid. The design of the nozzle grid allows for controlled stoichiometric ratios of NH₃ to NO_x on a localized scale over the cross-section of the SCR inlet duct. This is critical in order to optimize system NO_x removal efficiency since any unreacted NH₃ which "slips" across the SCR will be oxidized in the SO₂ Converter downstream to water (H₂O), nitrogen (N₂), and NO_x.

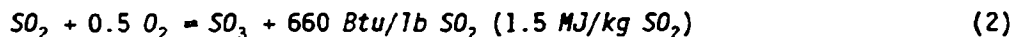
The flue gas/NH₃ mixture enters the SCR and contacts the Haldor Topsøe DNX monolithic catalyst which has been demonstrated to reduce 97%+ of the entering NO_x to N₂ and H₂O. The reduction of nitrogen oxide (NO) follows Equation 1.



The small amount of nitrogen dioxide (NO₂) present in the flue gas is reduced similarly. The general arrangement of the SNOX Process equipment offers one significant advantage over other SCR technologies in that those processes are limited to NH₃/NO_x molar ratios of less than 1.0. This is necessary to limit the NH₃ "slip" past the SCR to 5 ppm or less. Higher levels may result in ammonium sulfate or bisulfate scaling in lower temperature areas downstream. The NO_x removal efficiency of these processes is thus limited. Any NH₃ slip in the SNOX Process, however, is oxidized as it contacts the SO₂ Converter catalyst downstream. This allows stoichiometric ratios in excess of 1.0 and consequently higher NO_x removal efficiencies without adverse downstream effects. Ammonium "salting" does not occur in the duct between the SCR and the SO₂ Converter because the temperature is well above the dewpoints of ammonium sulfate and ammonium bisulfate. Excess NH₃ slippage, however, must still be minimized in order to maximize system NO_x removal due to the NO_x forming oxidation of NH₃ in the SO₂ Converter.

Sulfur Dioxide Oxidation

The SCR effluent is heated slightly with natural gas, oil or steam to reach the optimum SO₂ Converter inlet temperature of 770°F (410°C) and passed through beds of Haldor Topsøe sulfuric acid catalyst. This catalyst has seen wide use in the U.S. sulfuric acid industry for the past decade with a high degree of success. The efficiency of the Topsøe catalyst is not affected by the presence of water vapor or chlorides in concentrations up to 50% and several hundred ppm, respectively. Without any reagents or additives, over 95% of the entering SO₂ is oxidized via Equation 2.



Due to surface fouling by flyash, the oxidation catalyst requires screening to maintain a minimum converter pressure drop. The screening frequency is dependent on the removal efficiency of the particulate collection device upstream. The required screening frequency will range from once every two weeks to once a year. Regardless of the efficiency of the particulate collector, however, virtually all remaining particulate is retained in the SO₂ Converter which results in the inherently minimal particulate emissions of this process.

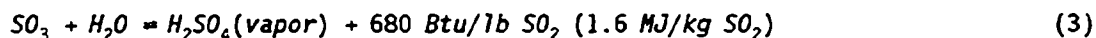
The screening procedure consists of the isolation of an individual catalyst bed, removal and mechanical screening of the catalyst in that bed, and refilling the bed

with the screened catalyst. Beds are sequentially screened in this manner. The procedure can be automated and is performed while the process is on-line at full load. This procedure separates and removes virtually all flyash and other contaminants from the surface of the catalyst pellets and restores SO₂ oxidation efficiency. Catalyst loss during screening is estimated at 2-3%.

An additional benefit of the sulfuric acid catalyst is that it oxidizes most of the carbon monoxide (CO) and hydrocarbons present in the flue gas stream to carbon dioxide and water. This is of importance since emissions of both these compounds have come under increased scrutiny as evidenced by the recent legislative actions.

Sulfuric Acid Condensation

The SO₃ in the gas leaving the SO₂ Converter is hydrated and condensed in two steps. First, the bulk of the SO₃ is hydrated to sulfuric acid vapor (Equation 3) as the flue gas passes through the hot side of the GGH and the temperature drops approximately 300°F (165°C).



At this point the flue gas is still well above the acid dewpoint thus avoiding acid condensation and corrosion of the ductwork. The flue gas, at around 500°F (260°C), is passed through the proprietary WSA-Condenser developed by Haldor Topsøe. The WSA-Condenser is a unique tube and shell falling film condenser with ambient air used as the cooling medium on the shell side. Proprietary borosilicate glass tubes are used to convey and cool the flue gas. There are several design features of these tubes which make possible the virtually complete condensation and capture of sulfuric acid at concentrations of 94 to 97 wt.%. The precipitation of the sulfuric acid from the gaseous phase to the liquid phase is also an exothermic reaction which releases 460 Btu/lb SO₂ recovered as H₂SO₄ (1.1 MJ/kg SO₂). The flue gas is cooled to about 210°F (100°C) at the outlet of the condenser which, combined with the presence of approximately 5 ppm of uncollected sulfuric acid mist, will require the downstream ductwork and stack to be lined. The condensed sulfuric acid product is funnelled through an acid brick lined trough at the bottom of the WSA-Condenser into the acid conditioning and storage system.

The WSA-Condenser's discharge cooling air represents the only other by-product of the SNOX Process. In an integrated system, the bulk of this heated ambient air at

about 400°F (200°C) will be passed through the furnace air preheater and used as combustion air. A small percentage of the product air is used for system auxiliaries such as ammonia evaporation and dilution, support burner combustion air, and coal milling. The WSA-Condenser, in effect, collects the heat released from the reactions in the SCR and SO₂ Converter, the hydration of SO₃, the condensation of H₂SO₄, the support burner, the booster fan compression and the overall decrease in flue gas temperature. This results in a considerable amount of thermal energy which can be easily utilized as preheated furnace combustion air to increase boiler efficiency. Steam production can increase on the order of 1% per each percent of sulfur in the fuel. At 2-3% sulfur, the SNOX Process energy requirements are compensated. These heat recovery characteristics make the use of high sulfur, low cost fuels economically attractive with this process.

Acid Conditioning and Storage Systems

The hot concentrated sulfuric acid product at about 400°F (200°C) is collected and circulated through a fluoropolymer lined system consisting of a holding tank, circulation pumps, and a water cooled heat exchanger. The purpose of this loop is to cool the acid to more manageable temperatures (70-100°F or 20-40°C) and to allow for dilution of the acid to a specified concentration, normally 93.2 wt.%. As acid collects in the conditioning loop, it is metered off at a rate which maintains a constant level in the holding tank. This product acid is stored in carbon steel tanks prior to removal by tanker truck. It should be noted that the sulfuric acid produced by the SNOX Process meets or exceeds U.S. Federal Specification O-S-801E Class I and is expected to be commercially tradeable without limitation.

Pilot Results

The performance characteristics of the SNOX Process as seen at the Haldor Topsøe 3.5 MW equivalent pilot facility in Skærbæk, Denmark over the past three years are summarized below:

- FABRIC FILTER - less than 0.0004 gr/SCF (1 mg/Nm³) of particulate leaving the filter which operates at about 4 in w.c. (10 mbar) of pressure drop and an air to cloth ratio of 3.3 fpm (60 m/h).
- SCR - 98% NO_x removal with 400 ppm inlet NO_x, an NH₃/NO_x ratio of 1.02 and a space velocity equal to that of a full-scale plant. Only minimal deactivation of the SCR catalyst has been observed.
- SO₂ CONVERTER - 97% and 95% SO₂ conversion at inlet SO₂ concentrations of 500 and 1,700 ppm, respectively, at 20% higher

than full-scale space velocities. The SO_2 catalyst has been screened successfully several times and only minimal deactivation of the catalyst has been observed.

- WSA-CONDENSER - high SO_3 capture efficiency with an acid mist carryover of 5 ppm normally and never greater than 10 ppm even through an operating range of 30 to 120% of design gas flow. The sulfuric acid by-product is consistently 95 wt.% with water clarity and no heavy metals present at greater than 0.5 ppm.

It should also be noted that all design heat and material balances have been substantiated and verified from Skærbæk data.

A 30 MW PETROLEUM COKE APPLICATION

The Gela Power Plant is owned by ENICHEM S.p.A. in Gela, Italy and contains a BREDA type boiler that supplies 380 t/h of steam at 1550 PSIA to a turbine and the adjacent petrochemical complex. The boiler was commissioned in 1960. The total flue gas from the boiler is about 250,000 SCFM (400,000 Nm^3/h), of which 25% is treated in the SNOX Plant. The normal fuel supply is pet-coke with a sulfur content of 6-7 wt.%. The boiler can also burn fuel-oil of 3.5 wt.% sulfur.

The Gela SNOX Plant

The Gela Plant represents the first industrial application of the SNOX technology according to the so-called "hot scheme" as shown in Figure 2. The key aspects of this type of application are as follows:

1. Flue gas is taken upstream of the boiler air preheater.
2. Particulate collection is accomplished with a hot side ESP at 730 to 750°F (390-400°C).
3. A gas/air heat exchanger is used instead of a gas/gas heat exchanger for flue gas cooling prior to the WSA-Condenser.
4. Atmospheric air used to condense the product sulfuric acid is heated to 645-660°F (340-350°C) and sent directly to the furnace burners.
5. The flue gas fan is installed downstream of the WSA-Condenser, thus all process equipment operates under negative pressure.

The design specifics of each major piece of process equipment are discussed below.

Electrostatic Precipitator. As stated before, the ESP at the Gela Plant is of the hot-side design. Its design inlet flue gas conditions are:

• Flowrate	62,400 SCFM	100,000 Nm ³ /h
• Temperature	790°F	420°C
• Dust load (pet-coke)	2.9 gr/SCF	7.0 g/Nm ³
• Dust load (fuel oil)	0.5 gr/SCF	1.3 g/Nm ³

This ESP normally operates with five fields in service. The dimensions (LxWxH) of the casing are 72x33x46 ft (22x10x14 m). This precipitator is designed to limit outlet dust emissions to .004 gr/SCF (10 mg/Nm³) for all operating conditions.

SCR Reactor. Flue gas enters the reactor from the top and exits via the bottom passing through two catalyst layers. Inside the reactor there are actually four catalyst support grids that make it possible to change the arrangement of the layers for experimental purposes. The reactor operates near 690°F (365°C) and utilizes a type of the Topsøe DNX catalyst known as "medium dust."

SO₂ Converter. The SO₂ Converter for this plant consists of six catalyst panels built into one casing. The flue gas leaving the reactor is conveyed through three ducts, each provided with a damper which allows the catalyst screening without interrupting plant load. The catalyst cleaning is done by means of an automated system. This converter also operates near 790°F (420°C) using Topsøe sulfuric acid catalyst.

WSA-Condenser. In the WSA-Condenser the flue gas is cooled to about 210°F (100°C) with air from the existing boiler air fan. This condenser contains 5800 glass condensing tubes, each about 20 ft (6 m) long. The WSA-Condenser's casing is constructed of carbon steel and has dimensions (LxWxH) of 23x23x20 ft (7x7x6 m). The acid collecting bottom of the condenser is lined with a PTFE membrane and acid brick.

Demonstrated Performance

The main objective of the Gela Plant's test program is to demonstrate the application of the "hot scheme" SNOX Process on a full-scale power station. During the two-year test program, a parametric study of different operating conditions will be performed on various fuels. The information and data collected will be mainly used to identify the factors which affect process reliability.

During the first operating period (March 1991-July 1991), the plant was tested at the following conditions:

• Fuel	Pet-coke	Pet-coke
• Flue gas flowrate	50,000 SCFM	80,000 Nm ³ /h
• Cooling air flowrate	62,000 SCFM	100,000 Nm ³ /h
• Hot air to boiler	53,000 SCFM	85,000 Nm ³ /h
• Process temperatures:		
• Inlet ESP	735°F	390°C
• Inlet SCR	690°F	365°C
• Inlet SO ₂ Converter	790°F	420°C
• Outlet WSA-Condenser	225°F	106°C
• Hot air to boiler	645°F	340°C
• Sulfuric acid production	1800-2400 lb/h	800-1100 kg/h
• Sulfuric acid concentration	≥ 94 wt.%	≥ 94 wt.%

Dust Removal. The ESP performance has been evaluated by isokinetically measuring outlet dust conditions and values less than .002 gr/SCF (5 mg/Nm³) have been found. No inlet loadings have been measured thus far. The minimal pressure drop increase across the SO₂ Converter confirms these very low outlet measurements.

NO_x Removal. The system NO_x removal, calculated from process instrumentation, was greater than 96% with SCR inlet and WSA-Condenser outlet NO_x concentrations of 350 and 9 ppm, respectively. This data was collected at an NH₃/NO_x ratio of 1.0.

SO₂ Conversion. The system SO₂ conversion, calculated from the plant's Continuous Emissions Monitoring System (CEMS) and confirmed by lab analyses, was greater than 96% throughout the operating period. The plant inlet SO₂ concentration varies widely between 2400 and 4000 ppm depending on fuel sulfur content. Even through this wide range of inlet sulfur loadings, outlet emissions are maintained between 70 and 140 ppm - greater than 96% SO₂ removal. The wide range of SO₂ inlet concentrations caused no operating problems with the SNOX Plant.

Sulfuric Acid Condensation. Apart from a light turbidity for the first few days of start-up, the sulfuric acid product has been perfectly colorless. The acid concentration has remained between 94 and 94.5 wt.%. Based on lab analyses, the

sulfuric acid is of good industrial quality with a very low heavy metals content and is normally used inside the Gela petrochemical complex for fertilizer production. The thermal exchange characteristics of the WSA-Condenser have been in accordance with expected values.

Initial Operating Experience

The main problems during the first operating period of the test have not been directly connected with the SNOX Process. For instance, during the final ESP commissioning phase, it was necessary to replace certain electrical insulators. This changeout resulted in a corresponding delay in the expected plant start-up date.

A persistent mechanical problem, which has affected plant availability, has been improper balance of the flue gas fan. This problem is being investigated by the fan vendor.

It should be noted that the SNOX Plant start-up and shut-down procedures have not caused any problems with the normal boiler operation. Also, SNOX Plant operation is fully automatic.

A 305 MW COAL-FIRED APPLICATION

The power station of Vendsyssel is owned by I/S NEFO, the North Jutland Electricity Supply Company, and is the northernmost power station within the ELSAM (Jutland-Funen power pool) cooperation. This power station consists of 2 coal/oil-fired units of 137 MW and 305 MW, respectively. The SNOX Plant is to clean 100% of the flue gas from Unit 2, the larger, which is of the Benson type with a nominal steam production of 910 t/h (235 kg/s) at 2900 PSIA and 1000°F.

The NEFO SNOX Plant

The equipment supplied at the NEFO Plant is shown as a simplified process flow schematic in Figure 3. A discussion of each major piece of equipment is provided below.

Fabric Filter. The fabric filter is arranged in sections with common inlet and outlet manifolds. Thus, each section, or compartment, can be isolated and maintained during full operation. Cleaning of the bags is done according to the reverse air principle. The filter material was supplied by Gore-Tex® and consists of a glass fiber backing laminate coated with a Teflon (PTFE) membrane. The

filtration itself is accomplished by the so-called membrane filtration technique which allows a maximum dust detention simultaneously with high filtration speed and low pressure loss.

Start-Up Burner. For preheating the SNOX Plant to operating temperature before treating flue gas, two light oil-fired start-up burners heat a partial flow of the cooling air leaving the WSA-Condenser. The preheated air is introduced to the system prior to the flue gas blowers. Preheating the SNOX Plant from a cold condition requires six to eight hours.

Flue Gas Blowers. In order to overcome the pressure loss across the SNOX Plant, two 50% axial fans are provided - each with a motor rating of approximately 4 MW.

Gas/Gas Preheater. For heating the flue gas after the flue gas fans, a rotating regenerative gas/gas preheater is installed. The preheater is designed to heat the SCR inlet flue gas to approximately 725°F (385°C) while simultaneous cooling of the stream exiting the SO₂ Converter. In order to reduce the temperature differences which normally occur across the cross section of a rotating gas/gas preheater, the speed of the rotor is increased from 0.6 rpm to 1.2 rpm in the high load area.

The thermal efficiency of this preheater is designed at 85% with a maximum leakage of 2% at full load. The heating surface area totals approximately 915,000 ft² (85,000 m²). This preheater, which follows the Ljungström principle, is provided with a leakage minimizing system in order to maximize system SO₂ and NO_x removals. Any leakage across the preheater, in effect, bypasses the catalytic reactors and results in a decrease in system removals.

SCR Reactor. The SCR reactor contains two layers or beds of catalyst and one blank bed grid. When the catalyst activity has degraded to a certain limit, a third layer is added. The catalyst is built up into box-shaped modules, each module consisting of six cassettes. The catalyst design allows the passage of any dust particles. For this reason the SCR reactor does not require cleaning equipment such as steam lances. The construction of the reactor allows for easy exchange of the catalyst modules by means of equipment specially designed for this purpose. A plant outage is, however, required.

Steam/Gas Preheater. Having passed through the SCR reactor, the flue gas is heated in order to obtain the reaction temperature necessary in the SO₂ Converter. This heating is done by a steam/gas preheater which uses superheated steam taken after

the second high pressure superheater of the boiler. Having been cooled by approximately 210°F (100°C), the steam is returned to the boiler circuit prior to the third high pressure superheater. The heat exchanger is designed as a finned tube heat exchanger with a total heating surface area of approximately 44,000 ft² (4,100 m²).

SO₂ Converter. The SO₂ Converter consists of 36 catalyst panels built into one casing. The lateral faces of the panels are perforated allowing flue gas flow horizontally through the panels from a central inlet chamber to the outlet chambers. The panels can be isolated from the flue gas flow during the filling and discharge of catalyst. The catalyst is a vanadium-containing oxidation type formed as rings. Catalyst addition is performed through top mounted feed chutes on each panel. Discharge is done at the bottom of the beds through discharge chutes.

Unless major leakage occurs in the bag filter, the catalyst is expected to be cleaned only once a year - at the time of the annual outage. The cleaning of the catalyst material in the SO₂ Converter is executed with a mobile screen system. The screen system is connected to each panel sequentially after isolation from the flue gas flow. The cleaned catalyst material flows to a heated container. The container is then moved to the top of the panel where the catalyst material is deposited into the panel.

WSA-Condenser. The WSA-Condenser consists of six sections, each containing twelve modules. Each module consists of a bundle of vertically mounted glass tubes. As the flue gas is cooled to about 210°F (100°C) in the WSA-Condenser, the sulfuric acid vapor from the SO₂ Converter is condensed and concentrated on the glass tubes. The condensed sulfuric acid is collected in lined vessels placed under the glass tubes and cooled in an acid cooling circuit with a sea-water cooled heat exchanger. Having been cooled to approximately 100°F (40°C), the sulfuric acid is conveyed to the acid storage tanks by means of conveying pumps. These steel storage tanks contain up to 3,750 tons of sulfuric acid, corresponding to approximately six weeks of full load coal-fired operation with 1.6% sulfur fuel.

The cooling air to the WSA-Condenser is delivered by two existing secondary air fans. Having been heated in the WSA-Condenser, the discharge cooling air passes through a trim cooler and then to the existing air preheater to be used as furnace

combustion air. The trim cooler is cooled by condensate taken after the first low pressure preheater and returned to the feed tank. This brings about a gross increase of the efficiency of the turbine generator of approximately 2.2 MW at 100% load.

Chimney. At the WSA-Condenser outlet the flue gas temperature will be 190-230°F (90-110°C) dependent on the ambient temperature. The flue gas will contain small quantities (5-10 ppm) of sulfuric acid mist. Therefore, the flue gas duct after the WSA-Condenser is provided with an acid-resistant coating and the new SNOX chimney is provided with a chimney pipe constructed of acid-resistant brick. Technical and economic estimates showed that the cheapest alternative was to build a new SNOX chimney since the existing chimney would, among other things, have required the application of a protective coating. Now, the pre-existing chimney is used only during bypass operation and start-up of the SNOX Plant.

Consumption and Production Data

With a coal sulfur content of 1.6%, the full load consumption and production data for this SNOX Plant will be as follows:

• Flue gas loading, SCFM (Nm ³ /h)	562,000 (900,000)
• Sulfur dioxide removal, %	93+
• Nitrogen oxide removal, %	90+
• Water consumption, gpm	0
• NH ₃ consumption, t/h	0.38
• Acid production (95% H ₂ SO ₄), t/h	5.2
• Reduced efficiency of power plant, %	0.2

THE U.S. SNOX DEMONSTRATION PROJECT

The U.S. SNOX Demonstration Project will be located at the Ohio Edison Niles Power Plant near Niles, Ohio in Trumbull County. The plant is situated on 130 acres along the southern bank of the Mahoning River. The Niles Plant is part of the Ohio Edison System with over 6000 MW of capacity serving central and northeastern Ohio and western Pennsylvania. This project is one of 10 clean coal projects Ohio Edison currently has underway or has recently completed.

Ohio is a high sulfur coal state and clean coal research and development is supported by government, business and labor. Ohio is one of the leading states in

the consumption of coal. In 1989, the State of Ohio produced 31.4 million tons of coal and has demonstrated reserves of 19 billion short tons. Coal will likely continue to be the cornerstone of Ohio's energy supply. However, largely as a result of the Clean Air Act, the demand for Ohio-produced coal, both domestic and out-of-state, has fallen considerably since 1970.

One of eleven power plants in the Ohio Edison system, the Niles facility was commissioned in 1954. The main power plant structure covers an area of approximately 166 ft by 200 ft, and houses two cyclone coal-fired steam electricity-generating units with a net demonstrated total capacity of 216 MW for both units. The boiler units burn high-sulfur coal with a capacity factor of approximately 67 percent. Flue gases from both boiler units are dispersed into the atmosphere by a single 393 ft tall dual flue stack. Each unit utilizes an ESP to control particulate emissions.

The SNOX Demonstration Project will treat about one-third of the flue gas stream from Unit 2 or approximately 16 percent of the total flue gas generated at the plant. The flue gas is taken as a slipstream just upstream of the Unit 2 ESP. Flue gas cleaned by the SNOX Plant will be returned directly to the existing stack breeching. Project facilities will be installed on a 150 ft by 120 ft unoccupied area southeast of the plant building.

Demonstration Objectives

The SNOX technology and all the mechanical components which are required for its successful application have completed both the bench and pilot phases of development. The 30 MW application in Italy and 300 MW application in Denmark are evidence that this technology has also entered a commercialization phase. Thus, the SNOX facility at the Niles Station is not a developmental project but a demonstration of this technology's readiness for commercial use in the United States.

The first and foremost objective of the project is to successfully apply the technology and proprietary equipment to a North American power plant firing high sulfur coal to confirm the capability to economically meet the pollution control needs of the utility market. Several supporting objectives are in place to meet this primary objective. These supporting objectives are to confirm the results achieved at the Skærbæk pilot facility, demonstrate the marketability and economic credits of the sulfuric acid and heat energy by-products, confirm the estimated low O&M costs, and define any limitations of each piece of major equipment with respect

to a utility environment. This demonstration facility began operation in November of this year.

SUMMARY

The SNOX Process has been developed with the objective of near complete removal of sulfur oxides, nitrogen oxides, and particulate from flue gas with minimum consumption of resources and maximum recovery of valuable by-products without the creation of any secondary environmental problems. All indications to date are that this ambitious objective has been achieved and that the full-scale capital and O&M costs of this technology are comparable to or lower than those of currently utilized technologies.

The SNOX Process has several distinct advantages over other de-NO_x/de-SO_x processes and conventional technologies which will rate it as a desirable and superior technology in the coming decade of increased environmental concern. These advantages include:

- High SO₂ removal
- No alkali reagent required
- High NO_x removal
- Very low particulate emissions
- Low CO and hydrocarbon emissions
- Only by-product is salable sulfuric acid
- Operating costs decrease with increasing fuel sulfur content
- Furnace integration of recovered heat increases plant thermal efficiency and compensates for backend energy requirements.

SNOX INTEGRATED PROCESS FLOW

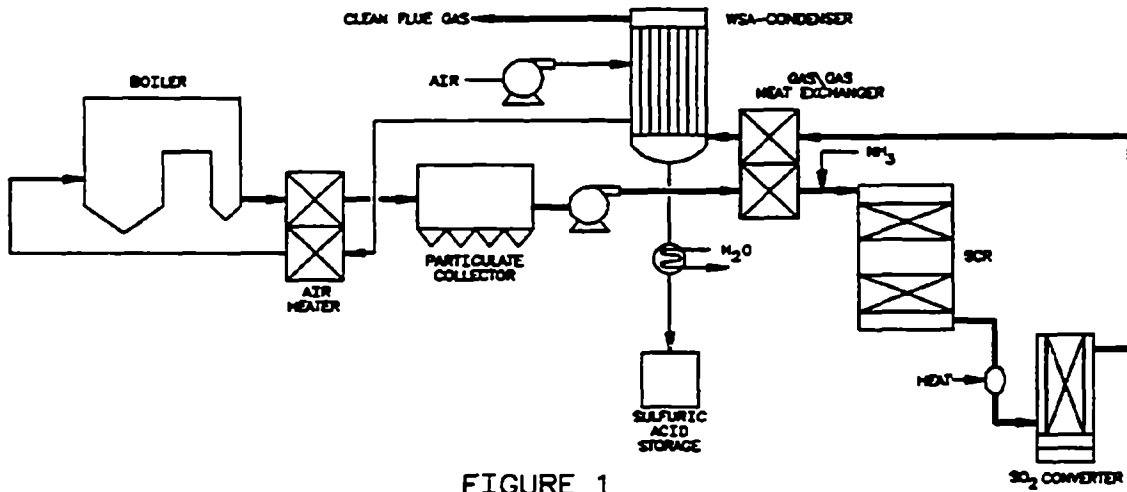


FIGURE 1

SNOX HOT SCHEME PROCESS FLOW

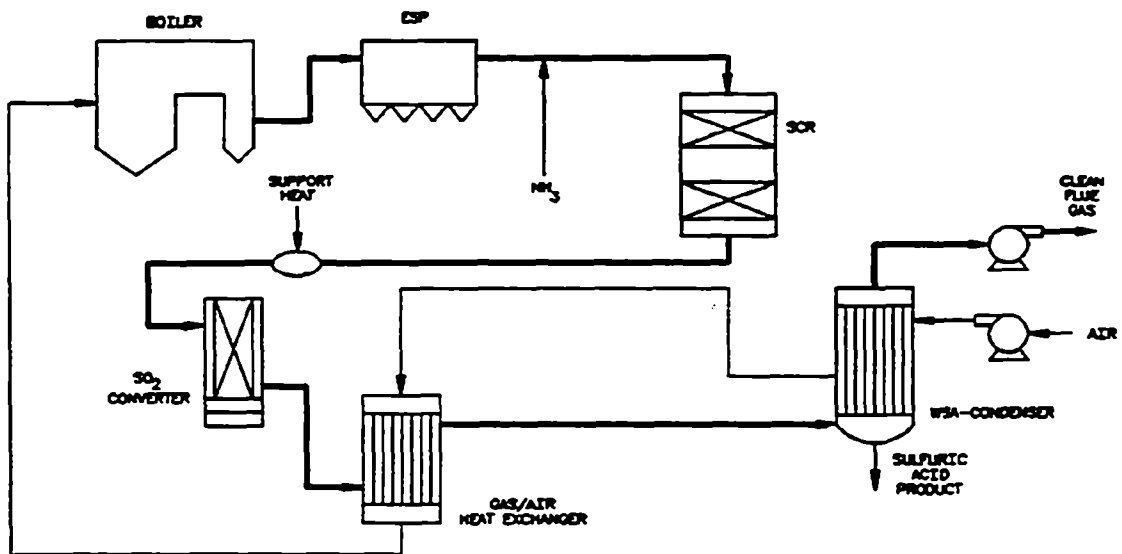


FIGURE 2

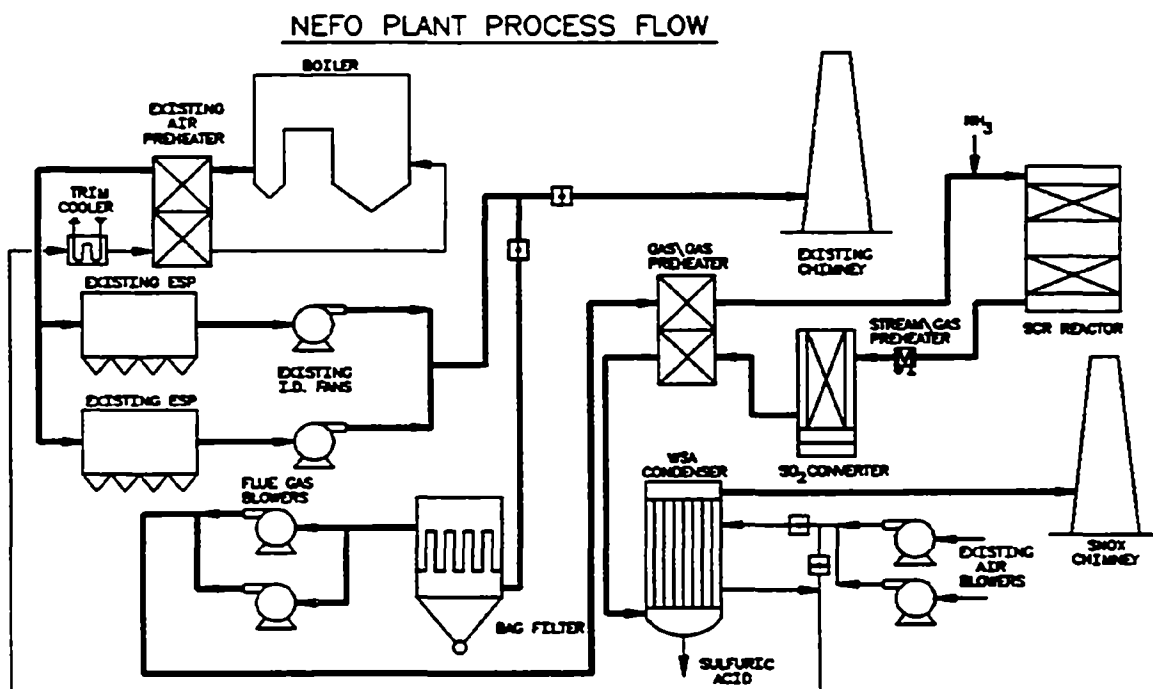


FIGURE 3

**PROGRESS REPORT OF THE
NIPSCO - PURE AIR - DOE
CLEAN COAL II PROJECT**

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ABSTRACT

The paper will describe the current status of the NIPSCO - Pure Air - DOE Clean Coal II Project at the Northern Indiana Public Service Company's Bailly Generating Station. It will describe the site features, layout, configuration, and current construction status. The paper will also cover the results of pilot plant design confirmation testing done with actual coal and limestone samples. The testing was performed at the Mitsubishi Heavy Industries test facility in Hiroshima, Japan. These tests confirmed the design calculations for the plant.

Pure Air, a general partnership between Air Products and Chemicals, Inc., and Mitsubishi Heavy Industries America, Inc., was established in 1985 to market flue gas desulfurization (FGD) systems and services in North America. MHIA is a wholly-owned subsidiary of Mitsubishi Heavy Industries, Ltd. (MHI). MHI has sold more than 90 FGD units worldwide, with a total of over 500 years of operating time on all the units combined. The general partnership combines the Mitsubishi Advanced Flue Gas Desulfurization (AFGD) technology with Air Products' plant design, construction, and operating capability to form a company that can either sell FGD systems on a turnkey basis or design, construct, finance, own operate and maintain FGD plants. Air Products pioneered the "on-site" concept over 40 years ago, and currently owns and operates over 165 industrial gas, chemical, cogeneration, and waste-to-energy plants worldwide.

In 1988, Pure Air was selected by the U.S. Department of Energy (DOE) under the second solicitation of the Clean Coal Technology Program to install an AFGD system at Northern Indiana Public Service Company's (Northern Indiana) Bailly Generating Station. Pure Air will design, construct, finance, own, operate, and maintain the AFGD facility, and has signed a contract to provide these services to Northern Indiana at Bailly Station for a 20 year term. During the initial three years of operation, a demonstration test plan will be conducted to confirm that the Pure Air AFGD system will perform at high removal efficiencies, in an economic fashion over a wide range of midwestern high sulfur coals. The economics of this system were previously presented at the 1990 SO₂ Control Symposium.

The Project will demonstrate the following novel features:

Single 600 MW Module

A single 600 megawatt module will treat flue gases from two boilers, Bailly Units #7 and #8. No spare modules are necessary. Pure Air is providing an availability guarantee to Northern Indiana for the entire life of the contract.

Co-current Module With In-Situ Oxidation

The facility is designed to produce high quality gypsum by-product while operating on a range of coals. Oxidation is performed in the absorber tank rather than a separate vessel.

Own and Operate Concept

The FGD system supplier will own, operate, and maintain the SO₂ removal, dewatering, and wastewater system for a period of 20 or more years. Pure Air will provide ongoing performance guarantees for the life of the plant, which reduces risk to Northern Indiana and its customers.

Saleable By-Product Gypsum

The by-product gypsum produced by this facility will meet specifications established by the wallboard industry for use in gypsum wallboard, thus avoiding landfill costs associated with disposable systems and providing an additional revenue service to Northern Indiana to partially offset the costs of SO₂ removal.

Dry Limestone Injection

Dry limestone powder will be directly injected into the absorber reaction tank below the liquid level. This system is of particular benefit where space limitations restrict on-site installation of wet grinding systems. For this project, limestone will be ground off site at a nearby processing plant and transported to the site in pneumatic vehicles.

High SO₂ Removal Efficiency

Removal efficiencies of 95% or more will be demonstrated.

Wastewater Minimization

Wastewater from the facility is minimized by adjusting the pH of FGD system blowdown, pressurizing a portion of the flow, and injecting it into the flue gas duct

upstream of the electrostatic precipitator. The water is vaporized and the solids removed with the fly ash (Figure 1). Note that the wastewater evaporation system was jointly developed by Kansai Electric Power Company and MHL.

A flowsheet of the project is shown in Figure 2.

Contracts

On 1 July 1989, Pure Air and Northern Indiana entered into a Flue Gas Processing Agreement whereby Pure Air agreed to finance, design, construct, own, operate, and maintain the FGD system at the Bailly Generating Station for a period of 20 years. In exchange for a monthly fee, Pure Air guarantees operating costs, capital costs, and availability to Northern Indiana on an ongoing basis.

Pure Air and the Department of Energy concluded negotiations and signed the Cooperative Agreement for the project on 20 December 1989.

Bids for pulverized limestone delivery were solicited by Pure Air on behalf of Northern Indiana. On 31 December 1990, a contract for supply of limestone was executed with the J. M. Huber Company.

Pure Air assisted Northern Indiana in marketing the gypsum by-product from this facility. On 1 June 1990, Northern Indiana concluded a gypsum sale agreement with United States Gypsum, whereby USG will buy the by-product output from the FGD facility for use at a nearby wallboard facility.

BAILLY PROJECT STATUS

Environmental Approvals

The Environmental Assessment required by the National Environmental Policy Act (NEPA) was prepared and reviewed by DOE officials. A finding of no significant impact was issued to the project on 16 April 1990.

The Air Permit to Construct was applied for on 23 August 1989 and officially approved by the Indiana Department of Environmental Management/Air Board on 7 November 1990.

The National Pollutant Discharge Elimination System (NPDES) Permit Modification was applied for on 24 August 1989 and officially approved by the Indiana Department of Environmental Management/Water Board on 15 November 1990.

All required state and local building permits have been applied for and received.

Design Confirmation Test

A two week design confirmation test for the Bailly AFGD Project was conducted at APC-200 test facility at MHI's Hiroshima Technical Institute. The APC-200 test facility (Figure 3) is a state-of-the-art pilot unit for total analysis and design confirmation of flue gas cleaning systems. A coal feed rate of 25 kg/hr. is used to generate 200 NM³/hr. of flue gas. The facility is capable of monitoring numerous flue gas process configurations and of analyzing the inter-related effects of various fuel and absorbent conditions. Predictions from the APC-200 unit have been confirmed against operating units. The Bailly plant design confirmation tests were conducted using samples of the coals and limestone that are expected to be used at Bailly. The purposes of the test were to confirm calculated performance for SO₂ removal efficiency and calcium utilization under design conditions, verify the reactivity of the limestone source, and confirm by-product gypsum quality.

Testing was performed using two grinds of limestone which previously had been qualified based on purity and reactivity. The testing involved combusting coal samples in the test unit furnace and treating the resultant flue gas in the test unit. The testing determined the SO₂ removal efficiency for different liquid to gas ratios and inlet SO₂ concentrations, and at the same time producing a gypsum by-product of greater than 95 wt. % purity. The results of this testing are summarized in Table 1. These results indicate that SO₂ removal efficiencies greater than 97.5% can be achieved processing flue gas from coals containing up to 4.5 wt. % sulfur.

Construction Status

Official ground breaking ceremonies for the project were held at the Bailly site on Earth Day 1990 (20 April 1990). As of 1 September 1991, Northern Indiana has completed necessary site fill and grading operations, the shell of the new chimney, and is in the process of installing the chimney liners. Northern Indiana is also constructing the

electrical and other utility feeders to the FGD system battery limits, and making necessary control modifications to the power plants.

Pure Air has completed Equipment Procurement and Detailed Design Engineering for the FGD facility. The absorber vessel has been erected and is being lined. Lining activities are approximately 75% complete. The absorber hold tank is complete; the recirculation pumps have been set and piping work is underway. Electrical construction is in progress.

In July, the circulating water lines leading into and out of the power plant collapsed causing significant damage to the power plant and lesser damage to the FGD facility. Although the cause of the collapse is still not known, immediately after the collapse, Pure Air and Northern Indiana formed a joint team to 1) complete efforts to ensure that safe conditions exist at the accident site and assemble an engineering team, including outside experts, to begin evaluating the cause of the accident and the degree of damage to all facilities, 2) develop an integrated approach to begin repairs to the power plant's water supply system and to resume operations as soon as possible, and 3) resume construction of the scrubber facility and minimize any delays in its completion.

Pre-commissioning activities are expected to begin in the first quarter of 1991, with commercial operation expected in July 1992.

FIGURE 1
WASTEWATER EVAPORATION SYSTEM (WES)

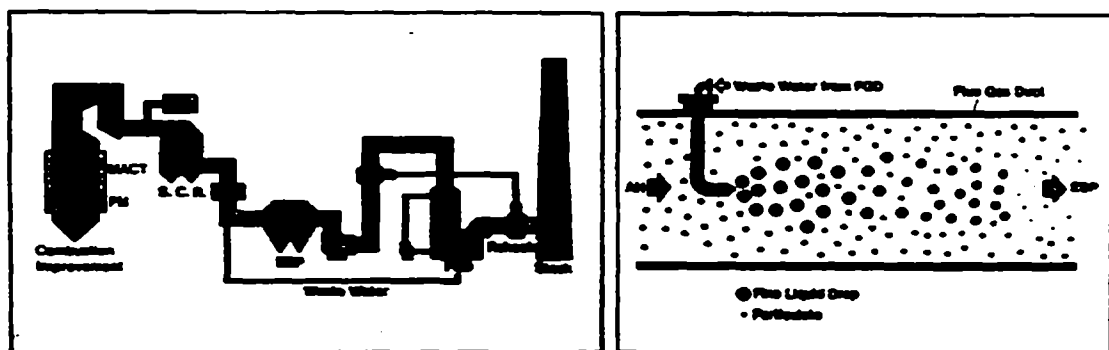


FIGURE 2
ADVANCED FLUE GAS DESULFURIZATION
PROCESS FLOW DIAGRAM

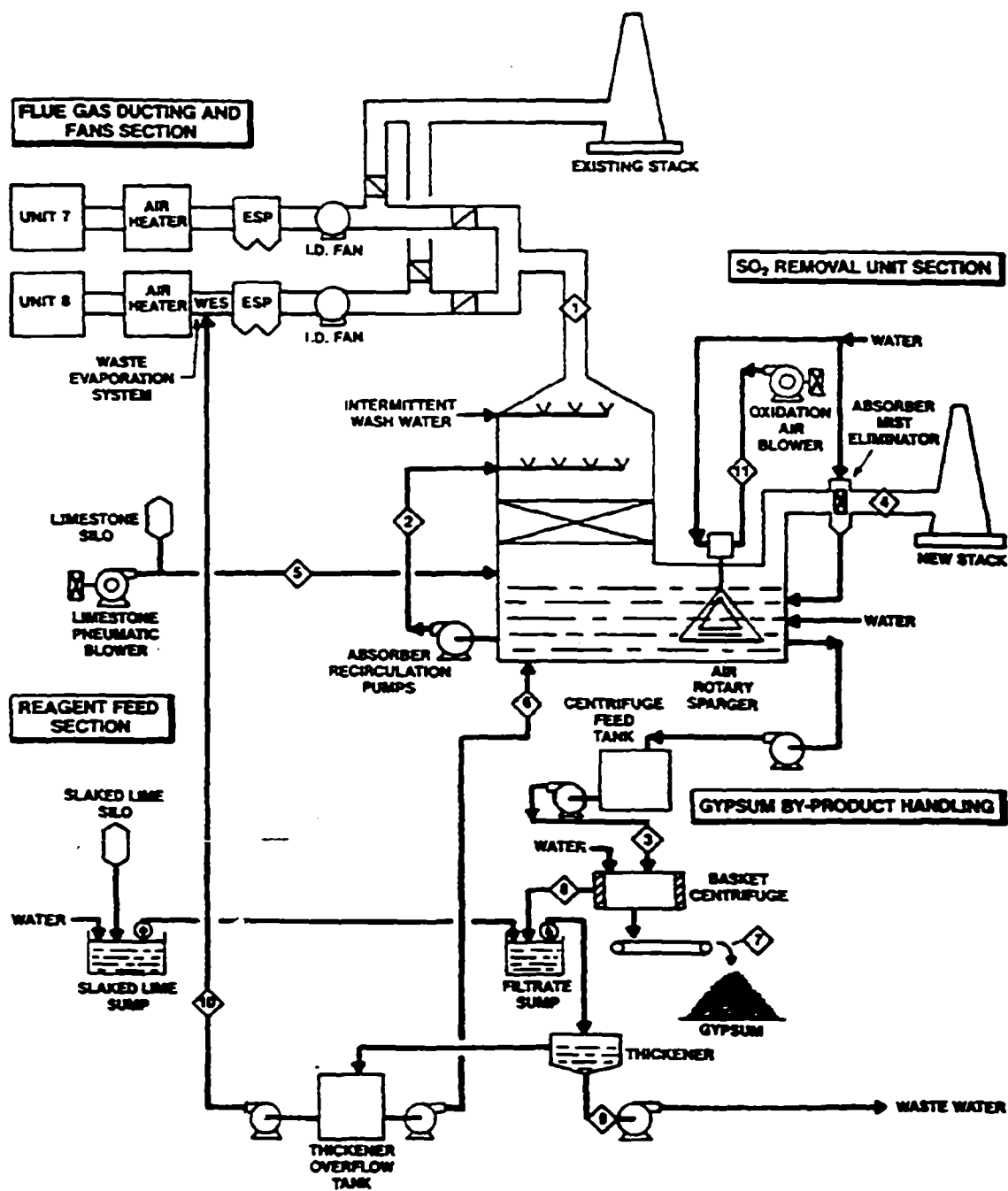
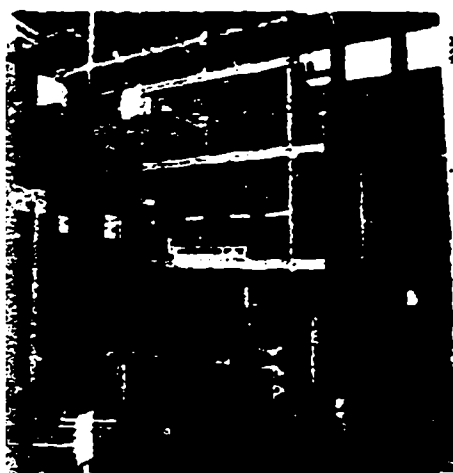


FIGURE 3



APC-200

200m³N/h TEST FACILITY



TABLE 1**RESULTS OF APC-200 DESIGN CONFIRMATION TEST****Limestone: NL-3**

<u>Inlet SO₂, ppmd</u>	<u>L/G, 1/Nm³</u>	<u>SO₂ Removal Efficiency, %</u>	<u>Calcium Utilization, %</u>	<u>Gypsum Purity, wt. %</u>
3,055	22.2	97.5	94.3	95.9
2,317	16.1	95.9	94.2	95.8

Limestone:>NNL-3

<u>Inlet SO₂, ppmd</u>	<u>L/G, 1/Nm³</u>	<u>SO₂ Removal Efficiency, %</u>	<u>Calcium Utilization, %</u>	<u>Gypsum Purity, wt. %</u>
3,040	22.2	97.7	93.8	95.5
2,330	16.1	96.1	94.1	95.7

DEVELOPMENT OF A POST-COMBUSTION DRY SO₂
CONTROL REACTOR FOR SMALL-SCALE COMBUSTION SYSTEMS

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ABSTRACT

Under a contract with the U.S. Department of Energy, Pittsburgh Energy Technology Center (PETC), Tecogen Inc. is developing an integrated emissions control system for use with small-scale, coal water slurry (CWS) furnace systems. This program focuses on the reduction of NO_x , SO_2 , and particulate emissions to levels of 0.2, 0.4, and 0.02 pounds per million Btu fired, respectively. With respect to particulate emissions, the objective is to capture 99.9 percent of the particles in the size range of 0.5 to 10 microns.

As part of this work, a unique emissions control reactor is being developed for the post-combustion reduction of SO_2 emissions. This reactor uses the principles of fluid mechanics and particle dynamics in an innovative way to enhance the capture of SO_2 by various sorbents. The SO_2 emissions control reactor is a vortical flow device designed to separate sorbent particles and then confine them within the reactor. This separation of particles within the reactor substantially increases their residence time relative to the gas and therefore provides an effective sorbent-to-sulfur ratio within the reactor that is many times greater than what was injected, providing a very high sorbent particle surface area concentration within a very compact reactor.

This paper describes the significant features of the SO_2 emissions control reactor, presents a simplified analytical model used to determine key operation parameters, and reports recent test results. These results include reductions in SO_2 levels greater than 90 percent.

DEVELOPMENT OF A POST-COMBUSTION DRY SO₂ CONTROL REACTOR FOR SMALL-SCALE COMBUSTION SYSTEMS

INTRODUCTION

The current contract Tecogen Inc. has with PETC (Contract No. DE-AC22-89PC8904) deals with the development of an integrated emissions control system for small-scale, CWS-fired furnace systems. This program focuses on the reduction of NO_x, SO₂, and particulate emissions to levels of 0.2, 0.4, and 0.02 pounds per million Btu fired, respectively. With respect to particulate emissions, the objective is to capture 99.9 percent of the particles in the size range of 0.5 to 10 microns.

The control of NO_x and particulate emissions is being achieved via staged combustion for NO_x control and the use of a high-efficiency baghouse for particulates. In order to control SO₂ emissions a dry sorbent post-combustion strategy was adopted. To achieve the program's SO₂ emissions goal, a separate high-temperature reactor is currently being developed.

The emissions control reactor currently being developed uses the principles of fluid mechanics and particle dynamics in an innovative way to enhance the capture of SO₂ by various sorbents. The SO₂ control reactor is a vortical flow device in which the products of combustion and sorbent particles enter tangentially at the reactor base and flow upward towards the discharge. Due to the vortical flow field within the reactor, the sorbent particles are separated and then confined within the reactor. Separation of the sorbent particles within the reactor substantially increases their residence time relative to the gas and therefore provides an effective sorbent-to-sulfur ratio within the reactor that is many times greater than what was injected, providing a very high sorbent particle surface area concentration within a very compact reactor.

The SO₂ reduction reactor was designed on the principle of axial recirculation. In a vortical flow field, the pressure at the periphery is greater than that at the centerline. By connecting one end of a tube tangentially from the periphery at one axial location and the other end at the centerline, an external axial recirculation flow path is established that operates only on the natural pressure difference present in the vortical flow field without requiring external assistance.

When the principle of axial recirculation is used in a gas/solids system, the residence time of the solids within the reactor can be significantly increased relative to that of the gas, and can provide good solids distribution throughout the reactor as well. A schematic diagram of both the internal and external particle recirculation paths is shown in Figure 1, and a photograph of the external particle recirculation is shown in Figure 2.

ANALYTICAL MODELING

In developing an analytical model of the SO₂ reactor, several complexities are encountered due to the coupling of the flow field in the main body of the reactor to that of the axial recirculation loop. These two highly coupled flow fields result in the need to solve a three-dimensional, highly nonisotropic turbulent flow field with a dispersed second phase of particles that undergo chemical reactions.

Resolving the flow field, tracking the sorbent particles, and accounting for changes in chemical species require an extremely high computational effort. As an alternative to this approach, a simplified model of the reactor was developed. The purpose of this model was to determine the dominant parameters that govern the reduction of SO₂ within the reactor as well as to provide performance estimates under various operating conditions.

One of the prime areas of concern is the ability of the reactor to detain particles of a given size for given gas-flow conditions. Though the flow within the reactor is quite complex, except for the recirculation line effect, the reactor is quite similar to a cyclone separator. The ability of cyclones to collect particles of a given size has been well documented; by Zenz, for example.¹ For a given geometry and gas flow conditions the theoretically smallest-size particle size that a cyclone can collect, typically called the cut point diameter, can be found by:

$$D_{pm} = \left[\frac{9 \mu_g L_w}{\pi N_s V_{in} (\rho_p - \rho_g)} \right]^{\frac{1}{2}} \quad (1)$$

where:

μ_g is the gas viscosity

V_{in} is the inlet velocity

ρ_p, ρ_g are the particle density and gas density, respectively

N_s is the number of spiral turns, which is found from experiment

L_w is the cyclone inlet width

For application of this equation to the axial recirculation reactor, L_w is defined as the radial distance between the reactor wall and the outside radius of the recirculation tube.

Once the cut point diameter is determined, the separation efficiency of any other size particle can be determined from normalized separation efficiency data, as shown by Zenz.¹ Knowing the separation efficiency of a given-size particle allows one to determine its residence time in the reactor relative to the gas. Under steady-state conditions and assuming that the reactor is capable of fluidizing all the particles within it, as one particle is added to the reactor, one particle must leave. However, the particle that is added to the system will be recirculated N times before it leaves. The number of times a particle of a specific diameter within the reactor circulates — N — is dependent on the separation efficiency for this size particle. This relationship can be expressed as:

$$N = 1 + \eta + \eta^2 + \eta^3 + \dots \quad (2)$$

where η is the separation efficiency. This relation can be expressed in closed form as:

$$N = \frac{1}{1 - \eta} \quad (3)$$

Once N is determined, the amount of solid material in the reactor that can participate in the reduction of SO₂ can be found since it is equal to N times the inlet solids flow rate.

When the amount of solids present in the reactor is known, one-dimensional species-continuity equations for the concentration of SO₂ in the gas phase and CaO in the solid phase can be written as:

$$\frac{d [SO_2]}{dz} = \frac{-6 (1 - \epsilon) [SO_2]}{\epsilon D_p V_g \left(\frac{1}{k_c} + \frac{1}{k_d} \right)} \quad (4)$$

$$\frac{d [CaO]}{dz} = \frac{-6 [SO_2]}{D_p V_s \left(\frac{1}{k_c} + \frac{1}{k_d} \right)} \quad (5)$$

where

[SO₂] is the concentration of SO₂ in the gas phase

[CaO] is the concentration of CaO in the solid phase

V_g, V_s are the gas and solid phase velocities, respectively

ε is the void fraction (adjusted to account for particle recirculation)

k_c, k_d are the chemical kinetics and diffusion resistances, respectively

D_p is the particle diameter

The diffusion resistance, k_d, can be found from the relationship:

$$Sh = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad (6)$$

where:

Sh is the Sherwood number defined by:

$$Sh = k_d \frac{D_p}{D} \quad (7)$$

D is the diffusivity

Re is the Reynolds number based on the slip velocity

Sc is the Schmidt number

The chemical kinetics resistance is determined by using Borgwardt's² model, which takes into account the decrease in the rate of reaction due to pore plugging.

$$k_c = A_o \exp \left(- \beta \frac{n'}{w} \right) \exp \left(- \frac{E}{RT} \right) \quad (8)$$

where:

A_o is the frequency factor

n' is the sulfate in the stone

W is the weight in the solid sample

R is the universal gas constant

T is the absolute temperature

E is the activation energy

β is the stone-dependent constant determined by experiment

Model Parametric Study

The model was used as part of a parametric study to determine the effect of such parameters as reactor diameter, Ca/S, and particle diameter on the SO₂ capture. For this analysis, the reactor model was operated with the combustion products of the CWS specified for this program. The parent coal in this CWS is an Illinois No. 6 coal, which contains 2.63-percent sulfur and has a higher heating value of 13,579 Btu/lbm. This provides the potential of 3.87 lbm/MMBtu of SO₂. When this CWS is burned with 20-percent excess air, this SO₂ potential translates into a concentration of 1,950 ppm on a dry basis. The parameters used in this analysis are shown in Table 1.

The effect of sorbent particle diameter on reactor performance is shown in Figure 3 for reactor diameters of 4, 6, and 8 in., operating with a Ca/S mole ratio of 3:1. The interesting feature of Figure 3 is that for each reactor there is an optimum particle diameter for SO₂ capture. This optimum diameter is based on the reactor's ability to capture particles of a given size. Particles smaller than the optimum diameter cannot be detained in the reactor and pass through without participating to a great extent in the SO₂ capture process. Particles that are larger than the optimum diameter are able to be detained in the reactor; however, since the sorbent particle surface area to volume ratio decreases as the diameter increases, there is less available surface area in the reactor to participate in the SO₂ capture process compared to the optimum.

The effect of Ca/S mole ratio on reactor performance is shown in Figure 4 for reactor diameters of 4, 6, and 8 in. For each of these cases the model used the optimum particle diameter for these operating conditions, as shown in Figure 3. For the sorbent properties used in this analysis, the required 90-percent reduction in SO₂ emissions is achieved at a Ca/S mole ratio of about 4.5 for the 8-in.-diameter reactor.

The effect of input rate on reactor performance is shown in Figure 5 as a function of particle diameter. For this case, only an 8-in.-diameter reactor is considered since at the higher flow rates, the pressure drop becomes excessive in the smaller units. Figure 5 shows that as the input rate is increased, reactor performance decreases. This is due to the reduction in gas phase residence time associated with the fixed reactor height.

An interesting feature of Figure 5 is that as the input rate is increased, the optimum particle diameter for SO₂ capture decreases. This is due to the fact that at the higher tangential velocities associated with the increased flow rates, the reactor has a greater ability of capturing smaller sized particles. This provides a greater surface area concentration within the reactor.

Figure 5 indicates that if operation at higher input rates is required and comparable performance with lower input rate operation is required, provisions must be made to compensate for the reduction in gas phase residence time. This can be accomplished by increasing either the reactor length or diameter.

The specified coal for this program, when burned with 20-percent excess air, has the potential to produce 1,950 ppm of SO₂ on a dry basis. Operation of the reactor with the products of combustion of other slurries yields the potential for different SO₂ inlet concentrations. The performance of the reactor as a function of inlet SO₂ concentration is shown in Figure 6 for a Ca/S mole ratio of 3:1 and reactor diameters of 4, 6, and 8 in. Figure 6 shows that the percent reduction in SO₂ increases as an exponential function of inlet concentration, approaching a limiting value of close to 100-percent reduction.

The fact that the percent reduction in SO₂ approaches an exponential limit at near 100 percent as inlet concentration is increased indicates that in absolute terms, i.e., with respect to the actual outlet concentration (ppm), the reactor would have a lower outlet SO₂ concentration when operated with higher sulfur coals. To illustrate this, the percent reduction results shown in Figure 6 are plotted in Figure 7 in terms of the actual outlet concentration of SO₂ (ppm on a dry basis). Figure 7 shows that particularly for the 6-in.-diameter and 8-in.-diameter reactors, as the inlet concentration is increased, for a fixed Ca/S ratio there is more sorbent within the reactor and the outlet SO₂ concentration decreases. For example, consider the 8-in.-diameter reactor. Using this particular sorbent, an outlet concentration of about 400 ppm would be expected with the reactor operating at the 1,950 ppm level expected for this coal. This result is about 200 ppm higher than the level required to meet the 0.4 lbm/MMBtu program goal. However, if the reactor was operated with a coal that produced about 3,500 ppm of SO₂, the outlet concentration would meet the goal of 0.4 lbm/MMBtu (200 ppm).

SO₂ REACTOR TEST RESULTS

A schematic diagram of the SO₂ reduction test facility is shown in Figure 8. In order to have more control over the operation of the SO₂ reactor, it was decided to operate the facility with flue gases produced from an oil burner and inject SO₂ as required in order to obtain desired inlet concentrations. Also, since oil burners can operate over a very wide range of input rates, typically from 68,500 to over 400,000 Btu/hr for residential scale burners, they provide a great deal of flexibility in reactor operation.

The reactor tested in this facility had the following geometry:

Inside Diameter:	8.329 in.
Outlet Diameter:	1.5 in.
Active Reactor Height:	43 in.
Inlet Area:	4 in. ²

Four different calcium-based sorbents were tested in the 8-in.-diameter reactor, and a summary of these sorbents in terms of specific calcium compound, weight percent, and mean particle diameter is shown in Table 2. The sorbent used in this work represented a cross section of various products found throughout the United States. Sorbent A-1 was a dolomite from northwest Connecticut. The as-received version of this sorbent, called Sorbent 1, had a mean diameter of 194 microns. In order to obtain the as-tested size distribution, the as-received dolomite was sieved and then selectively blended. Sorbent 2 was a high-calcium limestone from Pennsylvania that was received in pulverized form. Sorbent 3 was a pulverized lime that was calcined from the same limestone used in Sorbent 2, and Sorbent 4 was an as-received limestone from Illinois.

The SO₂ reduction test facility operates with the products of combustion from an oil burner using Number 2 heating oil. Gaseous SO₂ is injected to achieve the desired reactor inlet concentration. Tests conducted with the 8-in.-diameter reactor were designed to simulate operation with the specified CWS for this program. The coal in this slurry contained 2.36-percent sulfur and had a heating value of 13,579 Btu/lbm, yielding a potential for the formation of 3.87 lbm/MMBtu of SO₂.

The products of combustion of Number 2 oil differ in composition from those of CWS, and it becomes necessary to put these results on a coal-equivalent basis to allow weight-based, not volume-based results to be reported. In order to establish this equivalent basis, it was decided to equate the oxygen content in the products of combustion of heating oil with that of CWS. With an equivalent oxygen level for CWS combustion established, the stoichiometric ratio can be determined and the volumetric measurements recorded by the analyzers can be converted to a weight basis.

Results of 8-in.-diameter reactor testing are shown in Figure 9 in terms of SO₂ content, lbm/MMBtu, as a function of Ca/S mole ratio along with lines that represent a least squares method fit of the data (exponential fit). Figure 9 shows that the SO₂ emissions goal for this program — 0.4 lbm/MMBtu — was reached at a Ca/S mole ratio of about 5:1 for Sorbent 1-A.

The data shown in Figure 9 bring up an interesting feature about the reactor and the SO₂ capture process itself. Consider the results for Sorbents 2 and 3, which have essentially the same mean particle diameter and distribution. Sorbent 3 is made from the calcination of the material used in Sorbent 2, and since it is CaO that captures SO₂ directly and not CaCO₃, it was expected that better SO₂ capture would be achieved with Sorbent 3 since the calcination step within the reactor was eliminated. This was not the case. Sorbent 2, which undergoes the calcination process within the reactor, exhibited a much greater ability to capture SO₂ and at much lower Ca/S mole ratios than Sorbent 3. In fact, Sorbent 2 achieved an SO₂ emissions level of 0.54 lbm/MMBtu, an 88.3-percent reduction at a Ca/S mole ratio of 4.12 compared to 0.73 lbm/MMBtu, and an 80-percent reduction at a Ca/S mole ratio of 7.53.

In addition to reporting SO₂ reduction as a function of Ca/S mole ratio, it is also desirable to use as an independent variable the sorbent mass loading, i.e., the mass of sorbent injected into the reactor for each unit mass of SO₂. These results are shown in Figure 10. The main difference between Figure 9 and Figure 10 is with respect to Sorbent 1-A, which achieved 0.39 lbm/MMBtu at a Ca/S mole ratio of about 5:1. However, since Sorbent 1-A is a dolomite that contains approximately 40-percent MgCO₃, it takes considerably more sorbent on a mass basis to achieve a given Ca/S mole ratio compared to any

of the other high-calcium-based sorbents. Therefore in order to achieve the required reduction in SO_2 , over 13 pounds of Sorbent 1-A are required for every pound of SO_2 in the gas stream. For purposes of comparison, consider achieving a reduction in SO_2 to 0.6 lbm/MMBtu. For Sorbent 1-A, this would require 12 pounds of sorbent for each pound of SO_2 ; however, for Sorbent 2, less than 6 pounds of sorbent are required for each pound of SO_2 .

The results shown in Figures 9 and 10 are SO_2 content on a lbm/MMBtu basis versus Ca/S and sorbent loading ratio, respectively, which represent absolute values. In some instances, it is desirable to present the data on a relative basis; i.e., percent reduction in SO_2 . This is shown in Figure 11, in which percent reduction in SO_2 is plotted against Ca/S mole ratio. This plot shows in a very simple manner how each sorbent performs relative to the others. For example, at a Ca/S mole ratio of 1:1, Sorbent 2 exhibits an almost 60-percent reduction in SO_2 whereas Sorbent 4 at this Ca/S mole ratio exhibits only about 15-percent reduction.

In comparing the data obtained in the SO_2 reduction test facility with the analytical model, three constants are needed in order to characterize the sorbents' chemical kinetic behavior. These constants are the activation energy, E; the frequency factor, A_0 ; and the pore plugging parameter, beta. Based on test results obtained with Sorbent 3, a high-CaO lime product taken at three temperatures, these constants were determined to be:

Activation Energy:	11,750 cal/gmole
Frequency Factor:	243,100 1/s
beta:	0

which are well within agreement of published data.²

With an estimation of the sorbent properties, the computer model comparison was performed for two different cases. These results are shown in Figure 12 in which percent reduction in SO_2 is plotted against Ca/S mole ratio. Figure 12 shows that a fairly good agreement exists between the model and data.

SUMMARY AND FUTURE WORK

Test results obtained with the 8-in.-diameter reactor using calcium-based sorbents have achieved over a 90-percent reduction in SO_2 emissions. Emission levels of as low as 0.39 lbm/MMBtu have been obtained, which are lower than the 0.4 lbm/MMBtu program goal.

Reactor performance was found to be a function of both the sorbent used in the capture process and its mean particle diameter. A noticeable increase in reactor performance was observed when the sorbent used in the SO_2 capture process was calcined within the reactor as opposed to using a precalcined product.

In future work, parametric investigation of the SO_2 reactor will continue. This work will include testing various other sorbents as well as baffles and other devices to aid in particle separation. In addition to

parametric testing, the SO₂ reactor will be integrated into a complete small-scale CWS-fired furnace and will be tested extensively.

ACKNOWLEDGEMENT

This work was funded by the U.S. Department of Energy, Pittsburgh Energy Technology Center under Contract No. DE-AC22-89PC8904. The author would like to express his appreciation for the financial support to accomplish this development effort. The valuable guidance and encouragement given by Mr. Thomas Brown, DOE's Project Manager, is gratefully acknowledged.

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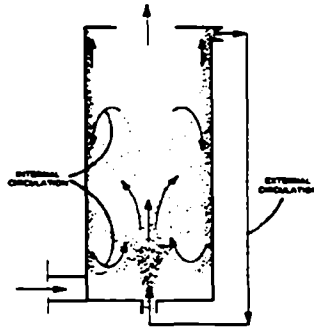


Figure 1. External and Internal Circulation in the Emissions Control Reactor



Figure 2. Emissions Control Reactor Model (High Load) Intensive External and Internal Circulation

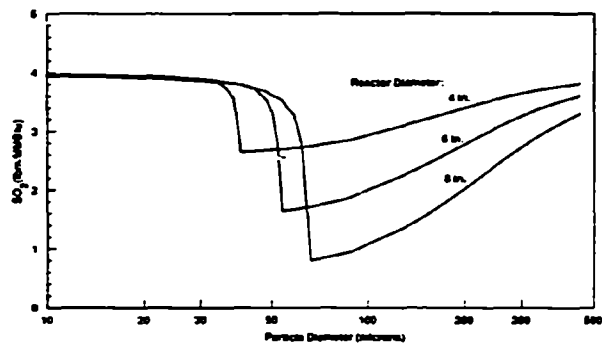


Figure 3. Effect of Particle Diameter on Reactor Performance (Operating with a Ca/S Ratio of 3:1)

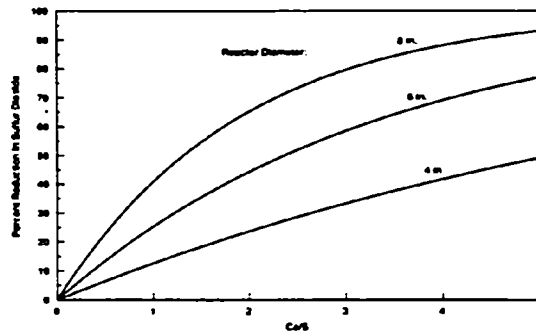


Figure 4. Effect of Ca/S Mole Ratio on Reactor Performance

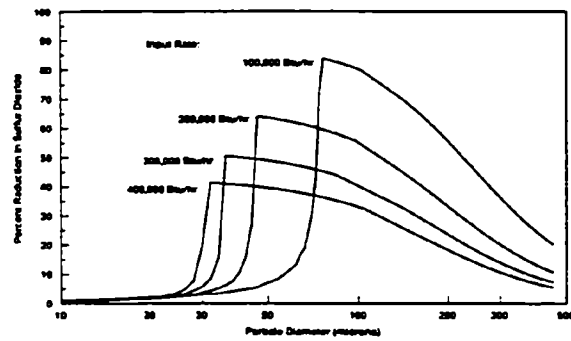


Figure 5. Effect of Input Rate on Reactor Performance
(For an 8-In.-Diameter Reactor Operating
with a Ca/S Ratio of 3:1)

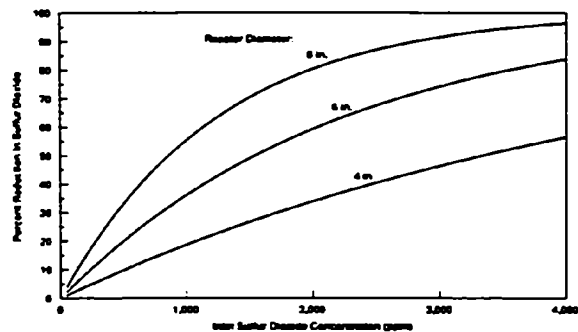


Figure 6. Effect of SO₂ Concentration on Reactor Performance
(Operating at a Ca/S Ratio of 3:1)

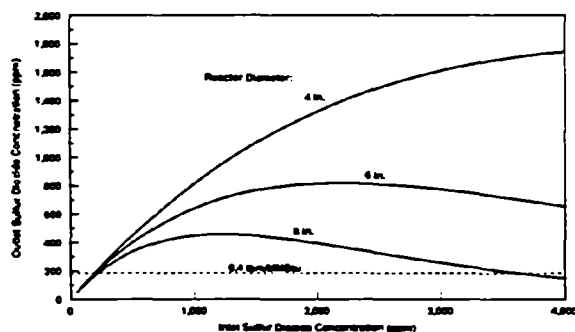


Figure 7. Effect of Inlet SO_2 Concentration on Reactor Outlet Concentration (Operating with a Ca/S Ratio of 3:1)

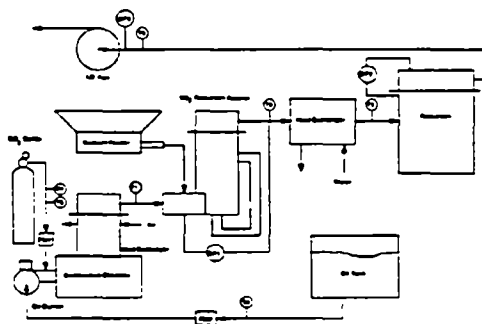


Figure 8. SO_2 Removal Test Facility

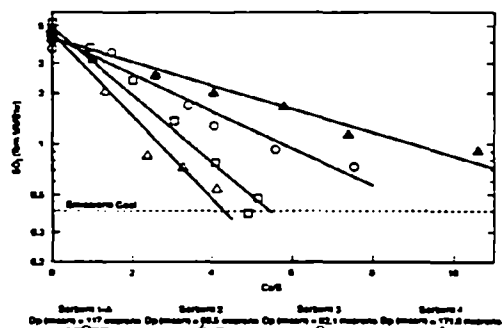


Figure 9. Effect of Ca/S Mole Ratio on 8-In.-Diameter Reactor Performance

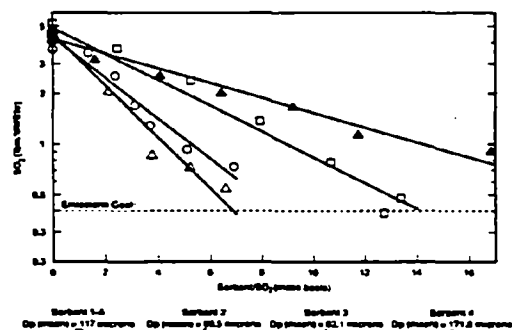


Figure 10. Effect of Sorbent Loading (Weight Basis) on the Performance of the 8-In. Reactor

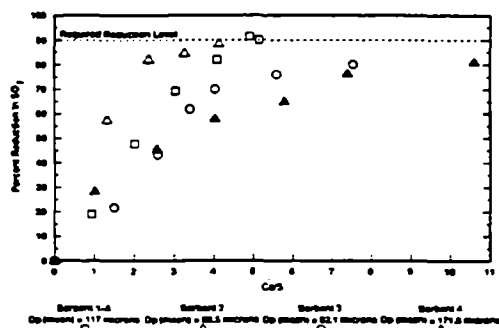


Figure 11. Effect of Ca/S Mole Ratio on 8-In.-Diameter Reactor Performance

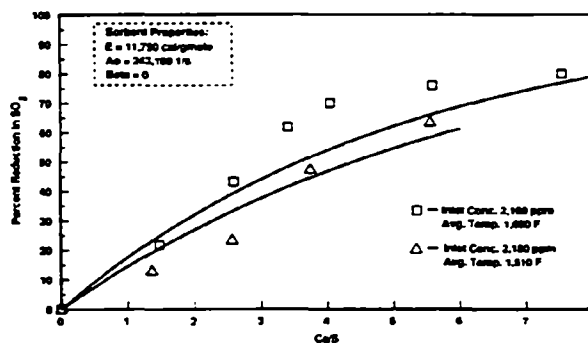


Figure 12. Comparison of Model Prediction and Reactor Data for the 8-In.-Diameter Reactor Operating with Sorbent 3

TABLE 1
MODELING PARAMETERS

Fuel: Coal Content (weight %) Higher Heating Value (Btu/lbm) Sulfur Content (coal)	IL6-248-MCW-G (Specified fuel for the program) 53.22 7,227 2.63
Input Rate (Btu/hr): Excess Air (%) SO ₂ (ppm dry basis) Reactor Operating Temperature (F)	120,000 (nominal) 20 1,950 1,600
Reactor Diameter (in.) Reactor Height (in.)	4, 6, 8 45 (nominal)
Sorbent Properties: Activation Energy (cal/g-mole) Frequency Factor (1/s) Beta (g/g-mole) Density (lbm/ft ³)	 10,000 335,000 333.3 150

TABLE 2
SORBENTS USED IN TESTING THE 8-INCH-DIAMETER SO₂ REACTOR

Sorbent	Calcium Compound	Percentage	Mean Diameter (microns)
1-A	CaCO₃	60	117
2	CaCO₃	97.8	88.5
3	CaO	95.4	82.1
4	CaCO₃	98.3	172

SCRUBBER REAGENT ADDITIVES FOR
OXIDATION INHIBITED SCRUBBING

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ABSTRACT

Gas film limited scrubbing (maximum removal for a given L/G) requires a high liquid phase alkalinity in the scrubbing liquor, most readily obtained in the form of buffered sulfite ions (SO_3^{2-}). The cations used as an ion pair with the sulfite are most often Mg (the Thiosorbic process by Dravo Lime) and Na (in dual alkali systems). Excessive amounts of MgO as an additive allows the more soluble sulfate to increase, thus depressing the sulfite solubility, and total alkalinity.

Manufactured minerals such as $\text{CaAl}_2\text{Si}_2\text{O}_8$, and $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, have a much greater buffering capacity for sulfite ions than $\text{Mg}(\text{OH})_2$, and more nearly match sulfite/sulfate solubility so that sulfite alkalinity is not diminished by small excesses of additive.

Because these mineral compounds are manufactured, small amount of sulfide can be included by reacting the minerals with weak solutions of hydrogen sulfide, thus providing a built-in oxidation inhibitor.

BACKGROUND

Wet FGD scrubbing is controlled almost entirely by liquid phase chemistry of the liquor being pumped to the absorber module(s). In the simplest terms, the capture of a given amount of sulfur dioxide requires a matching amount of alkalinity in the liquor. The required amount of alkalinity can be thought of as some number, A. A is the product of the volume of liquor, VL, and the concentration of alkalinity in the liquor, cB. Thus, $A = (cB) \times (VL)$. If the alkalinity concentration is high, VL can be small. As the concentration, cB, diminishes, a corresponding increase in VL is required to obtain the same A. In terms of a scrubber, the L/G ratio must increase as the concentration of alkalinity in the liquor declines in order to remove the same amount of SO₂ from the flue gas.

It is the liquor that reacts with sulfur dioxide in the absorber module to provide SO₂ removal. The role of limestone and lime in wet FGD systems is not to capture sulfur dioxide in the absorber, but rather to knock the absorbed sulfites/sulfates out of the liquor as precipitates in the recycle or mix tank. The liquor does the scrubbing in the absorber, and the limestone and/or lime reagent reconstitutes the liquor in the recycle tank. The soluble additives in the reagent define the liquid phase chemistry, and hence sulfur dioxide capture. The reagent itself removes the captured sulfur from the liquor.

If calcium is the only, or primary cation in the system, gypsum scaling is almost inevitable, because the absorption and precipitation phases overlap. There is too much Ca^{++} in solution in the absorber, thus the addition of more sulfur produces a gypsum precipitate. Additives are used to provide additional cations, which act to depress the calcium solubility, and lower the relative gypsum saturation.

Essentially, modern scrubbers are attempting to approach the dual alkali concept with a single loop. The dual alkali concept uses sodium as the cation to carry buffered sulfite alkalinity. The soluble sodium bi-sulfite solution, NaHSO_3 , is then reacted with calcium hydroxide to form calcium sulfite solids and reconstitute the sodium sulfite solution (scrubbing liquor). The Dravo Thiosorbic process uses the same idea, but with Mg rather than sodium, and the magnesium is included in the lime as MgO . Organic acids are intended to play a parallel role in limestone systems.

Oxidation of sulfite to sulfate in the absorber only serves to lower the available alkalinity for sulfur dioxide capture. Thus, ideally, oxidation only occurs in the recycle or mix tank, not in the absorber. The liquid phase should be oxidation inhibited in the absorber, and in the case of forced oxidation, the reaction should be delayed until the solution reaches the recycle tank.

Scrubbing systems have two exactly opposite demands. Lower pH values favor increased solubility of the reagents, limestone, or lime. But higher pH values provide greater alkalinity, hence better removal rates with lower L/G ratios.

MANUFACTURED MINERAL ADDITIVES

Synthetic minerals which dissociate incongruently in a scrubbing liquor can have the dual advantage of providing higher buffered sulfite alkalinity over a wider range of pH than single compounds, e.g., magnesium hydroxide, and can act to inhibit sulfite oxidation in the absorber, while also promoting large, simple crystal growth in the recycle tank.

At the present time, research indicates that as the mineral becomes increasingly more complex with a larger total amount of OH^- ions associated with its hydrated form, the buffering capacity of sulfite alkalinity is improved. A series of minerals have been investigated, starting with natural Kaolinite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The sulfite buffering capacity was improved by making a combined mineral of $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Still greater buffering capacity has been provided by $\text{Ca}_4\text{Al}_2\text{Si}_{12}(\text{OH})_{32} \cdot \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

Oxidation inhibition can be added by reacting the hydrated mineral compound with a weak solution of hydrogen sulfide, H_2S . Oxidation inhibition in the absorber and enhanced crystal growth in the recycle tank have been achieved by treating the hydrated mineral compounds with a mixed solution of hydrogen and iron sulfides.

It is unlikely that the ideal mix of calcium and magnesium carbonate will occur near every scrubber. Moreover, as a scrubber system becomes tighter (less and less make-up water is added) the optimal amount of additive will change (diminish). The two ingredients, calcite or calcium carbonate, and dolomitic stone or calcium-magnesium carbonate, can be viewed as two colors of paint: black and white, with which one can produce any shade of gray. Thus, reagent design can be defined in terms of high calcium lime, or limestone, and an additive that provides optimal

performance of a given combination of coal, boiler, scrubber, and scrubber operation.

Process Calx, Inc., is presently designing and building a pilot scrubber to provide utilities with a service that will simulate any major scrubber configuration, along with boiler quench rate, and use any coal, to determine the optimal mix of limestone, and/or lime, and additives.

The manufactured minerals, both composition and methods of production are the subject of a patent application by Process Calx, Inc.

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RECOVERY OF SULFUR FROM CALCIUM SULFITE
AND SULFATE SCRUBBER SLUDGES

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ABSTRACT

Calcium and sulfur can be effectively extracted from scrubber sludges so that the calcium can be re-used, and the sulfur sold off, through a two step process of bio-chemical reaction and smelting. Calcium sulfite/sulfate sludges are placed in a digester containing anaerobic bacteria, desulfo-vibrio, to which is added metal powders, e.g., electric arc furnace dust, or BOF dust. The resulting mixed metal sulfides are split by hydro-cycloning: calcium sulfide, and all other heavier sulfides, i.e., iron, manganese, chrome, etc. The sulfides are then smelted individually, calcium by itself, and the others. The calcium is returned to the scrubber, the combined metals are returned to the melt shop, and the sulfur is captured for commercial sale.

BACKGROUND

Reagent and disposal costs are significant factors in the decision matrix of comparing wet FGD options of enhanced lime (oxidation inhibited) vs. limestone/forced oxidation. While there is no debate over the chemical facts that higher pH scrubbing with buffered sulfite provides more NTU (Number of Transfer Units) at lower L/G ratios, the economics of the comparison is anything but obvious.

Reagent costs and disposal volume can be reduced by recycling the calcium used to precipitate the absorbed sulfur out of the scrubbing liquor, and extracting the sulfur from the calcium salt. Calcining calcium sulfate to recover calcium oxide and sulfur has been in commercial practice for a number of years by ICI in the UK, among others. This process requires a reducing atmosphere, and is as energy intensive as calcining limestone into lime. Moreover, the capital required and the expense of operating the sulfur dioxide recovery operation is relatively high compared to current sulfur prices. The commercial viability of this avenue is very sensitive to the prices of fuel and sulfur.

A much simpler method of calcium recycling and sulfur recovery was devised by Process Calx, Inc., in the course of defining methods for controlling the Hydrogen sulfide odor problem that is common to many FGD systems. Almost all rivers and streams used for process make-up water contain some concentrations of common anaerobic, sulfur reducing bacteria: primarily, desulfo-vibrio. The bacteria reduce the sulfites and/or sulfates (remove oxygen and add electrons) to yield sulfides and release hydrogen sulfide

(the source of the odor problem). While the objective of the study was to control the bacteria and eliminate the odor, a critical dimension was to define the conditions in which the bacteria flourish.

Typical fly ash from a utility boiler contains sufficient unburned carbon to apparently act as a food supply for the bacteria. Anaerobic digester conditions with a pH in the range of 8 to 9, and temperatures of 30 to 45 °C produced the most rapid growth of bacteria and reduction of the sulfite/sulfate sludges. Adding powdered metal oxides to react with the H_2S in solution (to keep the pH around 8.5) and produce a metal sulfide precipitate was more effective than adding additional hydrate, calcium hydroxide.

Electric arc furnace dust, EAFD or K-061 in the EPA list of Hazardous Wastes, was the most effective additive to remove the hydrogen sulfide in solution in the digester. EAFD itself has been the subject of investigation. The presently accepted method of destruction is to vaporize the EAFD in a plasma arc and then condense the metals from the vapor. Energy requirements for this technology are in the range of 1700 KWh/ton of EAFD. There are several problems with EAFD as more and more scrap metal is recycled. Recycling the EAFD has problems in that the melt shop doesn't want zinc and lead returned to the melt, as these concentrations build in the recycle dust. Reacting the EAFD, a very fine powder of mixed metal oxides, with H_2S in solution is an effective method of removing the hydrogen sulfide, and producing individual metal sulfides which are easily separated on the basis of density.

<u>sulfide</u>	<u>density</u>
CaS	2.5
FeS, FeS ₂	5.0 to 4.8
PbS	7.5
ZnS	4.0
NiS	5.3 to 5.6

The commercial interest for stainless steel shops is the recovery and recycle of the nickel along with the elimination of Pb, and Zn. It isn't necessary to separate the iron and nickel. The operation is set to yield four catagories of sulfides: the lightest fraction (calcium, along with fly ash, etc.); light middle (zinc); heavy middle (Fe, the bulk of the metal oxides, along with Ni for stainless shops); and the heaviest fraction (Pb).

Roasting a sulfide to recover a metal with a nearly pure sulfur atmosphere is much simpler system than calcining sulfites and/or sulfates to recover sulfur dioxide.

PROCESS DESIGN

A typical 500 MWe boiler, 60% load factor, uses 1 million tons per year of coal. With a 3% sulfur content in the coal, the reagent requirements are approximately 58,000 tons per year of lime (including a 4% MgO, or other additive), and the disposal of almost 130,000 tons of scrubber solids. With this sulfur extraction and calcium recycle system, the reagent requirement is only 6,000 annual tons, and the disposal is 15,000 tons of dry solids from the slaking operation. The essential dimension of this technology is the rate at which the bacteria can process (reduce) the sulfites and sulfates.

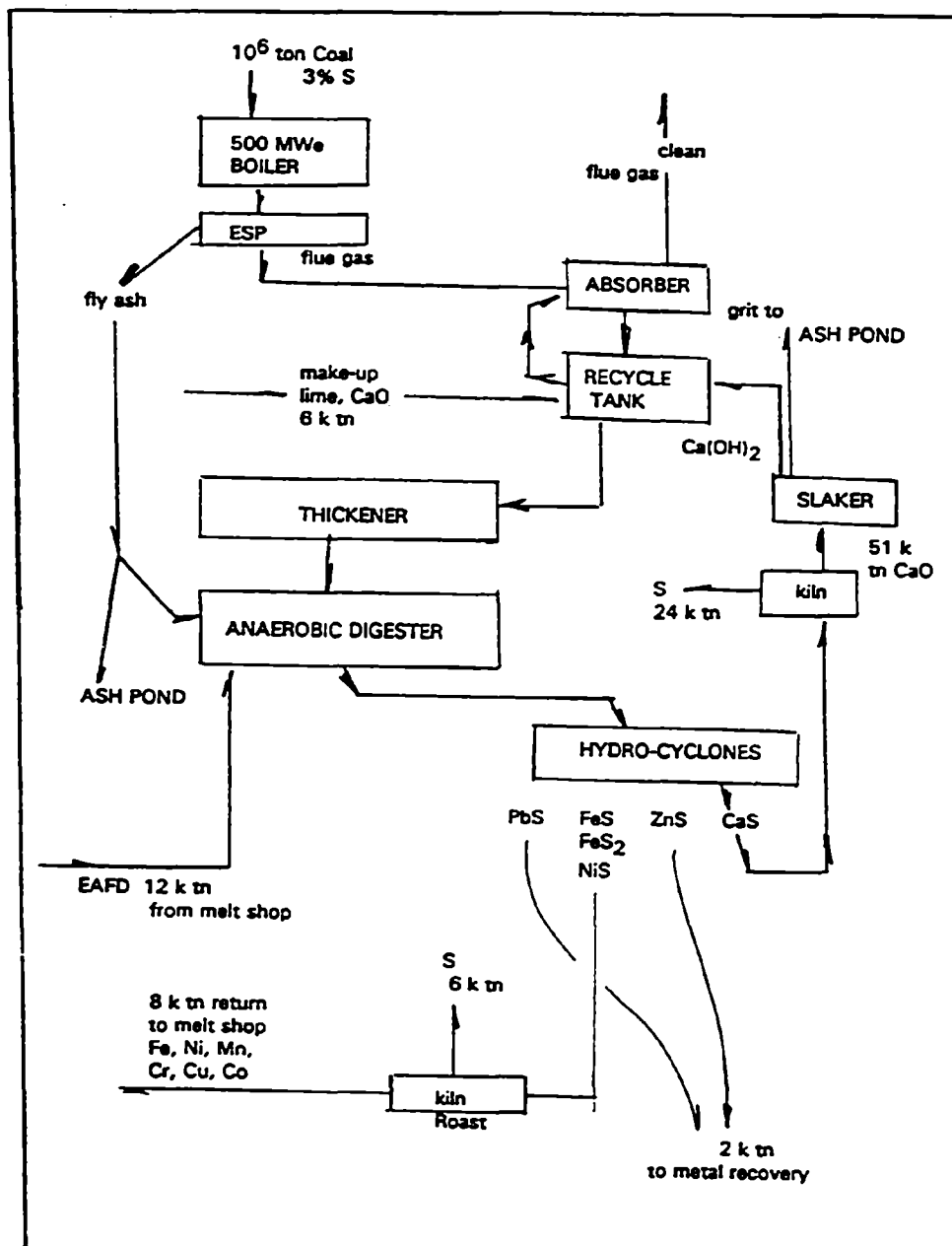


Figure 1. Flow diagram for the extraction of sulfur from sulfite and sulfate scrubber solids by means of a biochemical process, including the recycle of calcium, and the production of reduced metals.

Bench scale work has maintained conversions of scrubber solids sulfites to calcium and metal sulfides at a rate of 0.1 lbs/(hr ft³) of active digester volume, or 1.6 g/(hr liter).

This process has two revenue streams: a fee charged to the melt shop to recycle the metals from the electric arc furnace dust; and the sulfur that is roasted from the sulfides.

A flow sheet for the process applied to a 500 MWe unit is shown above in Figure 1.

CURRENT STATUS

Increasing the rate at which the bacteria reduce the sulfites and sulfates to sulfides and producing cleaner separations of the sulfides are the critical parameters. Present rates of sulfite reduction are 0.1 lbs/(hr ft³), which does not increase with bacteria count (8.5 avg pH, and 100 °F). Present recycle of calcium can be maintained at 90+ % of total CaO in the system. Cleaner iron sulfide precipitate (free of Zn and Pb) would improve the value of the returned metals. A typical EAFD contains about 20% zinc oxide, and 2% PbO. Presently, the roasted iron/nickel metal contains less than 1% total Zn, and Pb.

The process as described has been studied at the laboratory, or bench scale, and is the subject of a patent application by Process Calx, Inc.

MAGNESITE AND DOLOMITE
FGD TECHNOLOGIES

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ABSTRACT

Solutions of calcined magnesite or dolomite are used as scrubbing agents. Useful by-products are produced. In the magnesite process MgSO_3 or MgSO_4 are produced; in the dolomite process a mixture of MgSO_3 and CaCO_3 is produced, all valuable agricultural fertilizers. Employing a unique purification based on the recrystallization of MgSO_3 from a metastable solution of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, 99.5% pure MgSO_3 can also be obtained. Both magnesite and dolomite technologies are described. Results of tests conducted on a pilot plant at the OR facilities are summarized. 75 t.h⁻¹ steam boiler desulfurization is described. Attention is given to agrochemical properties of the products.

BACKGROUND

Ore Research Institute has developed magnesite FGD technology which uses low quality calcined magnesites as scrubbing agents. It is an open technology (as opposed to regenerable technology) which produces MgSO_3 as by-product, valuable fertilizer. The technology has been tested on a $2,000 \text{ Nm}^3.\text{h}^{-1}$ pilot plant at the Ore Research Institute facilities in Mnisek pod Brdy, Czechoslovakia since 1989. Technical studies for application on commercial size projects have been done. One of them is being considered for 200 MW power plant at Tusimice, Czechoslovakia, where a desulfurization plant was constructed by a team from the Soviet Union in years 1983-1990, but was never brought to operation. Ore Research Institute is proposing 10% MgSO_3 to be taken out of regenerable cycle and to be used as fertilizer. This will prevent build up of ash and other insolubles in the circulating sorbent. Experience gained during pilot testing and at 200 MW Tusimice power plant gives ORI desulfurization team confidence to evaluate their open magnesite technology as one of FGD technologies that is ready to be used on commercial scale projects.

DESULFURIZATION OF 75 t.h^{-1} STEAM BOILER BY ORI MAGNESITE TECHNOLOGY

Data

Flue gas	$100\ 000 \text{ Nm}^3.\text{h}^{-1}$
SO_2 content	$8.42\text{g}.\text{Nm}^{-3}$
Fly ash content	$0.24\text{g}.\text{Nm}^{-3}$
SO_2 capture	92% minimum
Fly ash capture	90% minimum
MgO content	75%
SO_2 captured	775 kg.h^{-1}

Process

Please see Figure 1.

In the process the flue gas passes through heat exchanger 1 (where it exchanges heat with scrubbed exhaust) into absorber 2 where it is scrubbed. Suspension flows into circulating tank 4 from which it is pumped through hydrocyclones 6 into spraying floors of the absorber 2. The flow from hydrocyclones enters distributor 7 where it is distributed either to circulation tank or to centrifugal separator 12. The cake is dried in drier 14. Dry product is sorted 15, crushed 16, and transported into expedition tank 19.

MgO is transported from storage tank 8 into operational tank 10 from which it is distributed into suspension tank 11 which overflows into circulation tank 4.

Energy, labor, sorbent

Calcined magnesite (75% MgO)	720kg .h ⁻¹
H ₂ O	1 800kg .h ⁻¹
Gas	120 Nm ³ .h ⁻¹
Product (MgSO ₃)	2 200kg .h ⁻¹
Labor	2 workers per shift

Product

MgSO ₃ . 3H ₂ O	82%
MgSO ₄	7%
MgO	2%
Inerts	8%
Fly ash	1%

This product is an excellent fertilizer for Mg-deprived soils. Tests done at Ministry of Agriculture and Ministry of Health in Czechoslovakia proved that this fertilizer is comparable to or better than other Mg fertilizers (Kieserit, MgSO₄). During testing period content of heavy metals have been found acceptable to Czechoslovak regulations.

Content.

<u>Metal</u>	<u>Czech regulations</u>	<u>MgSo₄ fertilizer</u>
As	10	1.5
Cd	50	1.5
Cr	200	5
Hg	2	0.1
Pb	30	15

The open Magnesite technology doesn't produce any waste products, is very flexible, and production of fertilizers lowers the operational cost.

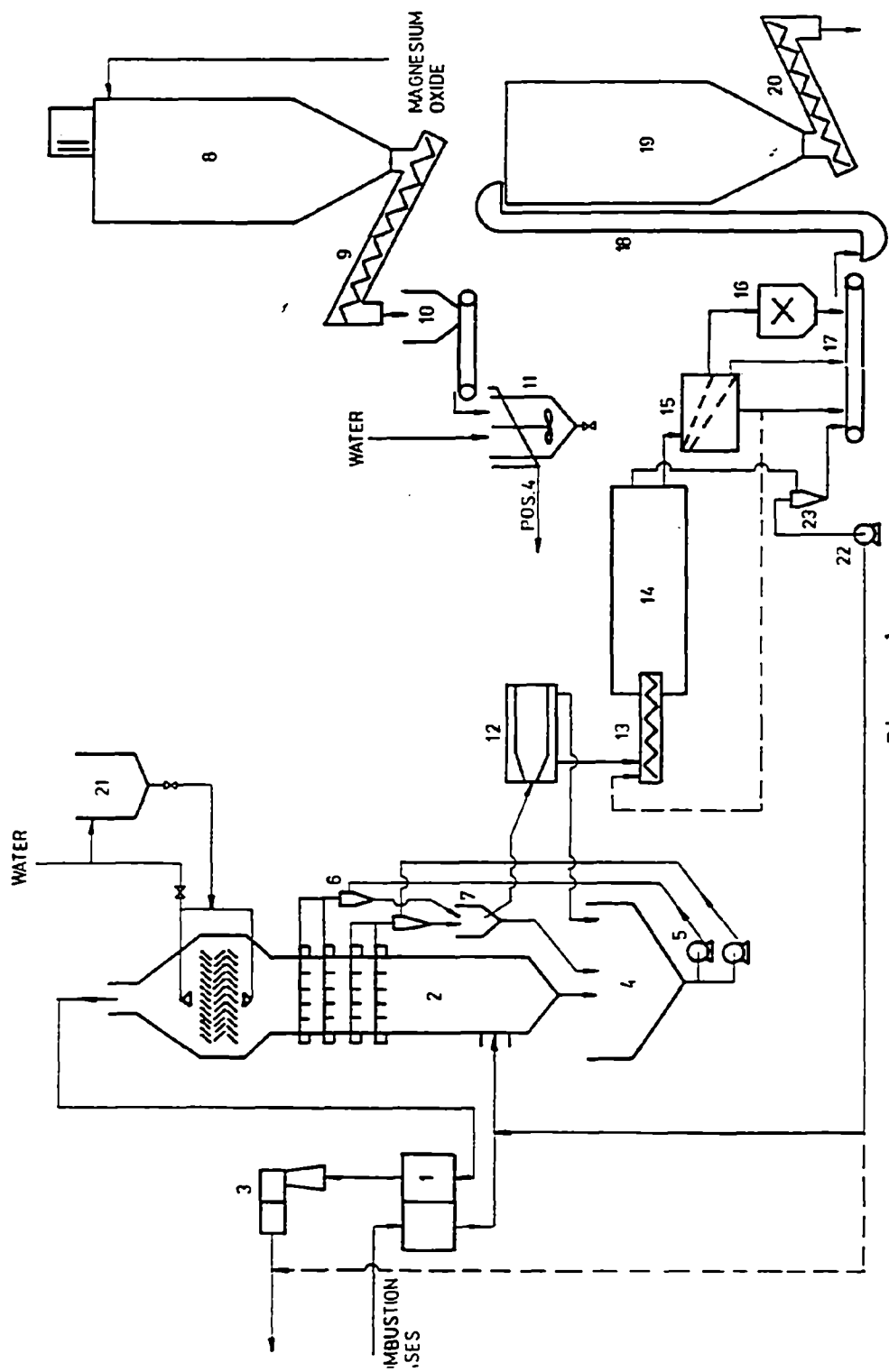


Figure 1.

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**SO₂ AND PARTICULATE EMISSIONS REDUCTION IN A PULVERIZED COAL UTILITY BOILER
THROUGH NATURAL GAS COFIRING**

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ABSTRACT

A field test was conducted in the fall of 1989 to evaluate cofiring of gas in a 450 MW coal-fired utility boiler. The boiler was commissioned by Public Service Company of Oklahoma in 1979 and is a tangentially-fired, supercritical unit. It normally burns a blend of Western subbituminous and Oklahoma bituminous coals. The main purpose of the tests was through natural gas cofiring to improve the boiler operation - reduce slagging and fouling and provide added life for critical boiler components. Stack emissions reduction was not the main goal, but was also under consideration.

During the tests, substantial leveraged reductions of 30% for opacity and 15% for SO₂ were obtained for 10% natural gas cofiring. The fuel gas was injected through existing corner gas burners, parallel to the main coal flame. These gas burners were mid-level in the burner bank so that most of the flue gas from the coal flame was either processed through or exposed to a higher temperature combustion zone.

A possible mechanism for the leveraged reduction of SO₂ and particulate emissions is suggested.

Comparison of tests with 100% coal firing and 90% coal with 10% natural gas cofiring showed a 280% increase in the sulfate content in the flyash. This resulted in a leveraged reduction in flue gas SO₂. The higher sulfate concentration in the flue gas reduced flyash resistivity, thereby enhancing ESP performance.

It is recommended that additional long-term testing be pursued on several different types of boilers and coal to determine how to optimize the cofiring configuration for maximum site specific emissions reduction benefits. The experience thus gained will facilitate future conversions to cofiring in utility boilers throughout the United States wherever the overall economics are favorable.

INTRODUCTION

In recent years the subject of cofiring gas with coal in boilers which usually operate on 100% coal has received increasing attention. A major reason for this is that cofiring can be a simple, effective technique for reducing stack emissions (including SO₂, NO_x, and particulates) by at least as much as the proportion of gas fired relative to coal.

In late 1988, Public Service Company of Oklahoma (PSO) explored the use of cofiring mainly for operational benefits to alleviate a slagging problem. Aptech Engineering Services, Inc. (APTECH) developed the project and performed the management, test, data reduction and boiler performance analysis.

TEST SITE DESCRIPTION

Public Service Company of Oklahoma Northeastern Station (NES) is located in Oologah, Oklahoma, 50 miles Northeast of Tulsa. Units 3 and 4 are two identical Combustion Engineering tangentially fired units rated at 450 MW, delivering 3,200,000 pounds of steam per hour at 3614 psi and 1005°F with single reheat. The boiler at NES 4 possesses burners for a variety of fuels including coal, natural gas, No. 4 oil, and refuse. Since start-up in 1979, however, both NES 3 and 4 have been operated exclusively on natural gas for start-up and warm-up and a coal blend for base-load service. Number 4 oil and refuse have never been fired in these units. There are five elevations of coal burners, with each set of four burners at a given elevation supplied by a separate mill. There are four levels of gas burners, and each level is situated between a pair of coal burner levels. Also at these four levels, but on the wall adjacent to the gas burners, are located four levels of gas ignitors. Finally, one elevation of gas warm-up guns is provided at the bottom of the burner bank. Regarding emission control equipment, these units are supplied with overfire air for NO_x control, a cold precipitator for particulates, and a single common stack. The coal blend consists of 90% Wyoming subbituminous and 10% Oklahoma bituminous on an annualized basis. Throughout the year, however, the coal blend can vary from 0% to 30% Oklahoma coal.

Tables 1 and 2 summarize the typical properties of Western subbituminous coal and Oklahoma bituminous coal used at NES 3 and 4, based upon coal analyses performed in the summer of 1989.

TEST RESULTS

Several different test series were conducted. The Baseline Performance Test was performed to characterize and optimize the unit on 100% coal. The coal blend was 100% Western, 0% Oklahoma. The data from this test were used for comparison and evaluation of further measurable improvement (or degradations) during subsequent gas cofiring.

The Exploratory Cofiring Test Series was a sequence of short tests to screen a variety of firing configurations. The following optimum configuration was determined: 4.5% to 5.0% excess O₂; 65% overfire air; windbox/furnace pressure differential of 7 to 8 inches H₂O; coal burner levels B-C-D-E in service with no mill bias, level A (bottom level) out of service; gas cofiring through gas burners between levels C and D; burner tilts on automatic. The gas cofired was tested in the range of 9% to 10% and only one level of four gas burners were used to keep the gas injection momentum sufficiently high to avoid the formation of "lazy flame."

This optimum was based upon the following considerations:

- Avoid clinker formation on the ash hopper slopes
- Minimize and potentially reduce waterwall slagging and convection pass fouling
- Maintain a "tight fireball"
- Maintain bulk superheated and reheated steam temperatures
- Do not increase stack opacity
- Do not increase superheater and reheater tube metal temperatures
- Keep percentage of excess O₂ at a minimum consistent with the above

Two long term test series were conducted. The Cofiring Test series consisted of four continuous days of cofiring, when about 10% as a heat input natural gas was burned through the gas burners between Levels C and D. A blend of 26% Oklahoma coal with 74% Western Coal was used.

The second long-term test series was the 100% Coal Test which also has a duration of four continuous days. The same coal blend was used for this second long-term test.

STACK SULFUR DIOXIDE AND NITROGEN OXIDES MEASUREMENTS

Figure 1 shows the stack sulfur dioxide and nitrogen oxides measurements each hour throughout the 24-hour period for November 5, and 16, 1989. Plotted are the actual hourly measurements, not the rolling three-hour averages. During full load, 100% coal firing, the average concentration of SO₂ is approximately 1.0 lb/MMBtu, while for full-load cofiring with 10% natural gas, it is approximately 0.82, representing an 18% reduction. This is typical of the results for all long-term cofiring testing.

Table 3 provides a more detailed analysis of the SO₂ data obtained during the long-term testing. The daily average SO₂ concentration for all times during the day for which the boiler was at full-load is tabulated for long-term 100% coal firing and cofiring. As indicated, percent reductions in SO₂ as high as 28% were obtained with no more than 13.3% gas cofiring.

Figure 2 graphically displays the leveraged SO₂ reductions obtained during the long-term cofiring testing.

STACK OPACITY MEASUREMENTS

Figure 3 shows the stack opacity measurements each hour throughout the 24-hour period for November 5 and November 16, 1989. Each hourly measurement is actually an average of ten instantaneous measurements recorded, one every six minutes, for that hour. As indicated, the mean during full-load 100% coal firing was 9.9% opacity, while during full-load cofiring, it was 5.5% opacity.

This represents a 44% reduction. The average opacity reduction for the entire long-term cofiring test period was 35% relative to the average opacity for the long-term 100% coal firing test.

Table 4 provides a more detailed analysis of the opacity data obtained during the long-term tests. Three different opacity values are shown for each day of the long-term cofiring tests. The first two opacity values are the instantaneous values for 10:00 and 16:00. These different times of the day are of interest because the precipitator performance is influenced by the ambient temperature level. The third opacity value is the average value for all times during the day for which the boiler was at full-load (including both 10:00 and 16:00). The opacity reductions resulting from cofiring for 10:00, 16:00, and full-load daily average are tabulated in Table 6.

Figure 4 graphically illustrates the leveraged opacity reductions achieved from cofiring for 10:00, 16:00, and the full-load daily average. As indicated, opacity reductions of almost 50% were obtained with no more than 13.3% gas cofiring.

TEST DATA INTERPRETATION

Introduction

In conducting this data interpretation, selected long-term test data from both gas cofiring and 100% coal firing have been considered. The emphasis has been to compare the results of the gas cofiring to those for 100% coal firing. Specifically, an attempt has been made to explain the changes in furnace temperatures and stack emissions that were observed as a result of going from 100% coal firing to gas cofiring while holding all other operational variables constant.

Firebox Flue Gas Temperature Evaluation

As a first step in interpretation of the test data, the firebox flue gas temperature distribution was evaluated. A one-dimensional heat transfer model was used to model the profile of bulk gas average temperature at different firebox horizontal cross sections. This one-dimensional model gives integrated combustion and heat transfer data at selected horizontal cross sections of the furnace which are relatively easy to interpret and relate to the coal properties and NO_x and SO_x formation.

Calculations of the flue gas bulk temperatures at the top of each of the three zones were performed with the one-dimensional model using the fundamental coal properties obtained from the analysis of coal samples taken in September prior to the test program. Table 5 summarizes the results of the ultimate analysis for the Western coal being used at NES 4 at that time. Table 6 presents an "equivalent" ultimate analysis for a fuel comprised of 90% Western coal and 10% natural gas.

Figure 5 presents the firebox bulk gas temperature profile predicted by the one-dimensional model for 100% coal, and that for 90% coal and 10% gas. The model predicts essentially no change in bulk gas temperature at the furnace exit (top of Zone 3) and the bottom of the bull nose (top of Zone 2) due to gas cofiring. However, at the top of the combustion zone (Zone 1) and in the combustion zone, the bulk gas temperature is 50°F to 100°F higher when cofiring. Specifically, at the top of Zone 1 just above the burners, the bulk gas temperature is 54°F higher with 10% cofiring, while down lower the flame temperature with heat transfer is 66°F higher while the adiabatic flame temperature is 94°F higher. Of course, in the very localized region where the natural gas is injected (Elevation CD gas burners), there are zones of much higher temperature through which the coal combustion products are processed.

SO_x Emissions

The organic and pyritic sulfur in coal oxidizes to SO_2 and SO_3 in the combustion process. Only a small portion of this sulfur is converted to SO_3 during combustion. Usually, for pulverized coal boilers, less than 1% of the sulfur is converted to SO_3 in the flue gas. However, in the flame (Zone 1) up to 5% to 12% of the available sulfur in the coal is oxidized to SO_3 .

The oxidation of SO₂ from molecular oxygen can be written as:



The equilibrium constant of this reaction is:

$$\log K_p = \frac{10373}{T} + 1.222$$

The equilibrium relationship between SO₂ and SO₃ is shown in Figure 6 for various conditions of temperature and molecular oxygen availability.

This reaction takes place in a temperature range below 1600°F and could be promoted by a catalyst. The chemical kinetics for SO₃ formation show that with a temperature increase, the role of molecular oxygen as an oxidizing agent is reduced and that of atomic oxygen is increased. The most probable reaction is:

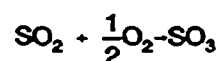


Figure 7 shows the conversion rate of SO₂ oxidation to SO₃ under adiabatic conditions. It also shows the atomic oxygen as a fraction of total oxygen as a function of excess air. This graph indicates that SO₃ concentration increases as atomic oxygen concentration decreases. This is due to the effect of temperature and also explains why after excess air reaches a certain value, the curve for SO₂ conversion rate begins to level off.

The effect of flame temperature on the SO₃ formation is shown in Figure 8. The amount of SO₃ formed increases with the flame temperature and is attributed to the greater concentration of atomic oxygen at higher temperatures. The curve leveling off at 3200°F is not well explained, but probably is due to the kinetic mechanisms of the reaction involving SO₂ and O₂ which also takes place. The equilibrium residence time of the reaction is about 200 msec. From experiments with different furnaces, it has been established that a shorter residence time of the gases in a higher temperature zone is favorable for production of SO₃.

When coal is burned, CaCO₃ and MgCO₃ are converted to CaO and MgO through a calcination process at high temperature conditions. Simultaneously, in the furnace CaO and MgO react with SO₂ and SO₃ in the presence of O₂ forming CaSO₄ and MgSO₄. The reactions with SO₂ are less probable than with SO₃ because of the lower

free energy available after the reactions are completed. This has also been established in experimental and full scale facilities for sorbent (CaCO_3 , MgCO_3) injection with coal burning for SO_2 reduction and oil burning for SO_3 reduction in the flue gas.

For the long-term 100% coal and cofiring tests, a sulfur balance was performed in order to determine the sulfur distribution in the combustion products. The results of the sulfur chemical analysis are shown in Table 7. The sulfur balance for both long-term tests is shown in Figures 9 and 10. From these results it is concluded that the fly ash in the cofiring test is significantly (approximately 50%) enriched in sulfur.

The sulfur reduction in the flue gas predicted from the sulfur balance is comparable with the reduction indicated from the direct flue gas SO_2 measurement data (Figure 11). The small difference is most likely a result of limitations on sample collection. These samples are not averaged from continuous sampling, but from samples extracted every four hours.

The results correspond well with the theory of SO_3 formation presented in the beginning of this section. For the NES 4 cofiring configuration, the natural gas was burned at the center of the coal flame, thus allowing coal combustion products to be processed in a higher temperature zone for a very short residence time. This promotes SO_3 formation in Zone 1 and in parallel, a sulfation process with CaO and MgO in the ash particles. In summary, this causes the SO_2 reduction in the flue gas to be higher than that expected due to the fuel sulfur reduction because 10% of the coal is replaced by natural gas. With special process designs and combustion process fine tuning, it is possible that this "leveraged" reduction in SO_2 can be even further increased.

PARTICULATE EMISSIONS AND STACK OPACITY

The flue gas opacity in the stack was measured during both 100% coal and cofiring tests with a Lear Siegler RM41 opacity meter. Calibration of the instrument was performed eight months before the tests, and after adjustment, the maximum error was in the range of 2% to 3%.

Since direct measurement of the particulate mass concentration via EPA Method 5 was not performed, the particle mass concentration was estimated based on experimental data relating mass concentration to light attenuation in the stack gas of a coal-fired boiler with ESP control. The experimental data for two different plants are shown in Figure 12. This graph shows significant differences between the mass concentrations for the same measured opacity for Plants A and B. This is due to differences in the particulate properties as well as possible errors in the determination of the mass concentration through the measurement technique.

Table 8 shows the results from the tests conducted in this project where the particulate emissions level, as indicated by opacity, is reduced over 30% when the particle loading input is reduced by only 10%. The estimates for particle mass concentrations reflect the range of the test data in Figure 12.

Generally, the level of particulate emissions is directly related to the electrostatic precipitator efficiency. The optimum ESP performance depends on the electrical resistivity of the flyash which should be high enough to result in electrostatic pinning of particles to the collecting surface, but not so high that electric discharge through the layer occurs as the corona current passes through it. The optimum flyash resistivity range measured in situ is considered to be 10^8 to 10^{10} ohm cm.

Flue gas produced by combustion of coals with low sulfur content in the range of 0.5% to 1% and at temperatures between 250°F to 300°F has a flyash resistivity higher than 10^{11} ohm cm, which is significantly above the desired 10^{10} ohm cm upper limit (Figure 13).

With the natural gas cofiring tests conducted here, the sulfate content in the flyash increased to 0.42% from 0.11% when 100% coal was fired. This results in lower electrical resistivity of the flyash and higher ESP current which improves ESP collection efficiency. Thus, a highly leveraged opacity reduction results because the flyash loading to the ESP is reduced by 10% when 10% of the coal is replaced with gas, and the collection efficiency for this flue gas with already reduced particle concentration is significantly increased.

CONCLUSIONS AND RECOMMENDATIONS

Overall, the results of this test program indicate that gas cofiring offers significant technical promise as a practical means for reducing stack SO_2 and particulate emissions. The circumstances surrounding this project should be kept in mind. The field testing was performed under the utility's normal operating conditions (except for gas cofiring) and only routine plant instrumentation was used. Also, the cofiring testing involved a specific boiler design, a specific coal, and a specific cofiring configuration. Nevertheless, the very significant leveraged reductions in SO_2 and opacity were obtained as reported here. The emissions data obtained in these field tests were consistent and repeatable, and the leverage trends are outside the estimated data uncertainty bands.

With the caveat that the majority of the cofiring testing was limited to a maximum of 13% gas at 100% load, and the test was not designed specifically for stack emissions reduction, the following is the major technical conclusion:

- Cofiring at NES showed substantial promise as an emissions reduction technique, particularly for opacity and SO₂. Substantial leveraged reductions were obtained with 13% cofiring: over 40% for opacity and over 20% for SO₂ were typical results. These leveraged reductions were attributed to significantly greater sulfur retention in the flyash during cofiring: sulfates content increased almost 400%, and sulfur content increased 16%. This was speculated to be a result of slightly higher combustion temperatures during cofiring (predicted not measured) which increased the conversion of SO₂ to SO₃, the latter being more reactive with flyash mineral matter. The increased sulfate content lowers the flyash resistivity and improves the ESP collection efficiency. These conclusions are supported by a detailed sulfur balance. The higher combustion temperatures promoted the formation of thermal NO_x which offset the inherently lower fuel NO_x, so that total NO_x concentrations for 100% coal firing and cofiring were essentially the same. This suggests that it will be difficult to simultaneously lower both SO₂ and NO_x in basic cofiring configuration similar to that available in the NES 4 boiler. Cofiring could be extremely cost beneficial in reducing emissions to remain in compliance without incurring very large capital expenditures for scrubbers and ESP or baghouses.

Concerning cofiring in coal-fired boilers in general, the following recommendations are made:

- Long-term cofiring tests should be conducted with a variety of boiler designs, loads, coal properties, firing configurations, and gas percentages.
- The results of these tests can be used to develop a cofiring field test data base from which site-specific technical guidelines can be developed for new users. These guidelines would tell users how to optimize cofiring for their desired site-specific benefits.

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Table 1
COAL PROPERTIES, WESTERN COAL

	<u>As-Received</u>	<u>Moisture Free</u>
Moisture	15.64%	
Ash	5.47%	6.48%
Volatile Matter	38.85%	46.05%
Fixed Carbon	40.04%	47.47%
Sulfur	0.45%	0.53%
BTU/lb	10,068	11,934
Ultimate Analysis		
Carbon	58.83%	69.74%
Hydrogen	4.27%	5.06%
Nitrogen	0.88	1.05%
Sulfur	0.45%	0.53%
Ash	5.47%	6.48%
Oxygen	14.46%	17.14%
Total Moisture	15.64%	

Table 2
COAL PROPERTIES, OKLAHOMA COAL

	<u>As-Received</u>	<u>Moisture Free</u>
Moisture	10.38%	
Ash	12.75%	14.22%
Volatile Matter	28.57%	31.88%
Fixed Carbon	48.30%	53.90%
Sulfur	0.35%	0.39%
BTU/lb	10,984	12,256
Ultimate Analysis		
Carbon	63.81%	71.20%
Hydrogen	3.84%	4.29%
Nitrogen	1.45%	1.62%
Sulfur	0.35%	0.39%
Ash	12.75%	14.22%
Oxygen	7.42%	8.28%
Total Moisture	10.38%	

Table 3
SO₂ DATA ANALYSIS

1. 100% Coal (Test 6, Long-Term 100% Coal Firing)

<u>Date</u>	<u>Average SO₂ @ Full-Load</u>
11/3/89	1.06
11/4/89	1.05
11/5/89	1.00
11/6/89	0.99
Daily Average	1.025

2. Gas Cofiring (Test 4, Long-Term Cofiring)

<u>Date</u>	<u>Percent Gas</u>	<u>Average SO₂ @ Full-Load</u>	<u>Percent Reduction Relative to Daily Average @ Full-Load on 100% Coal</u>
11/16/89	11.0	0.87	15.1
11/17/89	10.5	0.84	18.0
11/18/89	9.9	0.90	12.2
11/18/89	13.3	0.82	20.0
11/19/89	13.3	0.74	27.8
11/19/89	9.0	0.85	17.1

Note: All SO₂ values are lb/MBtu

Table 4
OPACITY DATA ANALYSIS

1. 100% Coal (Test 6, Long-Term 100% Coal Firing)

<u>Date</u>	<u>Opacity @ 10:00</u>	<u>Opacity @ 16:00</u>	<u>Average Opacity @ Full-Load</u>
11/3/89	8.8	9.7	9.1
11/4/89	8.3	10.8	9.2
11/5/89	10.3	12.2	9.9
11/6/91	8.7	10.8	8.9
Daily Average	9.0	10.9	9.3

2. Gas Cofiring (Test 4, Long-Term Cofiring)

<u>Date</u>	<u>Percent Gas</u>	<u>Opacity @ 10:00</u>	<u>Opacity @ 16:00</u>	<u>Average Opacity @ Full-Load</u>
11/16/89	11.0	5.8 (35.6)	6.2 (43.1)	5.9 (36.6)
11/17/89	10.5	6.0 (33.3)	7.5 (31.1)	6.2 (33.3)
11/18/89	9.9	5.1 (43.3)	—	6.3 (32.3)
11/18/89	13.3	—	5.6 (48.6)	5.4 (41.9)
11/19/89	13.3	6.8 (24.4)	—	4.9 (47.3)
11/19/89	9.0	—	7.4 (32.1)	7.3 (21.5)

() = Percent opacity reduction relative to daily average opacity at full-load on 100% coal

Note: All opacity values are percent opacity

Table 5
FUEL CHARACTERISTICS - 100% WESTERN COAL
ULTIMATE ANALYSIS FROM COAL
SAMPLE TAKEN SEPTEMBER 1989

C 58.83%

H 4.27%

S 0.45%

N 0.88%

O 14.46%

A 5.47%

W 15.64%

Total 100%

LHV - 10068 Btu/lb

Stoichiometric combustion air = 93.56 scft/lb

Stoichiometric flue gas = 103.81 scft/lb

Table 6
FUEL CHARACTERISTICS - 90% WESTERN COAL, 10% NATURAL GAS

<u>Natural Gas</u>	<u>Equivalent in Mass %</u>
CH ₄ - 98.9%	C - 74.31%
C ₂ H ₆ - 0.3%	H - 24.62%
C ₃ H ₈ - 0.1%	O - 0.39%
C ₄ H ₁₀ - 0.1%	N - 0.70%
N ₂ - 0.4%	
CO ₂ - 0.2%	Total 100%

Total 100%

LHV - 897 Btu/scft

S - 0.0445/lb/cft

EQUIVALENT ULTIMATE ANALYSIS

C - 58.90%
H - 5.96%
S - 0.43%
N - 0.88%
O - 14.76%
A - 4.92%
W - 14.18%

Total 100%

LHV = 11227 Btu/lb

Stoichiometric combustion air - 100.77 scft/lb

Stoichiometric flue gas - 1663.04 scft/lb

Table 7
FORMS OF SULFUR IN THE COAL AND COMBUSTION PRODUCTS

Forms of Sulfur %						
Test	Sample (As- Received)	Pyritic	Sulfate	Organic	Total Sulfur %	Unburned Carbon %
100% Coal						
11/14/89						
	Coal	0.11	0.01	0.39	0.51	—
	Fly ash	0.37	0.11	0.08	0.56	0.08
	Bottom ash	0.09	0.06	0.12	0.27	0.15
Cofiring						
11/16/89						
	Coal	0.11	0.01	0.39	0.51	—
	Fly ash	0.17	0.42	0.06	0.65	0.08
	Bottom ash	0.09	0.17	0.01	0.27	0.70

Table 8
COMPARISON OF PARTICULATE EMISSIONS

Test	Percent Opacity	Estimated Particle Mass Concentration mg/m³
		Average/Range
100% Coal	9.6	103
		176 - 30
Cofiring - 90% Coal 10% Natural Gas	6.5	76
		134 - 19
Reduction Percent	32.3	26.2
		23.9 - 36.7

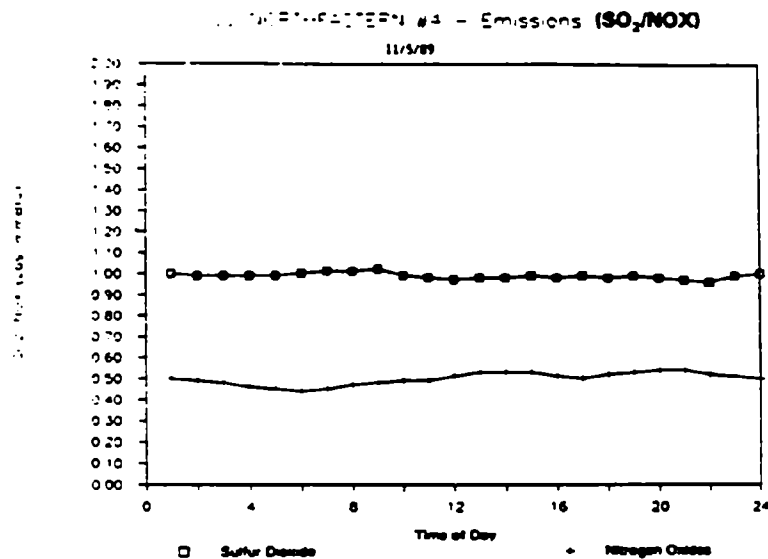


Figure 1A - Stack Sulfur Dioxide and Nitrogen Oxides Emissions, Long-Term 100% Coal Firing

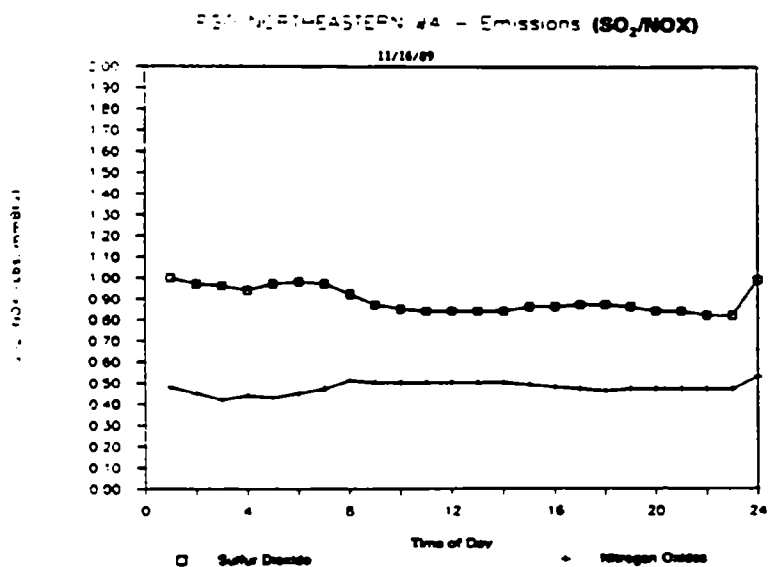


Figure 1B - Stack Sulfur Dioxide and Nitrogen Oxides Emissions, Long-Term Cofiring

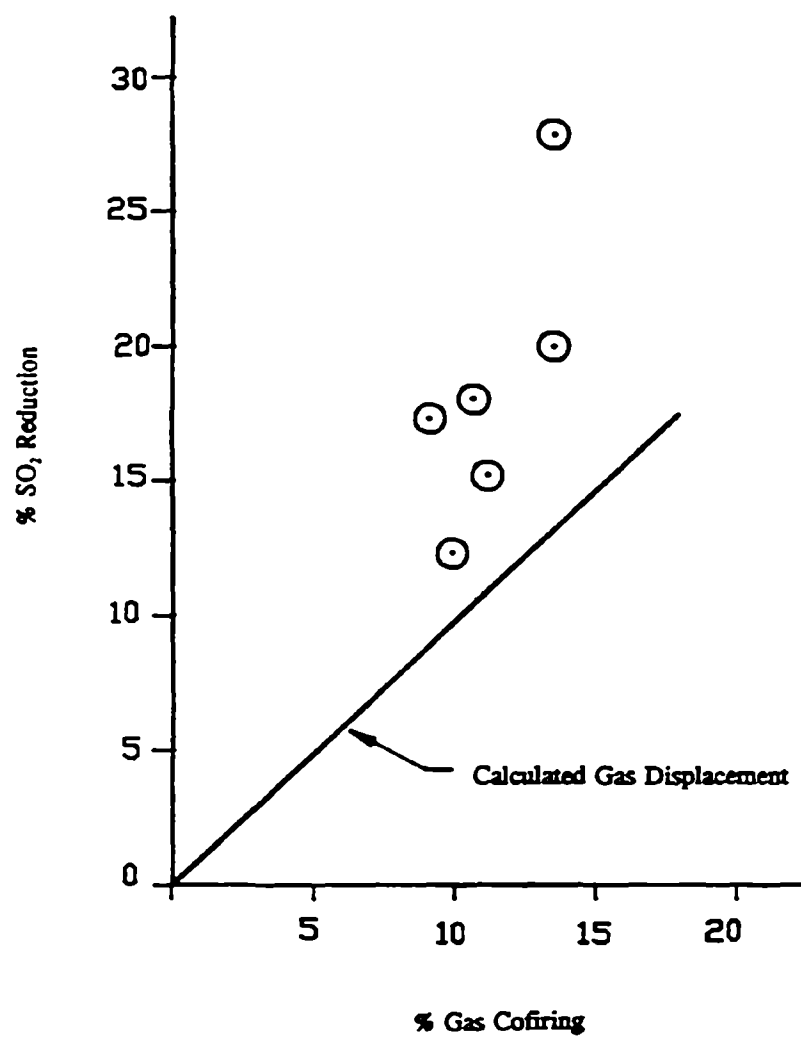


Figure 2 - Leveraged SO₂ Reductions Achieved From Long-Term Cofiring.

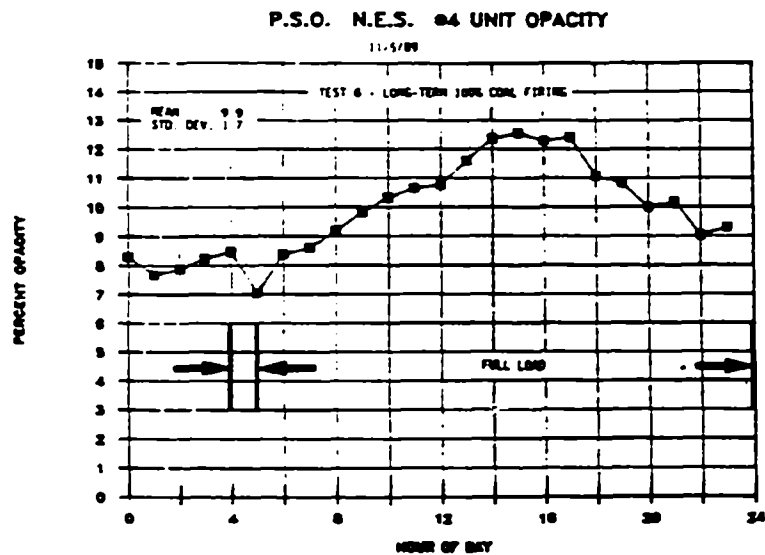


Figure 3A - Stack Opacity, Long-Term 100% Coal Firing.

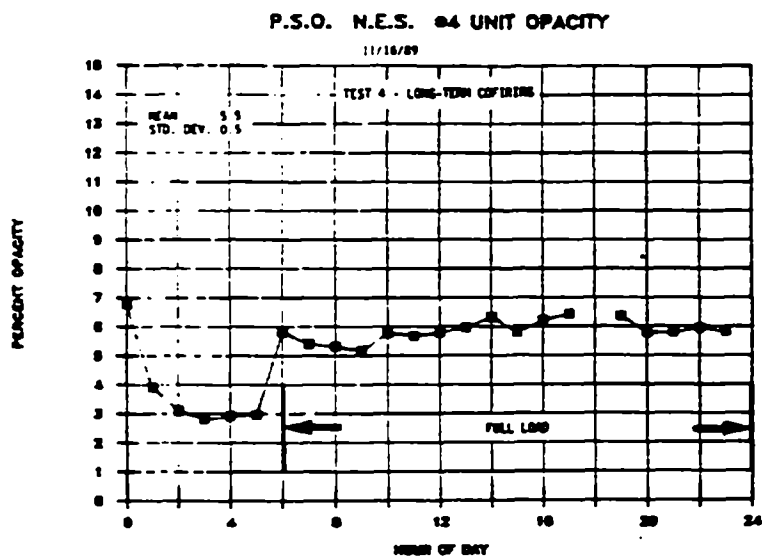


Figure 3B - Stack Opacity, Long-Term Cofiring.

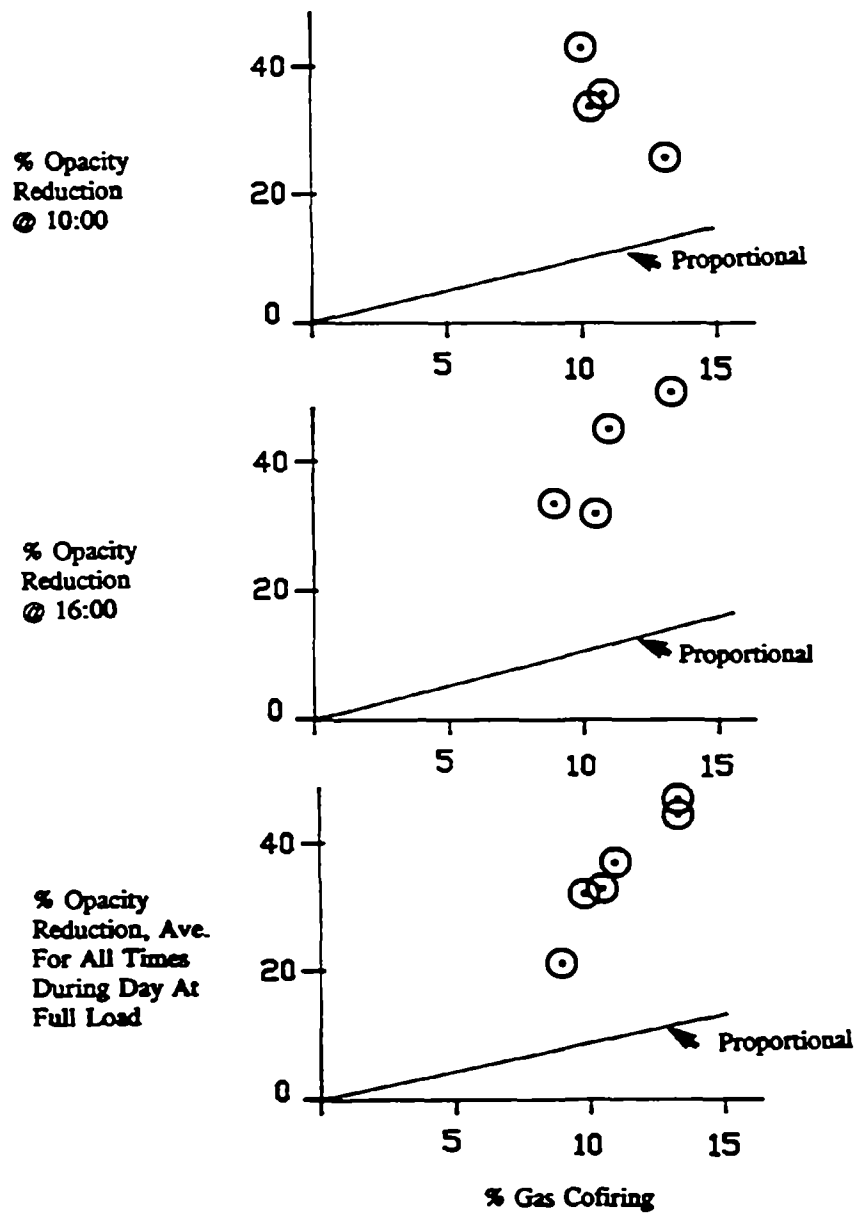


Figure 4 - Leveraged Opacity Reductions Achieved From Long-Term Cofiring.

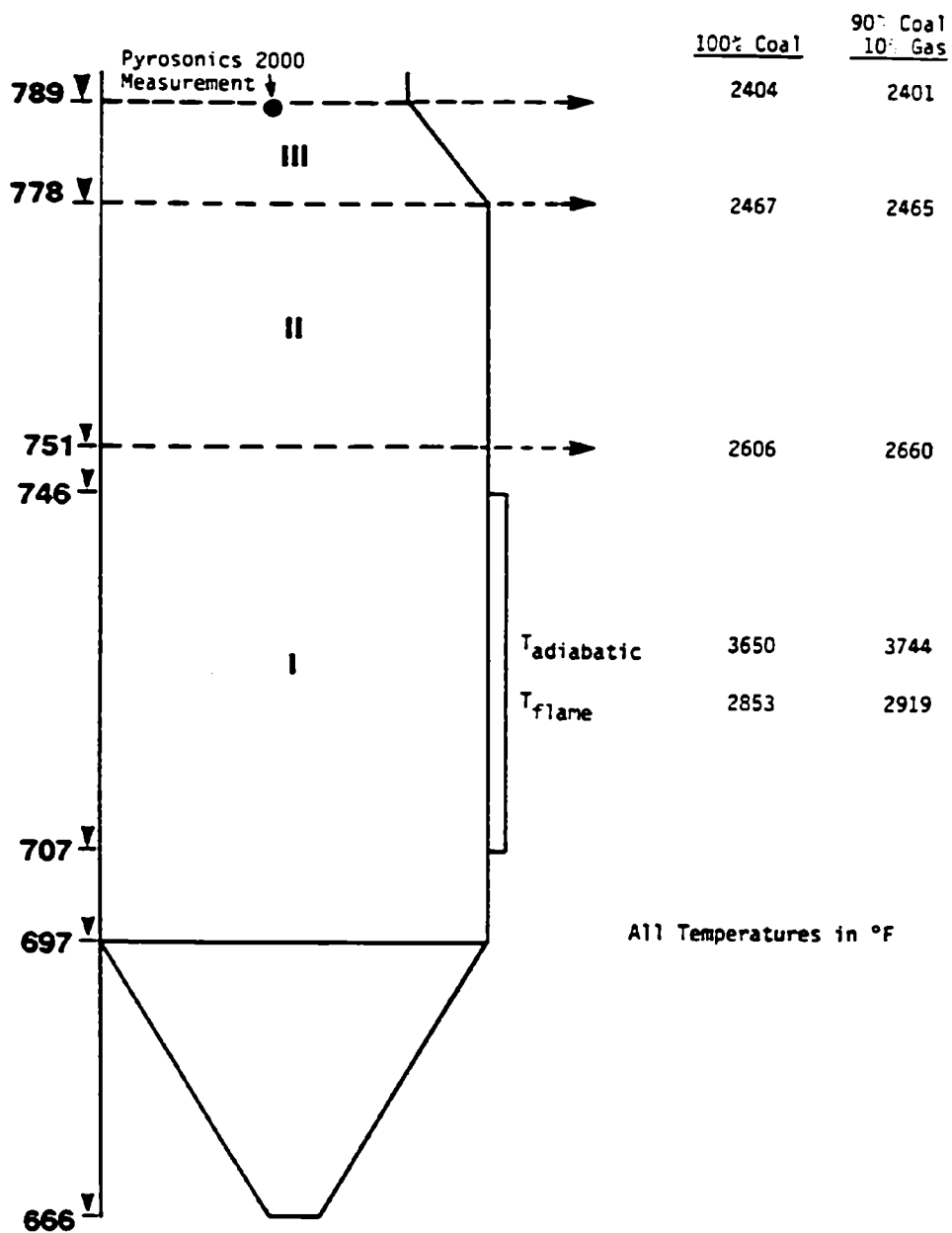


Figure 5 - Firebox Temperature Profile.

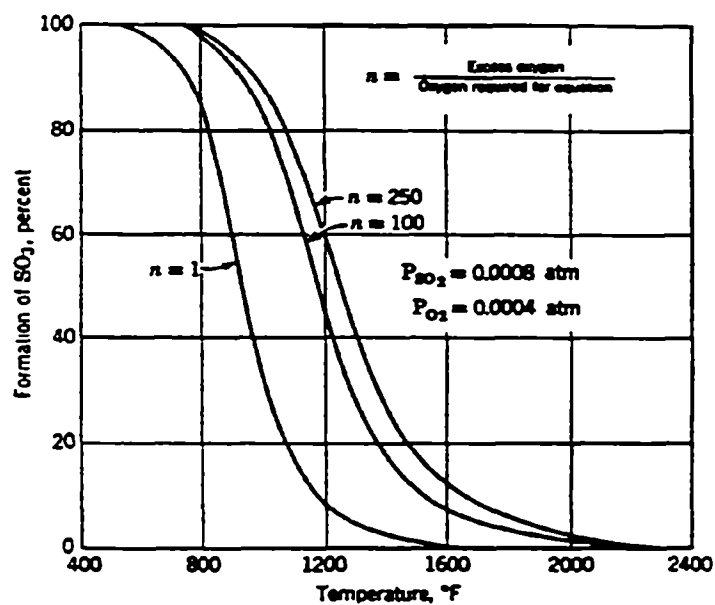


Figure 6 - Equilibrium Yields of SO_3 for the Equation $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$.

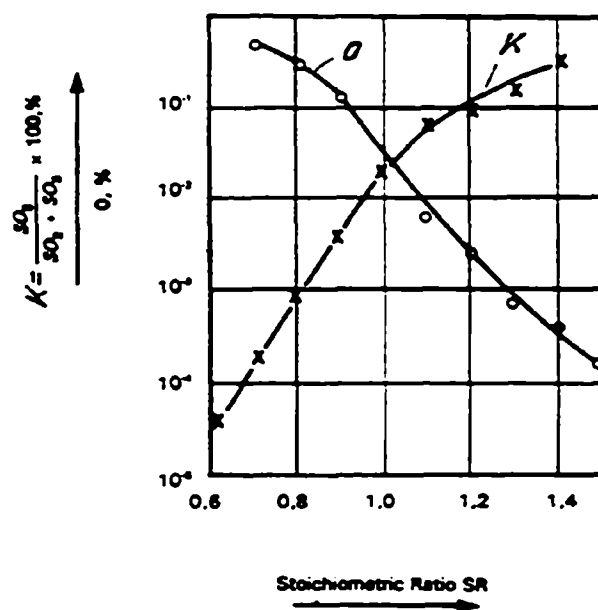


Figure 7 -

Equilibrium Conversion of SO_2 to SO_3 and Atomic Oxygen Concentration as a Function of the Stoichiometric Ratio.

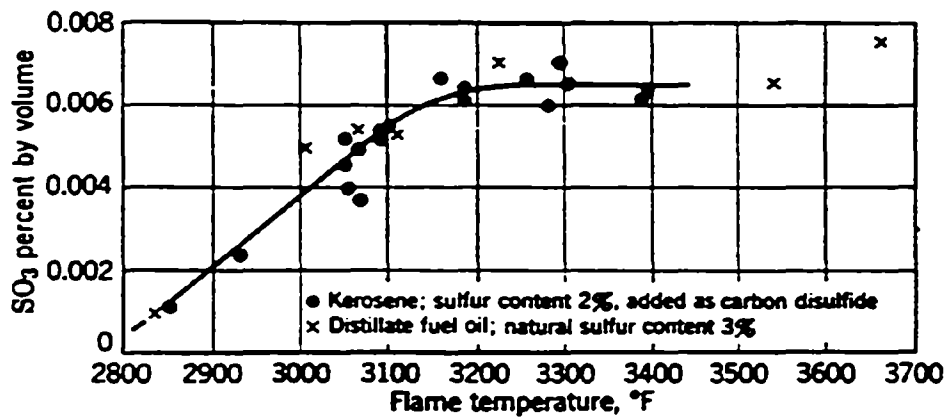


Figure 8 - Variation in SO₃ Content of Flue Gases Containing 12% CO₂ With Flame Temperature.

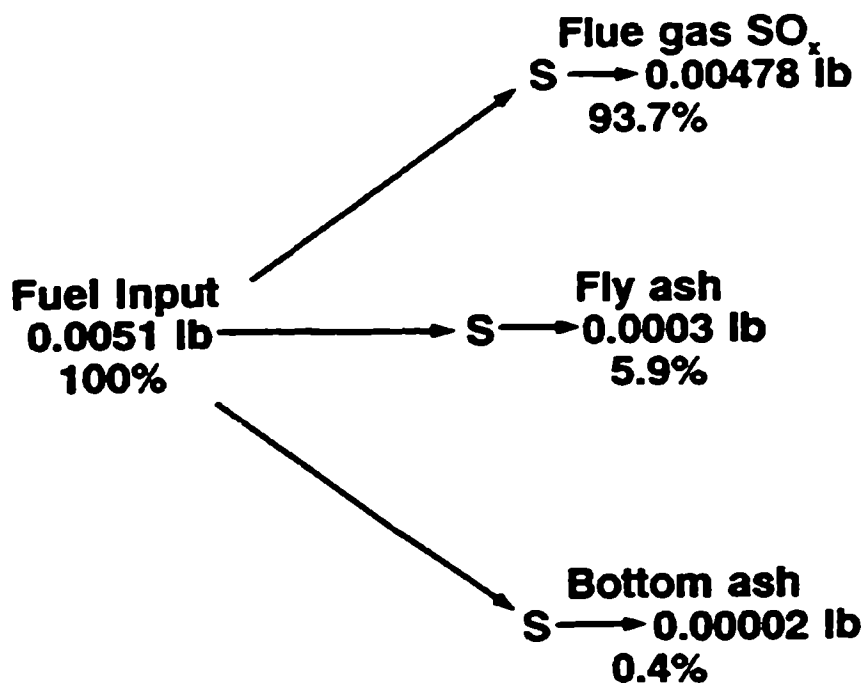


Figure 9 - Sulfur Balance (Per Pound Fuel) 100% Coal (November 4, 1989).

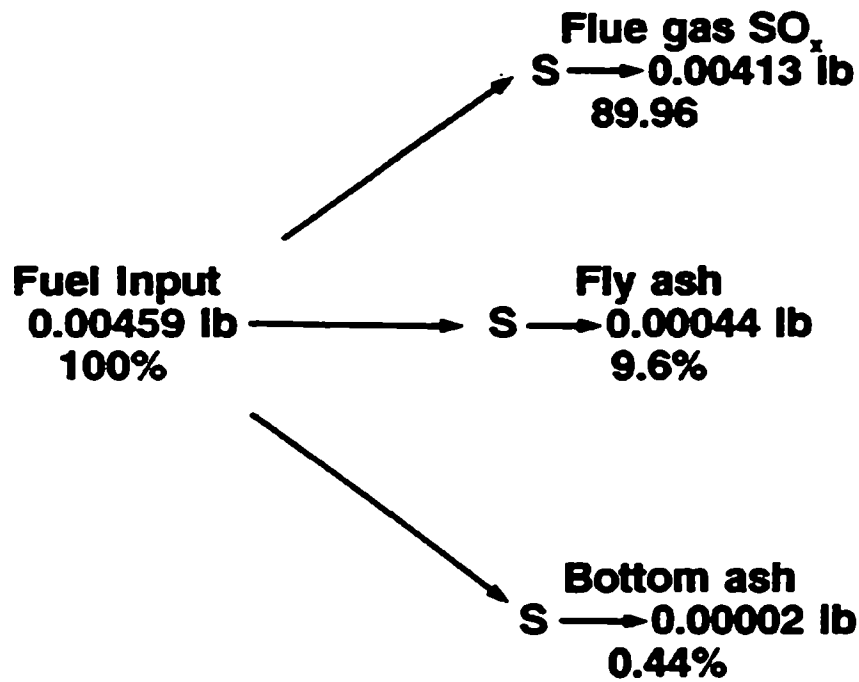


Figure 10 - Sulfur Balance (Per Pound Fuel) 90% Coal, 10% Gas (November 16, 1989).

FROM SO_x MEASUREMENT

100% coal (November 4, 1989) - SO _x = 1.04 lb/MBtu	} SO _x reduction - 15.4%
90% coal, 10% natural gas (November 16, 1989) - SO _x	
= 0.88 lb/MBtu	

FROM SULFUR BALANCE (Assumptions for coal ash distribution, 90% as a fly ash and 100% as a bottom ash)

SO_x reduction - 13.6%

Figure 11 - SO_x Emissions Reduction.

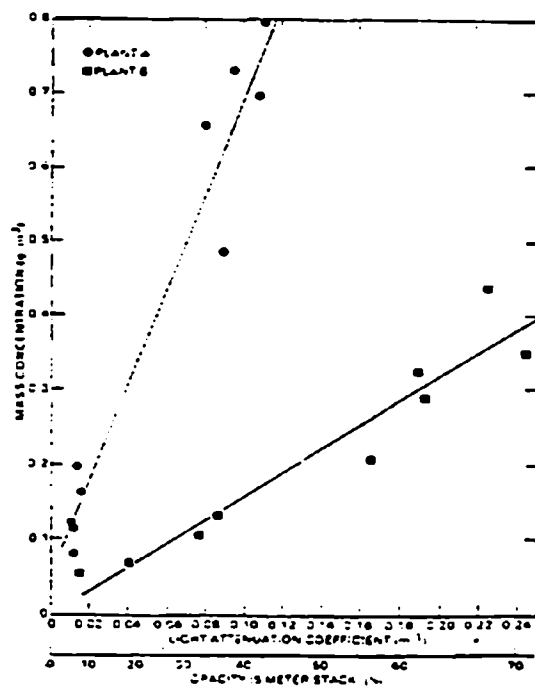


Figure 12 - Mass Concentration Versus Light Attenuation of Particulate Emissions at Coal-Fired Power Plants With ESP Controls.

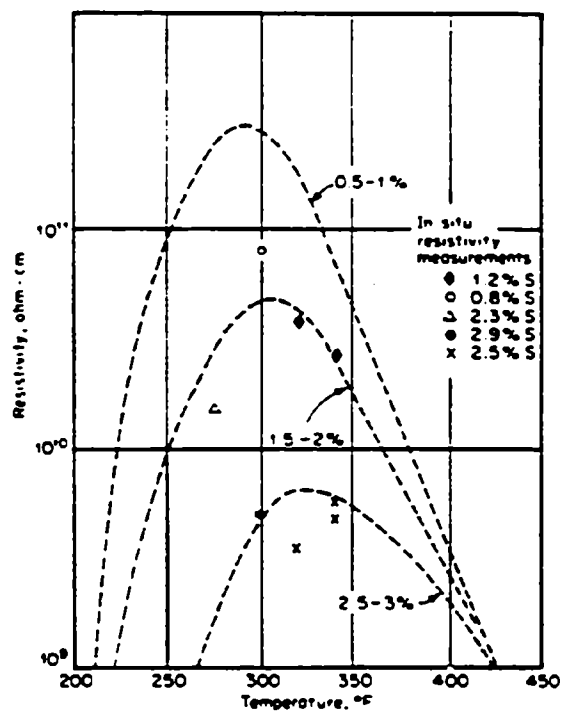


Figure 13 - Trends in Resistivity of Flyash With Variations in Flue Gas Temperatures and Coal Sulfur Content.

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**Design, Installation, and Operation of the
First Wet FGD for a Lignite-Fired Boiler in Europe at
330 MW P/S Voitsberg 3 in Austria**

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ABSTRACT

The FGD has been designed and constructed by Messrs. Waagner-Biro and incorporates the IFO-process of GEESI. The main features of the IFO-process (= Insitu Forced Oxidation) are the simultaneous removal of SO₂ and production of gypsum in the same vessel as well as the sophisticated limestone feed control which is essential to cope with the fluctuating SO₂-load in the range of 4000 to 7000 mg/m³ typical for lignite. The Voitsberg installation was the first wet FGD application for lignite in Europe.

The FGD is designed in two lines each rating 50 % of the total flue gas volume without spare vessels. Approx. 50,000 tons of gypsum have been produced annually and had been dumped in the exhausted strip mine nearby. Since 1990 100 % of the gypsum produced has been made use of in the cement industry. Further utilization possibilities are investigated and tested at present (e.g. high-grade sealing of disposals by residues from lignite fired P/S). Due to the specific site conditions no waste water is produced.

The desulphurization plant has been in operation for approx. 20,000 hours and has fulfilled all expectations regarding SO₂ reduction and reliability. Typical operating data are shown in the paper. The power plant availability never was influenced by the desulphurization plant. Operation and maintenance experience will be presented. The total project costs for the desulphurization plant were approx. 70 million US-\$.

- 1. General**
- 2. Furnace Limestone Injection (FLI)**
- 3. Wet Limestone Scrubbing (FGD)**
 - 3.1 Process Design and Arrangement**
 - 3.2 Operating Experience**
- 4. NO_x Reduction (DeNO_x-plant)**
- 5. Conclusion**
- 6. Figures**

1. GENERAL

The Österreichische Draukraftwerke AG (short: ÖDK), founded in 1947 with the main duty of developing the hydraulic power of the river Drau, decided to build the 330 MW Thermal Power Station of Voitsberg 3 (Fig. 1) on the basis of a long-term delivery contract for local lignite in July 1977.

The proven resources of 31 million tons of lignite have an average calorific value of approx. 10 500 kJ/kg and a sulphur content in the range of 0.5 to 1.5 % and is open-pit mined. This quantity is sufficient to guarantee the fuel supply of this unit-type power station for the duration of its actual life service (Fig. 1).

Voitsberg 3 has a once-through boiler with a steam generating capacity of 290 t/h and a triple-cased 330-MW-turbine.

The civil engineering and erection works for the plant started in autumn 1977 and were fundamentally completed by the commissioning date of the unit in April 1983.

Voitsberg 3 Power Plant is designed for approx. 4000 design load hours/year. A substantial portion of the total investment costs, i.e. approx. 1,6 billion ATS, has been spent for environmental precautions (ESP, LSI, FGD, DeNOx) Also see fig. 2.

2. FURNACE LIMESTONE INJECTION (FLI)

With this process limestone powder is injected into the furnace where it is calcined to CaO which reacts with the SO₂ to CaSO₄ (Fig. 4). The desulphurization product and the non-reacted additive are collected in the precipitator together with the fly ash. Testing numerous different injection points at different lignite fired plants, the limestone injection together with the combustion air brought the best results as the limestone is injected into a favourable temperature region and there is enough pulse with the overfire air of the burner to distribute the additive.

The plant was initially designed without an FGD. In order to fulfill emission requirements FLI was applied from the very beginning of commercial operation in April 1983 as an intermediate solution. The process was in operation for approx. 13,000 hours (Fig. 5). Depending on the boiler load a removal efficiency of 50 to 70 % was achieved. To reach this efficiency at design load a molar ratio Ca/S of approx. 3.5 was required. There were no reductions in plant availability when using the FLI process.

Advantages (+) and disadvantages (-) of this process are:

- + simple process, quick realization
- + low investment costs
- + low energy consumption
- limited removal of SO₂
- tendency of slagging in the boiler
- more difficult handling and disposal of ashes

3. WET LIMESTONE SCRUBBING (FGD)

To meet the new emission limits a wet limestone scrubbing process was retrofitted to Voitsberg 3. The FLI is now a stand-by to reduce SO₂-peaks from sudden changes of the sulphur content in the coal. Up to now this measure has not been used due to the excellent removal capacity of the wet-type FGD.

3.1 Process Design and Arrangement

The FGD has been designed and constructed by Messrs. Waagner-Biro and incorporates the GEESI-IFO-Process (Fig 3). The main features of the IFO-process (= Insitu Forced Oxidation) are the simultaneous removal of SO₂ and production of gypsum in the same vessel as well as the sophisticated limestone feed control which is essential to cope with the fluctuating SO₂-load typical for lignite. The Voitsberg installation was the first wet FGD application for lignite in Europe.

The FGD is designed in two lines each rating 50 % of the total flue gas volume. The flue gases discharged from the stack are led via two booster fans into the spray towers. Upstream of spray tower 1 a gas/gas heat exchanger is installed which cools down the flue gas before entering the spray tower and heats up the cleaned gas to approx. 100°C. In line 2 the flue gas is directly led into the spray tower. The cleaned and heated gas from spray tower 1 is mixed with the cleaned and unheated gas from spray tower 2. The gases leave the stack at a mixing temperature of approx. 80°C (Fig. 7a, 7b).

The FGD product (gypsum, Fig. 8) is thickened up to 30 % solid content and subsequently dewatered to 15 % moisture in a vacuum drum filter. Thickener overflow and filtrate are completely recycled to the process. No waste water is produced. Up to now approx. 25 % of the gypsum is utilized in the cement industry, the remaining part has been dumped in the exhausted coal mines (surface mining) together with the fly ash. Since 1990 100 % of the gypsum cake has been made use of in the cement industry.

3.2 Operating experience (Fig. 6)

In the following the experiences made during commissioning and the acceptance tests as well as during commercial operation will be presented.

The acceptance test measurements carried out by an officially authorized measuring institute showed that all guarantee values for the first large scale FGD working on the basis of limestone for a lignite fired power station in Europe could be fulfilled. Only in case of spray tower 2 there were slight excess values in mist carry-over.

In all details the problems that occurred during the operation of the plant and that mainly were due to the method of boiler operation and the use of new materials of construction as well as the failure of less important components will be presented below together with the solutions.

Mist eliminator

As can be seen in fig. 9 the mist eliminator was designed as a 2-stage-unit where the uppermost blades (at the clean gas outlet of the spray tower) initially was set in opposite direction to the flow. However, as in accordance with the contract the mist eliminator was designed for a wet flue gas capacity of $2 \times 625,000 \text{ st.m}^3/\text{h}$, wet and as due to a variety of modifications in the operation of the boiler the steam generator produced an approximate amount of $2 \times 685,000 \text{ st.m}^3/\text{h}$ wet flue gas or even more the mist eliminator clearly had to operate at the design limit.

This means that, as the flue gas velocity over the mist eliminator surface never has been constant there were local overloads that resulted in the following carry-over in the flue gas mainly but not only during the washing of the mist eliminator. The measurements were made by TÜV Hamburg acc. to the wet soot particles method.

	M.e. carry-over mg/m ³
Spray tower 1, design load	greater than 34
Spray tower 1, overload	greater than 100
Spray tower 2, design load	greater than 110
Spray tower 2, overload	greater than 1000
Guarantee value, design load	max. 100

The first possible means of improvement consisted in turning the mist eliminator packages so that the end blade of the uppermost mist eliminator was oriented toward the flue gas outlet of the spray tower. In addition catchment pockets were installed in the clean gas ducts.

Acceptance test measurements made then by Prof. Wurz showed the following results. At the design value the flue gas capacity upstream the critical components (gas reheater, clean gas damper, etc.) clearly was below the guarantee value and even in case of an overload of 10 % the amount of carry-over was acceptable.

	M.e. carry-over mg/m ³
Spray tower 1, design load	greater than 5
Spray tower 1, overload	greater than 28
Spray tower 2, design load	greater than 94
Spray tower 2, overload	greater than 153

Lining of the flue gas ducts

The flue gas ducts have been protected from the chemical attacks by clean gas by means of a fiber glass reinforced lining.

As Voitsberg 3 is a peak load power plant and frequently is stopped at weekends (when energy consumption is low in all of Austria) the components containing flue gases are subject to a very great number of changes from hot to cold states entailing considerable variations in the lengths and the resulting stresses.

After an approximate 3,000 operating hours the lining manifested cracks reaching deep down to the carbon steel surface. As these cracks occurred almost exclusively in the corner and edge zones the reason of these defects soon became very clear, unfortunately, only after the defect had occurred.

The lining had been applied by spraying and in the corner zones its thickness was 4 to 5 mm instead of the usual thickness of 1 to 1.5 mm upon plane surfaces. The glass fiber reinforced lining of that thickness could not bear the great number of changes in the expansion coefficients and the permanent heat stresses without cracking.

The defects were repaired by sandblasting the corners once again and applying the lining by means of a spatula, resulting in a thickness of about 1.2 mm.

For the plants being presently under construction we use flue gas ducts of slightly rounded corners ($r = \text{approx. } 20 \text{ mm}$) with which we have made the best experiences considering manufacturing, strength, and lining. This design permits treating all flue gas duct areas by means of the faster and less expensive spraying process.

For the flue gas ducts from the raw gas damper to the spray tower inlet a lining had to be retrofitted. Initially that section had been made of carbon steel only and because of the backflow of the wet and chemically aggressive vapours of the spray tower into the flue gas ducts (during the plant outages) that section began corroding within short.

During the plant outage this section incl. the gas reheater is dried by means of an air dehumidifier in order to minimize the production of sulphurous and sulphuric acid.

Oxidation air

As the process used for the present plant is the IFO-process where air – necessary for the reaction of calcium sulphite into calcium sulphate – is added in the same tank where SO_2 is removed and calcium sulphite is formed. Hence each spray

tower had been equipped with a rotary piston fan (Roots compressor) and a distribution level of glass fiber reinforced pipes.

Due to their function these compressors caused several problems, mentioned below.

- All of the system vibrates (the frequency is twice the speed) and at all "weak" points strong vibrations are produced.
- Like organ pipes the vibrating column of air excites the water injection cooler required for generating optimum conditions of reactions, i.e. a temperature of approx. 50°C, for the oxidation air, the compression temperature of which originally is at some 120°C. As a result of the excitation of the injection cooler the maximum admissible inhouse noise level of 85 dB(A) is markedly exceeded.
- The air distribution system in the spray tower which is equally vibrating manifests a substantial amount of wear due to the permanent movements and the considerably "abrasive" slurry.

In order to solve these problems fixtures were installed at short distances and the cooler (especially the one of spray tower 1) modified externally (i.e. shortened, special design of the water evacuation system).

It is true that these measures eliminated the vibrations but the sound radiation of the cooler had been improved only slightly. This problem was overcome by an absorption silencer that shifted the vertical air column out of the resonance range.

For the attachments of the air distribution systems within the spray towers a variety of solutions had been tried:

- Rigid connections by means of attachments of glass fiber reinforced material.
- Flexible connections by means of corrosion resistant rubber rings.
- Rigid connections by means of a combination of glass fiber reinforced bearings and attachment brackets of austenitic material.

We did not achieve a sufficient amount of continuous running hours using the first two of the variants.

Up to now the last variant has proven to be rather effective. However, it is to be underlined that the air pipes of glass fiber reinforced material themselves manifest

signs of material fatigue after approx. 15,000 running hours due to the permanent vibrations.

Hence, the conclusion to be drawn from the remarks made up to now is, that a lasting solution, i.e. 8 to 10 years, can be a distribution system of austenitic material (1.4539 or even better 1.4529).

Sound insulation

As the local hospital is only 420 m from the power plant particular attention had to be paid to sound reduction. Guarantee values of 50 dB(A) in 1 m from the contours of the building are required.

Considering the fact that during a normal conversation sound power levels of up to 60 dB(A) may be registered this demand illustrates the high requirements to the different sound insulating components and their detailed design in view of sound reduction.

Some detailed calculations and check measurements, e.g. sound damping over the complete stack height, were necessary in order to be able to install the proper and exhaustive sound reduction systems without incurring expensive modifications afterwards.

FGD operation without oxidation air

Due to a variety of experiences from other plants the taking out of service of the oxidation air seemed possible considering the flue gas and the ash composition. The following are the important parameters that had to be considered in this context:

- Oxygen content in the flue gas
- pH-value: It determines the ratio of sulphite and bi-sulphite. As only dissolved bi-sulphites can form oxides they finally have a decisive influence on the oxidation rate.
- Content of solids in gypsum slurry: The existence of superficially active fine particles and the concentration of dissolved and catalytically effective components like manganese or copper ions. The results can already be found in the specialized literature.

- Spray tower sump level and number and/or position of the spray levels in operation (retention time).
- Droplet size distribution: specific exchange surface.
- L/G = liquid/gas ratio.
- Temperature conditions: Influence on thermodynamic equilibrums, diffusion coefficients, kinetic processes, etc.
- Fluid dynamics: They determine remixing effects and residence time behaviour, above all the
- oxygen mass transfer from the gas into the liquid phase. This transfer is the slowest process phase and hence it determines the overall process velocity.

For the degree of oxidation the transport of oxygen is the most decisive factor.

As these are considerations mainly derived from theory but have not been studied completely on large scale a field test of 215 operating hours was conducted with spray tower 1 from Nov. 22 to Dec. 2, 1988.

For final and definitive statements the phases of the steady operation certainly were too short yet. Nevertheless, the preliminary results of this first large scale experiment at Voitsberg are rather encouraging in view of maintaining the proper operation of the spray tower without making use of the oxidation air fan.

However, the difficulties in measuring the pH-value turned out to be an important obstacle to the fast and exact dosing of limestone.

The pH-measurement determines only the liquid phase equilibrums. It is a complex system of liquid reactions, e.g. the absorption of HSO_3 , gas/liquid mass transfer, e.g. the absorption of SO_2 or O_2 , and interphase reactions, e.g. the dissolution of CaCO_3 and/or the precipitation of gypsum.

In case of instationary operating conditions like varying contents of SO_2 in the raw gas, as it is typical for lignite the common feed forward control of the limestone supply has to be improved by implementing sophisticated data collection and computer calculations to control the limestone feed accordingly.

Hence, for the optimum operation of the spray tower information on the exact content of residual carbonates and their reactivities are of decisive importance. The direct measurement of the content of carbonates and their reactivities permit the spray tower control by means of the limestone side. The quality of the produced gypsum as well as the SO₂ removal efficiency of the spray tower can be monitored and improved. So an appropriate measuring system had been designed and developed by Waagner-Biro Energy & Environment and shortly will be applied in Voitsberg.

The thickening function

Already at the first trial operation it clearly could be seen that brown sludge is carried over into the overflow tank.

During a plant inspection after some 4,000 operating hours it turned out that the overflow tank was partly filled with slurry.

So a dissolution and dosing unit for an organic flocculent (i.e. a liquid polymer substance) had to be retrofitted. The amount of dosing is appr. 2 to 4 g/ton of gypsum.

However, attention is to be paid to having the temperature of the mixing water of not more than 20°C as already at 30°C the undesired flocculation would result in the mixing with the concentrate.

Apart from finally having a clear overflow liquid the rake performance of the rake within the thickener also could be homogenized. This means that the concentration of the input liquid is more homogenous and the solid particles are moved better and more easily by the rake vanes as a certain amount of crystal glideability is given by the addition of the flocculent.

As during heating, resulting from the calcination of the gypsum, the liquid polymer is split up into CO₂ and H₂O there is no negative influence on the quality of the gypsum.

Special lining with Arbosol

In order to protect the spray levels of the two spray towers a new lining material had been used instead of the conventional rubber lining.

Arbosol is a PVC plasitsol that forms a homogenous and chemically highly endurable lining that is resistant to abrasion and corrosion.

Depending on the wall thickness of the pipe to be protected layer thicknesses of up to 6 mm may be created by means of a submerging process.

Since 1984 Waagner-Biro has been a licensee of Arbonite Corp., USA. A wide range of application is given above all in FGDs. Especially in case of the spray levels the seamless lining with Arbosol provides high resistance to abrasion compared to a conventional rubber lining. The areas of direct contact with droplets from the upper level have to be covered by wear layers of butyl rubber.

As has been learned by experience the service life of Arbosol is a little bit shorter than the standard rubber lining. Considering the considerably lower application cost there is an advantage in the total operating cost.

Agitators

Each of the two spray towers has been equipped with four horizontal agitators. The parts in contact with the medium were made of austenitic material (1.4539).

During a revision phase of approx. 7,000 operating hours slight erosion marks at the vanes were welded out and ground flush.

After the installation the agitators were running for another approx. 100 hours when strong vibrations occurred which were due to cracks in the agitator vanes close to the shaft.

The reason was that this material has no distinctive creep strength values for the given gypsum slurry data, i.e. pH-values of about 5.2 to 5.6, chloride ions of approx. 5000 mg/m³. This means the creep strength will decrease proportionally to the number of load changes.

The first damages occurred after an approximate 7,000 hours what corresponds to 10 to 100 million load changes. These were manifest as cracks in the weld seam area (transition from the shaft to the vane) along the grain boundaries of the microscopic structures.

As a first measure the thickness of the dampers was changed from 15 to 20 mm what corresponds to a theoretical life of approx. 1 billion load changes and/or a life of more than 6 years.

For small tanks vertical agitators were used the dampers of which are rubber lined. There also was one unexpected incident with one of these agitators.

In case of the limestone tank agitator used for homogenizing the limestone slurry with water (a content of solid particles of 20 %) there were signs of considerable wear at the soft rubber lining after approx. 4,000 operating hours despite the use of the double lining design, i.e. soft rubber lining applied to a base of hard rubber.

As a measure of improvement a highly wear resistant vane of cast fine steel was used as in case of high concentrations of solid particles the soft rubber lining literally is ground off. The metal propeller now used will permit a continuous running time of more than 25,000 operating hours.

Full metal pumps

Centrifugal pumps were used as recycle pumps as well as much smaller slurry and water recycle pumps.

The recycle pump is connected directly to the drive motor by means of an elastic coupling and mounted upon a common base frame (see fig. 10).

The parts of the centrifugal pump that are in contact with the medium are of material G-X3CrNiMoCu N 25 7 (1.4517 acc. to SEW-410). This material is characterized by its high resistance to corrosion and abrasion. Continuous running times of 30,000 operating hours are the best evidence of these qualities.

The impeller of the MFA centrifugal pump which is not completely covered and the weldability of the material permit a repair of wear spots and hence a further increase in the continuous running time. The robust design of the pump, i.e. heavily dimensioned and oil lubricated bearings with a shaft of stainless material, guarantee high availability and efficiency.

The installation of a single mechanical seal with a connection to the flushing water has proven to be completely effective and has been running for more than 20,000 hours up to now.

-

The full metal pump in FGDs has taken the lead in the European wet-type FGD technology.

Raw and clean gas ducts

For the flue gas ducts leaving the boiler steel structure 617 tons of structural steelwork had to be used. The design values were a temperature of 100 to 160°C and a design pressure of ± 50 mbar. The material used was RSt 37-2. In order to have an architecturally impressing design especially the clean gas duct was executed as a statically and structurally demanding component compared to the usual design of duct systems. In order to avoid thermal stresses due to the changes in the temperature a certain kind of static bearing had been chosen. Two bearing support points in the stack and one truss-type pendulum support close to the building of the FGD assured the transfer of the vertical forces into the ground. The branching of the big duct before the stack and the installation of a Y-piece required the welding in of torsional bracings in the flue gas flow.

Special dampers

For most of the FGD- and DeNOx-refits louvre and guillotine dampers were used. Later more and more large damper toggle arm dampers were preferred to shutoff and diverter dampers.

A typical example of application are the toggle-arm dampers which were developed for Voitsberg (see fig. 11).

For the operation of the flue gas by-pass three double louvre dampers of common design were necessary for each FGD-train.

Two toggle-arm dampers with an actuating toggle-arm system have been adopted instead of the double louvre or the guillotine damper.

The operating experience has proven that the large damper damper with toggle-arm systems are suited for the tightly sealing mansafe system. They meet all the requirements of the FGD, i.e.

- sealing absolutely tightly,
- minimum loss of pressure,
- corrosion resistance,
- fast switching time from FGD to by-pass operation,

- high availability, and
- minimum maintenance requirements.

Due to the toggle-arm principle used in the diverter strong forces are exerted just when the diverter is closing and in the middle of the damper where these forces are particularly necessary. The toggle-arm principle leads to independence from pressure or the direction of the gas flow.

In the beginning there were problems with the Viton sealings at the diverter damper. Those sealings had not been designed for loads sufficient for the contact pressure and the burst load. Then we have made use of Viton sealings with a wire mesh on the inside. These sealings have proven to be the best and up to now they did not have to be exchanged.

There also were some difficulties with the clean gas damper in the sealing air area where moisture may penetrate into the sealing air duct. Therefore sealing air valves have been developed that are arranged on the perimeter of the sealing seat and that are opened only when required by a separate actuator. The sealing air valves are designed so that the sealing air can be blown directly into the sealing air duct from the sealing air ring on the outside between the sealing elements of a double gasket. The outer ring duct can be opened when the sealing air valves are closed and can be inspected during operation.

The outer ring duct also has another advantage, i.e. that it is not a part of the frame and therefore no corrosion can occur when the sealing air is not blown in. The sealing air valves are sealed against humidity and dust.

Experience of Operation with the Gas-Gas Heater (GGH)

The fluegas from the boiler Voitsberg 3 is divided into two streams (2 x 50%). One stream passes the regenerative GGH with vertical shaft, cold side below.

There are two layers of heating elements – one double enameled sheet of 650 mm height and one plastic layer (Noryl) of 150 mm height.

The normal rotor speed is 1.5 rpm, during the cleaning the speed is reduced to 0.75 rpm.

The inlet temperature (untreated gas) is about 150°, the outlet temperature (untreated gas) about 100°C. The cold treated gas enters the GGH with about 63°C and leaves it with about 105°C.

The max. guaranteed pressure drop (sum of untreated and treated gas, untreated gas quantity is 625,000 st.m³/hr, untreated gas temperature 140°C) is 11.38 mbar.

If the pressure drop on treated gas side exceeds 10.5 mbar a high pressure washing program (40 bar cold side and 80 bar hot side) will be started by hand. For the first 3000 operation hours every 500 hours such a cleaning cycle of 8 hours duration is intended.

For the next period of operation the GGH has to be cleaned every 400 hours.

Besides this an everyday cleaning is intended by compressed air. The hot side elements (enamel) are blown with an air pressure of 5 bar and the cold side elements (plastic) 2 bar air pressure.

Duration of the blowing cycle 4.5 hours.

In the yearly revision time the scaling on the heating modules is cleaned by setting under freshwater till it is saturated, then it could be easily removed by flushing with low pressure water.

In Fig. 12 and 13 the chemical analysis from the scaling dated March 9, 1991 is given.

The low pH-value (sour character of the eluate), the high salt loads, especially of aluminium-, iron-, calcium-, and magnesium-sulphate and chlorides resp., have to be pointed out, e.g. $\text{Al}_2(\text{SO}_4)_3$.

The high Al-value is said to result mainly from the partly not intact enamel layer of the GGH, because between 13 and 28 % by wt. feldspar is used for the processing of enamel, that consists of complex aluminiumsilicate, composed of $\text{Me}(\text{AlSi}_3\text{O}_8)$;

Me = metal

The high iron values point to rust formations on the material below.

Due to the high salt load and the sour character of possible flushing waters the waste disposal without conditioning (at least dilution and neutralisation, resp.) is not possible.

The backwash in the spray tower during operation is basically possible as an alternative (high dilution and at the same time neutralisation by the absorber).

4. NO_x-REDUCTION (Fig. 14)

SCR-Process

Selective catalytic reduction (SCR) is a well-known technique especially when firing hard coal. For lack of sufficient experience regarding SCR techniques at lignite fired power plants, ÖDK tested this process at two pilot plants from 1985 to 1988.

The aim was to test catalyst behaviour in high dust arrangement.

The investigations showed that the SCR technology can also be used with high ash and high sulfur lignites. The large scale DeNOx-plant Voitsberg 3 has been commissioned in November 1990. It will be one of the first in Europe installed after a lignite fired boiler.

Primary measures

Parallel to the SCR tests the installation of primary measures (excess air, flue gas recirculation, overfire air) was investigated.

With investment costs of approx. 25 million AS (2 million US-\$) the NOx emission at design load could be reduced from approx. 500 to 550 to 300 to 350 (mg/st.m³, dry, 6 % O₂, as NO₂). As side effect the costs for the SCR plant could be decreased due to a reduction of catalysts.

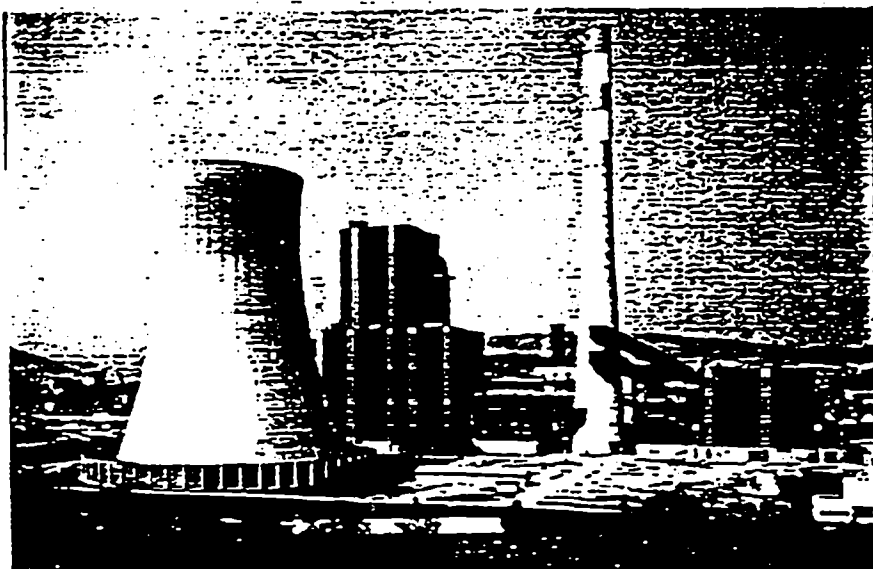
SNCR-Process

Seeing that the retrofitting of old plants with SCR is too expensive the SNCR (selective non catalytic reduction) process has been investigated very intensively since 1986.

Pure ammonia (NH₃), urea ((NH₂)₂CO) and ammonium water (NH₄OH) were tested. Comparable results (50–60% NOx-reduction at a stoichiometric ratio of 1.5 – 2.0) could be achieved with all three additives.

5. CONCLUSION

The FGD has been in operation for approx. 20,000 hours and has fulfilled all expectations regarding SO₂ reduction and reliability. Typical operating data are shown in Fig. 6. Power plant availability was never influenced by the FGD.



el output at MCR
 steam output (MCR)
 operating pressure
 steam/reheat temp.
 flue gas quantity

330 MW
 980 t/h
 184 bar
 535/535° C
 $1.25 \cdot 10^6 \text{ Nm}^3/\text{h}$

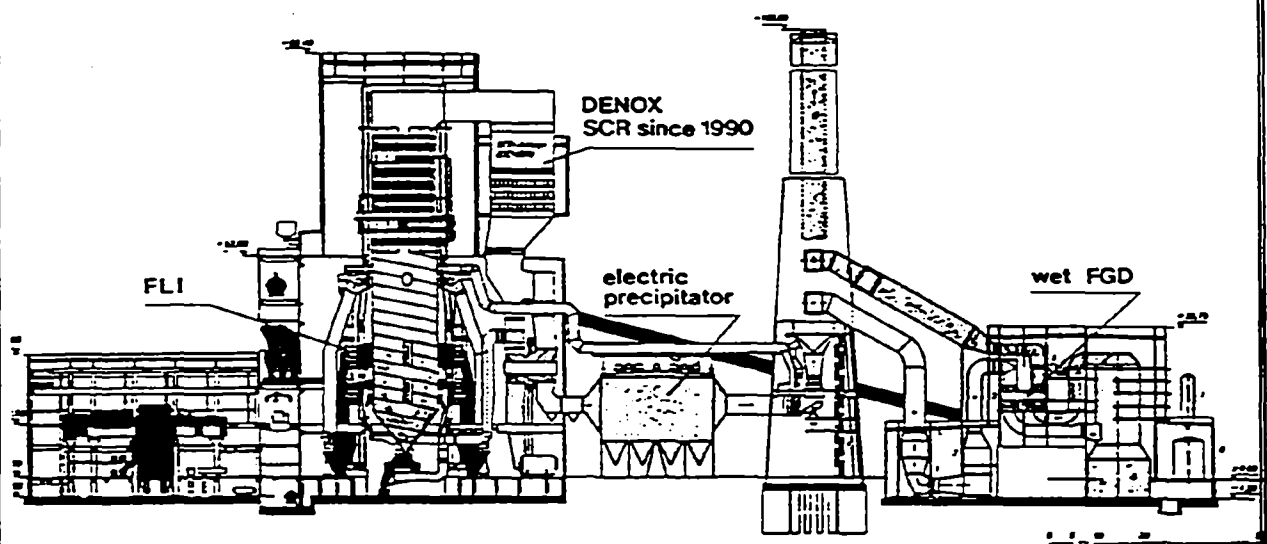
lower calorific value
 carbon content
 moisture
 ash
 sulphur content

9.2 - 11 MJ/kg
 23 - 40 %
 32 - 38 %
 15 - 30 %
 0.5 - 1.5 %

ÖDK
 1991

Fig. 1
 Thermal Power Plant Voitsberg 3

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 Energy & Environment GmbH



1st Step

Furnace Limestone Injection
Commissioned 1983
SO₂ Reduction >50%

3rd Step

SCR
Commissioned 1990
NO_x Reduction >80%

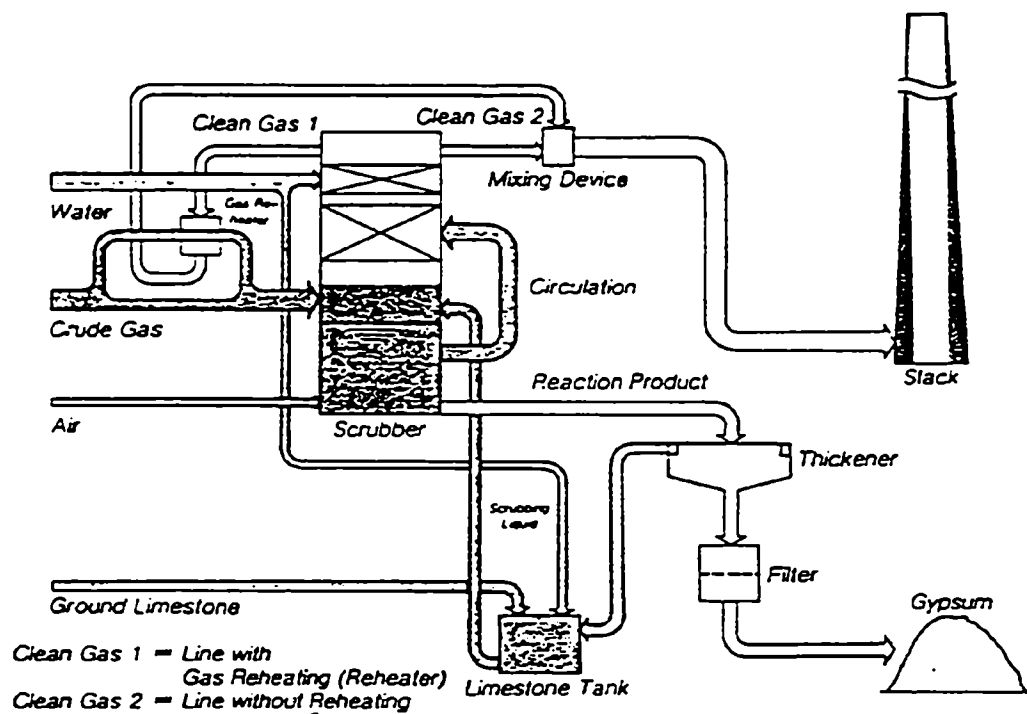
2nd Step

Wet FGD
Commissioned 1986
SO₂ Reduction >90%

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1991

Fig. 2
Voitsberg 3 FGD

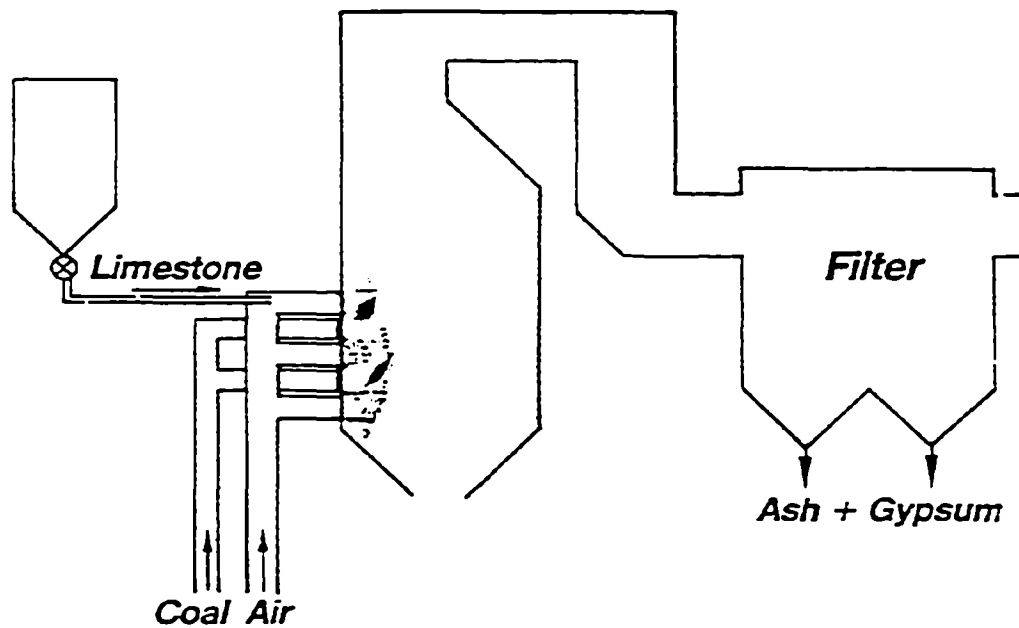
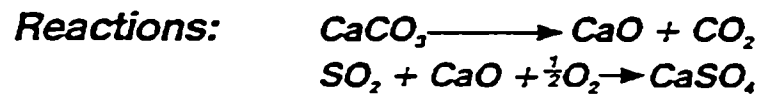
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Fig. 3
FGD Process Scheme

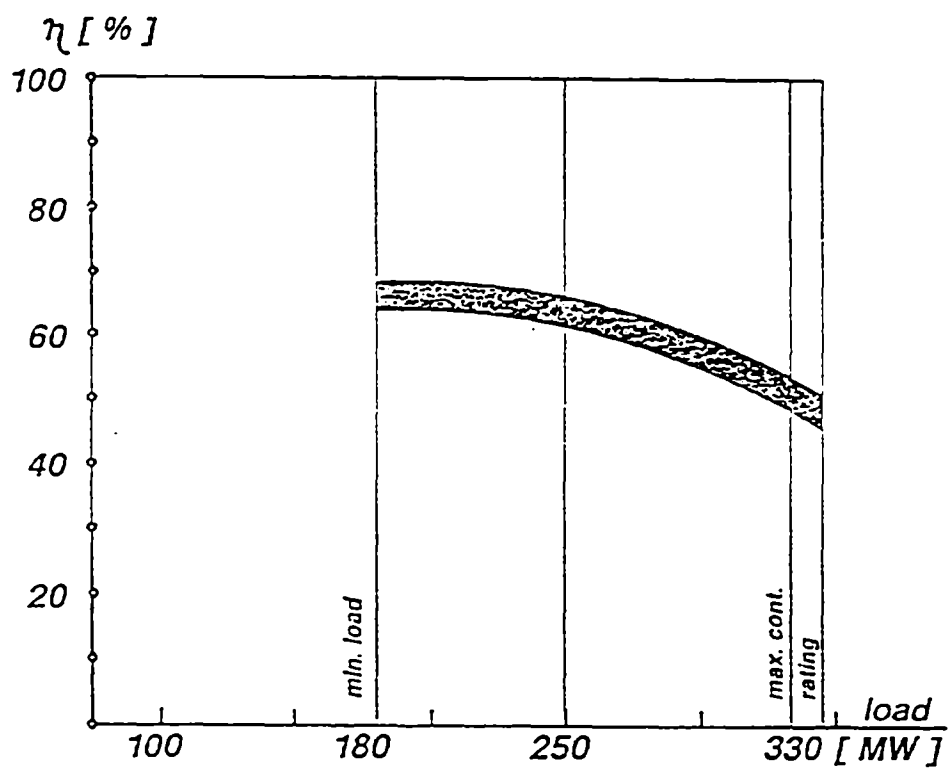
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Fig. 4
Furnace Limestone Injection (FLI)

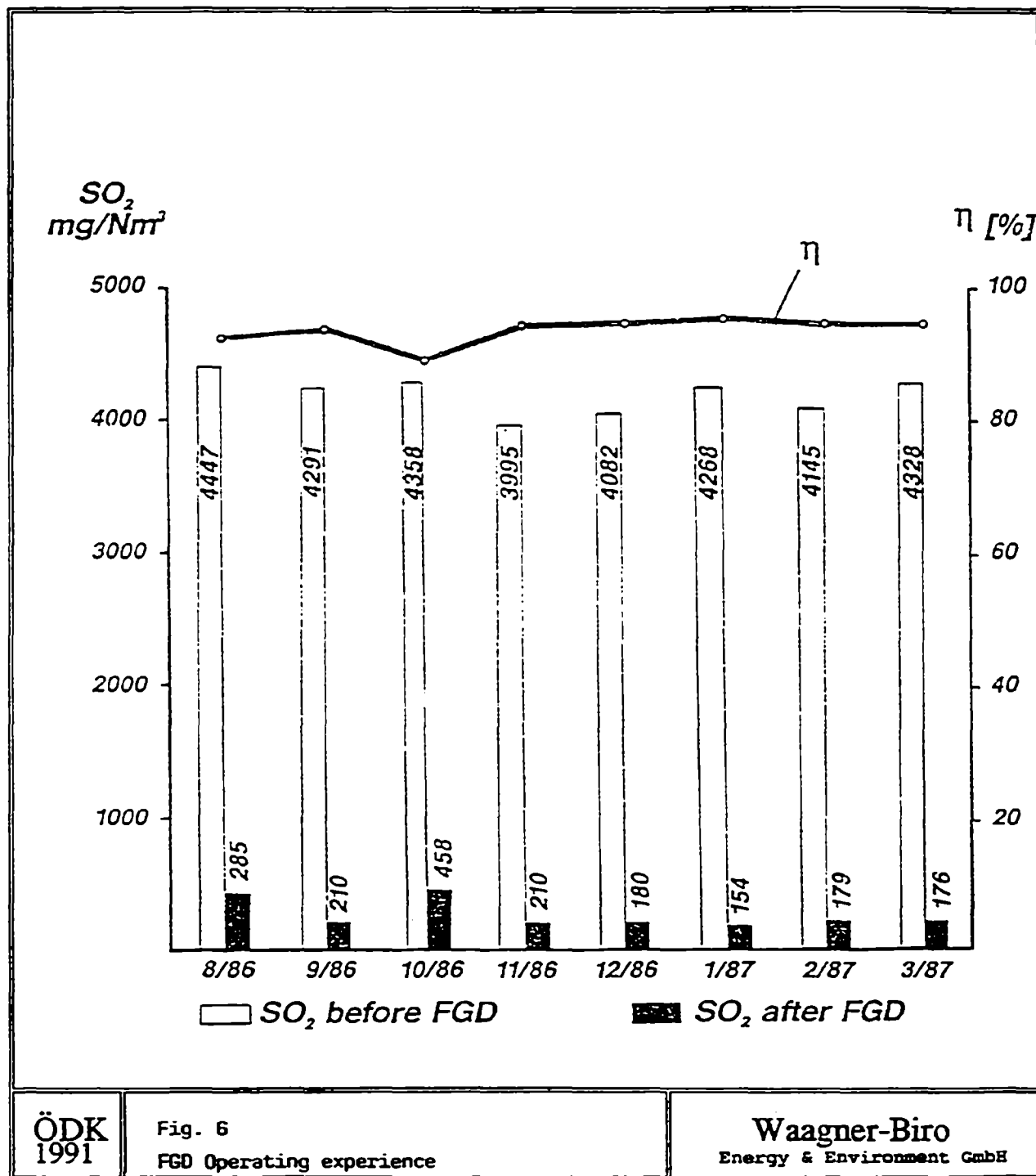
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Fig. 5
SO₂-Reduction by FLI

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Fig. 6
FGD Operating experience

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Fig. 7a

FGD-Arrangement (Train 1)

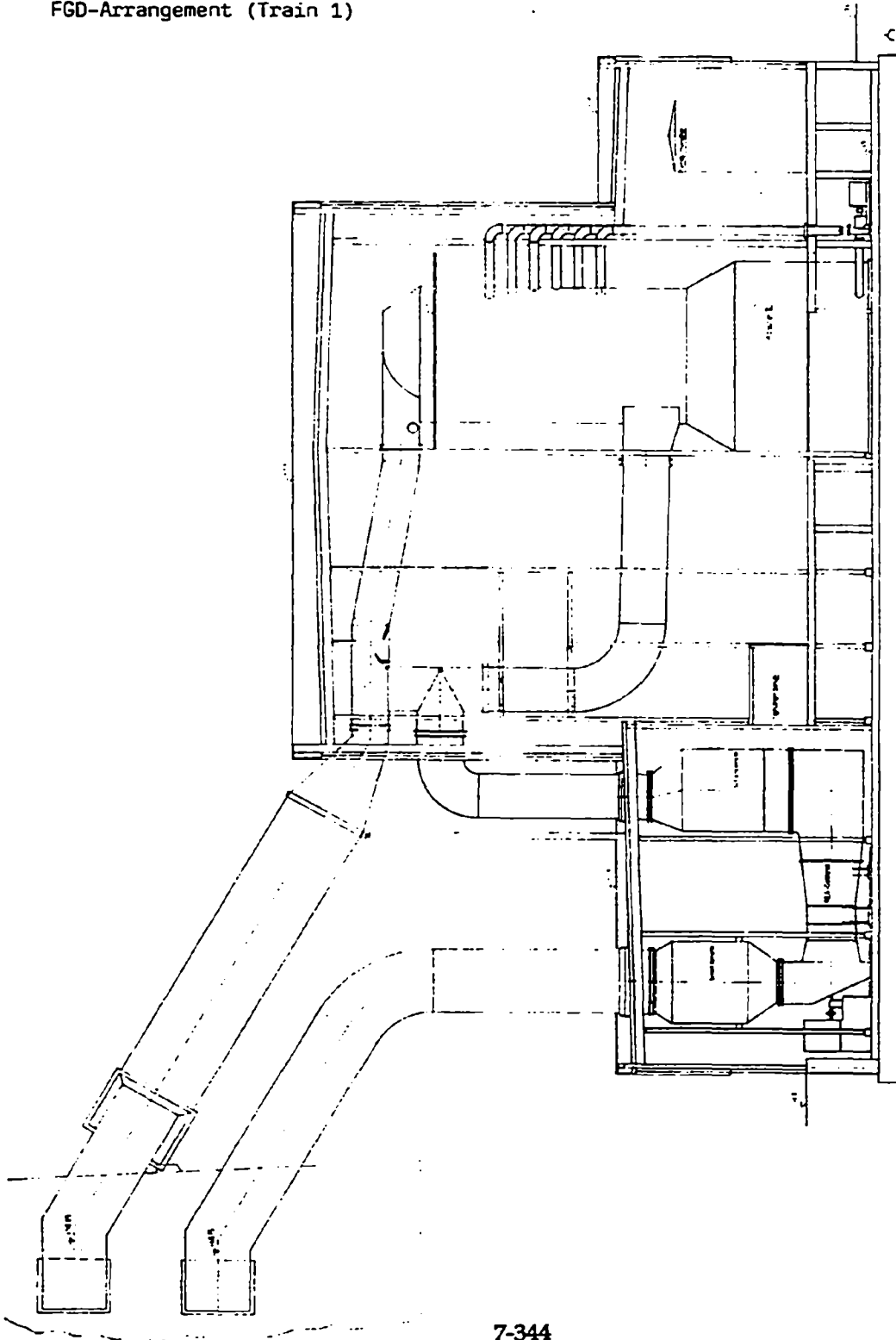
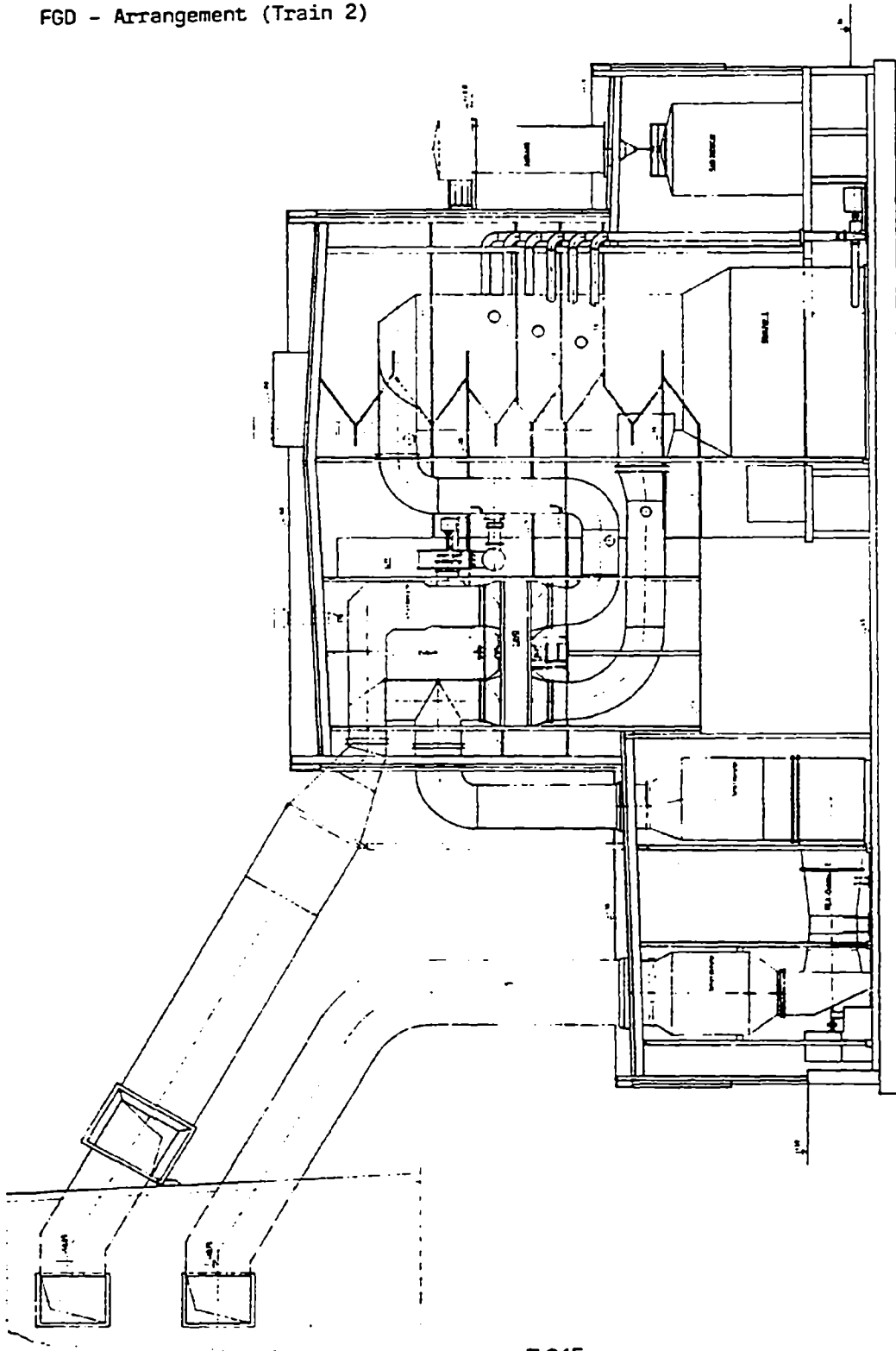


Fig. 7b
FGD - Arrangement (Train 2)

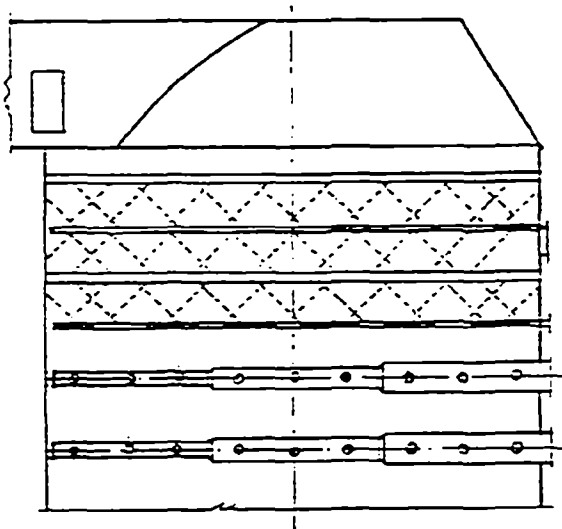


$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	97,4 weight %
$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$	0,32 —"—
CaCO_3	0,64 —"—
MgCO_3	0,21 —"—
Fe_2O_3	0,20 —"—
CL^-	0,02 —"—
Acid insolubles	1,21 —"—
<i>weight percentages related to dry substances</i>	



enlargement 300 fold

flue gas
outlet



m.e. 2nd stage

spray bank

m.e. 1st stage

spray bank

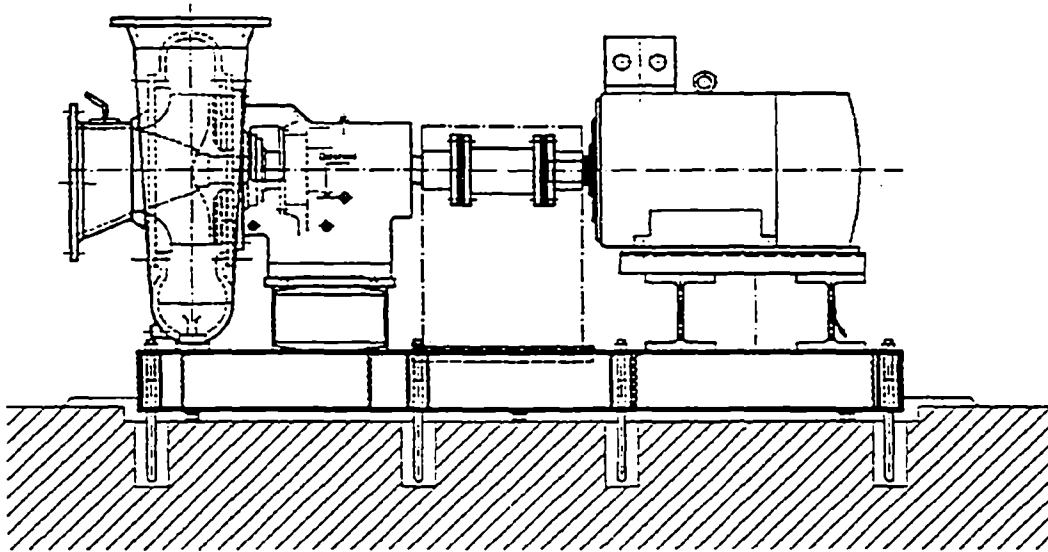
absorption spray
levels

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1991

Fig. 9
M. E. - Arrangement

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Fig. 10
Recycle Pump



Type: KS 500-750

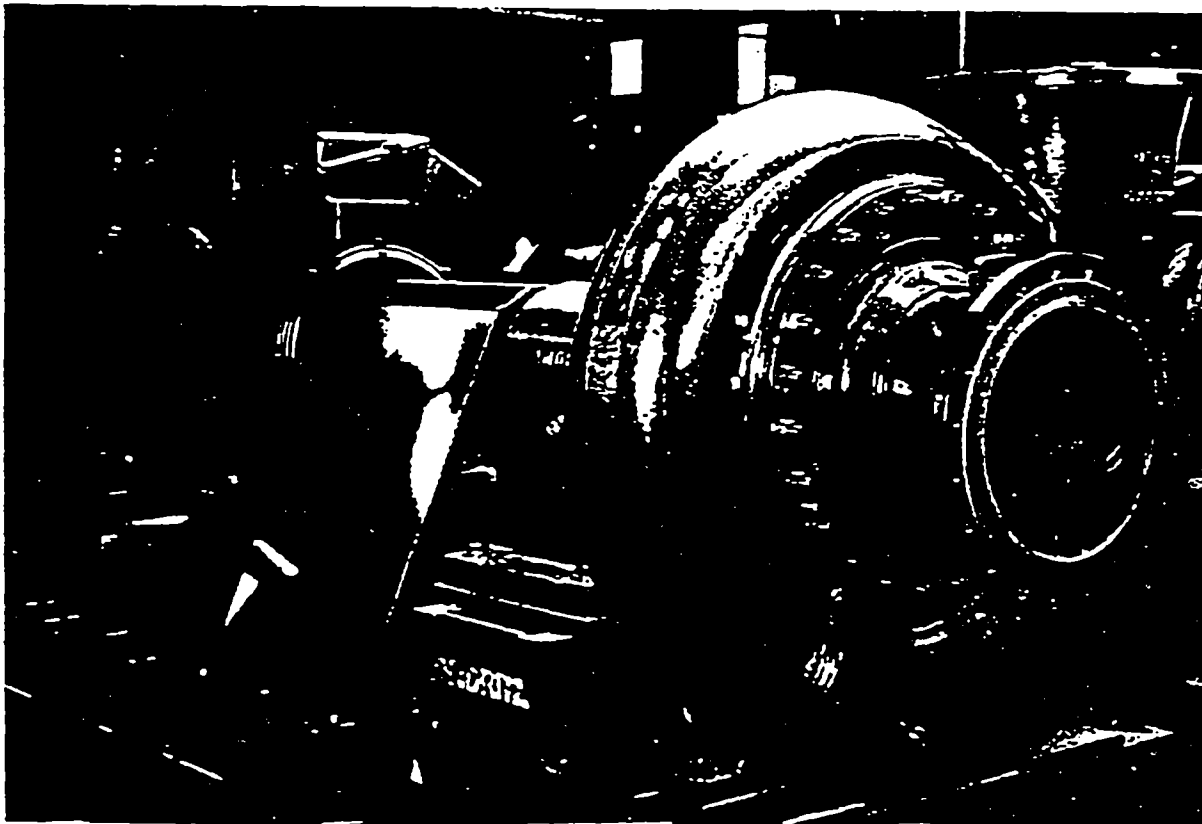


Fig. 11
Flue Gas Damper

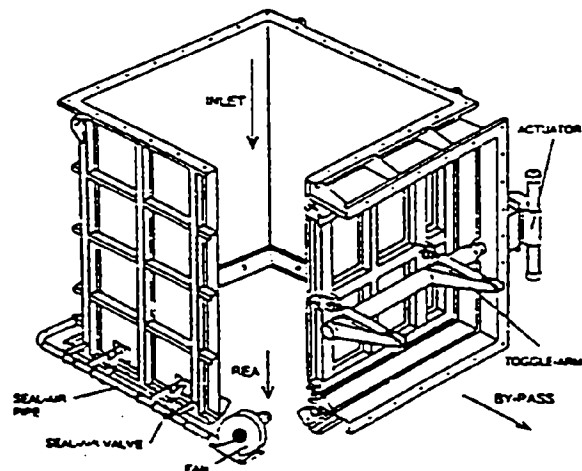
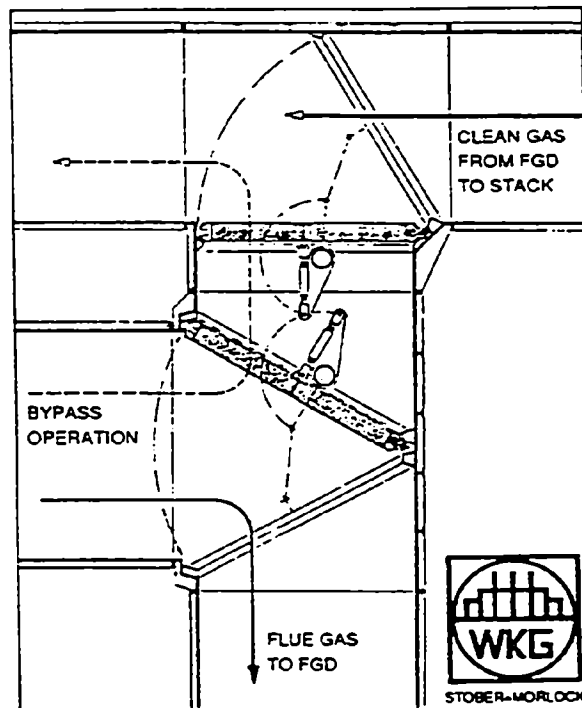
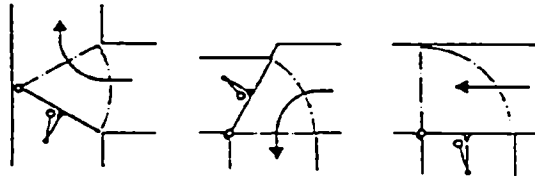


Fig. 12 GGH-Scaling

Data in wt.-% referred to the immediate sample:

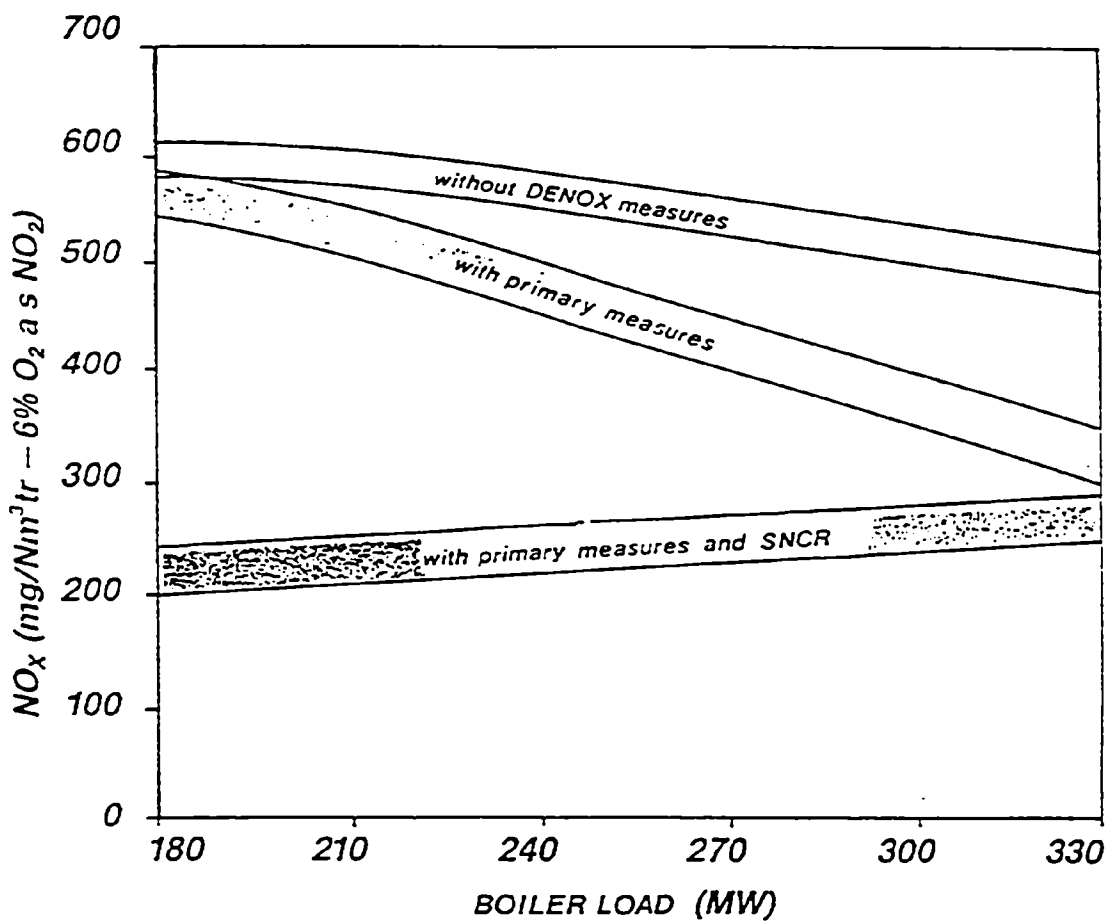
	GGH-plastic elements	GGH-beam
Annealing loss at 800°C	18.9	27.8
	(incl.) 11.8% SO ₃	(incl.) 15.6%SO ₃
Fe ₂ O ₃	7.56	6.23
Al ₂ O ₃	12.8	9.2
MgO	1.76	1.54
CaO	2.36	2.00
SiO ₂	32.7	23.8
TiO ₂	0.75	0.62
K ₂ O	1.67	1.07
Na ₂ O	0.34	0.26
SO ₃	19.4	26.1
	98.2	98.6
	=====	=====

Fig. 13 GGH–Scaling Elution Test

In order to check up all possibilities of cleaning the GGH from above mentioned scales a sample according to DEV S 4 was eluted and investigated:

Results:

pH-value	(–log H–)	1.3
conductivity	(μ S/cm)	23700
Cl [–]	(mg/l)	90
SO ₄ ^{2–}	"	> 39000
Al	"	4253
Fe	"	2228
Ca	"	825
Mg	"	647
K	"	401
Ti	"	136
Na	"	82
Zn	"	51
As	"	22
Mn	"	18
Cr	"	10
V	"	9
Cu	"	9
Ni	"	7
Pb	"	0.2
Cd	"	0.1



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1991

Fig. 14
NOx emissions at Voitsberg 3

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