



# Research and Development

PROCEEDINGS:

1991 SO<sub>2</sub> CONTROL SYMPOSIUM

Volume 5. Session 8

## Prepared for

Office of Air Quality Planning and Standards

## Prepared by

Air and Energy Engineering Research  
Laboratory  
Research Triangle Park NC 27711

TECHNICAL REPORT DATA <i>(Please read instructions on the reverse before complete)</i>		
1. REPORT NO. EPA-600/R-93-064e	2.	3. PB93-196137
4. TITLE AND SUBTITLE Proceedings: 1991 SO <sub>2</sub> Control Symposium, Volume 5. Session 8		5. REPORT DATE April 1993
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Miscellaneous		8. PERFORMING ORGANIZATION REPORT NO. TR-101054 (1)
9. PERFORMING ORGANIZATION NAME AND ADDRESS  See Block 12		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. NA (Inhouse)
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Proceedings; 1991
		14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES AEERL project officer is Brian K. Gullett, Mail Drop 4, 919/541-1534. Cosponsored by EPRI and DOE. Vol. 1 is Opening Session and Sessions 1-3, Vol. 2 is sessions 4 and 5A, Vol. 3 is Sessions 5B and 6, and Vol. 4 is Session 7.		
16. ABSTRACT The proceedings document the 1991 SO <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>x</sub> /NO <sub>x</sub> ) processes.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Sulfur Dioxide Nitrogen Oxides Flue Gases Desulfurization Coal	Pollution Control Stationary Sources	13B 07B  21B 07A, 07D 21D
18. DISTRIBUTION STATEMENT  Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 314
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

## **ORDERING INFORMATION**

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (510) 934-4212. There is no charge for reports requested by EPRI member utilities and affiliates.\*

---

(\*) Copies of this report are also available to the public, prepaid, through the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

Copyright © 1992, EPRI TR-101054, "Proceedings: 1991 SO<sub>2</sub> Control Symposium, Volumes 1, 2, and 3." Since this work was, in part, funded by the U. S. Government, the Government is vested with a royalty-free, non-exclusive, and irrevocable license to publish, translate, reproduce, and deliver that information and to authorize others to do so.

Electric Power Research Institute and EPRI are registered service marks of Electric Power Research Institute, Inc.

## **NOTICE**

This report was prepared by the Electric Power Research Institute, Inc. (EPRI). Neither EPRI, members of EPRI, nor any person acting on their behalf: (a) makes any warranty, express or implied, with respect to the use of any information, apparatus, method, or process disclosed in this report or that such use may not infringe privately owned rights; or (b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

EPA-600/R-93-064e  
April 1993

## Proceedings: 1991 SO<sub>2</sub> Control Symposium

Volume 5. Session 8

### For Sponsors:

#### **Electric Power Research Institute**

B. Toole O'Neil  
3412 Hillview Avenue  
Palo Alto, CA 94304

#### **U.S. Department of Energy**

Charles J. Drummond  
Pittsburgh Energy  
Technology Center  
P.O. Box 10940  
Pittsburgh, PA 15236

#### **U.S. Environmental Protection Agency**

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

## ABSTRACT

These are the Proceedings of the 1991 SO<sub>2</sub> 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 (SO<sub>2</sub>) control technologies, emerging processes, and strategies for complying with the Clean Air Act Amendments of 1990. This is the first SO<sub>2</sub> 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 SO<sub>2</sub> 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 (SO<sub>2</sub>/NO<sub>x</sub>) processes. Since the 1990 SO<sub>2</sub> 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.

## CONTENTS

PREFACE	xi
AGENDA	xii

### VOLUME 1

#### **Opening Session**

EPRI Perspective	OS-1
EPA Perspective	OS-5
DOE Perspective	OS-9

#### **Guest Speakers**

Shelley Fidler - Assistant, Policy Subcommittee on Energy and Power, U.S. Congress	OS-11
Jack S. Siegel - Deputy Assistant Secretary, Office of Coal Technology, U.S. Department of Energy	OS-19
Michael Shapiro - Deputy Assistant Administrator, Office of Air and Radiation, U.S. Environmental Protection Agency	OS-29

<b>Session 1 - Clean Air Act Compliance Issues/Panel</b>	<b>1-1</b>
--	------------

#### **Session 2 - Clean Air Act Compliance Strategies**

Scrubbers: A Popular Phase 1 Compliance Strategy	2-1
Scrub Vs. Trade: Enemies or Allies?	2-21
Evaluating Compliance Options	2-39
Clean Air Technology (CAT) Workstation	2-49
Economic Evaluations of 28 FGD Processes	2-73
Strategies for Meeting Sulfur Abatement Targets in the UK Electricity Supply Industry	2-93

Compliance Strategy for Future Capacity Additions: The Role of Organic Acid Additives	2-107
A Briefing Paper for the Status of the Flue Gas Desulfurization System at Indianapolis Power & Light Company Petersburg Station Units 1 and 2	2-129
Evaluation of SO <sub>2</sub> Control Compliance Strategies at Virginia Power	2-135
<b>Session 3A - Wet FGD Process Improvements</b>	
Overview on the Use of Additives in Wet FGD Systems	3A-1
Results of High SO <sub>2</sub> Removal Efficiency Tests at EPRI's High Sulfur Test Center	3A-25
Results of Formate Ion Additive Tests at EPRI's High Sulfur Test Center	3A-45
FGDPRISM, EPRI's FGD Process Model-Recent Applications	3A-63
Additive-Enhanced Desulfurization for FGD Scrubbers	3A-85
Techniques for Evaluating Alternative Reagent Supplies	3A-105
Factors Involved in the Selection of Limestone Reagents for Use in Wet FGD Systems	3A-119
Magnesium-Enhanced Lime FGD Reaction Tank Design Tests at EPRI's HSTC	3A-145
<b>Session 3B - Furnace Sorbent Injection</b>	
Computer Simulations of Reacting Particle-Laden Jet Mixing Applied to SO <sub>2</sub> Control by Dry Sorbent Injection	3B-1
Studies of the Initial Stage of the High Temperature CaO-SO <sub>2</sub> Reaction	3B-17
Status of the Tangentially Fired LIMB Demonstration Program at Yorktown Unit No. 2: An Update	3B-39
Results from LIMB Extension Testing at the Ohio Edison Edgewater Station	3B-57

VOLUME 2

**Session 4A - Wet FGD Design Improvements**

Reliability Considerations in the Design of Gypsum Producing Flue Gas Desulfurisation Plants in the UK	4A-1
Sparing Analysis for FGD Systems	4A-25
Increasing Draft Capability for Retrofit Flue Gas Desulfurization Systems	4A-41
Development of Advanced Retrofit FGD Designs	4A-61
Acid Rain FGD System Retrofits	4A-79
Guidelines for FGD Materials Selection and Corrosion Protection	4A-99
Economic Comparison of Materials of Construction of Wet FGD Absorbers and Internals	4A-125
The Intelligence & Economics of FRP in F.G.D. Systems	4A-141

**Session 4B - Dry FGD Technologies**

LIFAC Demonstration at Poplar River	4B-1
1.7 MW Pilot Results for the Duct Injection FGD Process Using Hydrated Lime Upstream of an ESP	4B-17
Scaleup Tests and Supporting Research for the Development of Duct Injection Technology	4B-39
A Pilot Demonstration of the Moving Bed Limestone Emission Control (LEC) Process	4B-61
Pilot Plant Support for ADVACATE/MDI Commercialization	4B-79
Suitability of Available Fly Ashes in ADVACATE Sorbents	4B-93
Mechanistic Study of Desulfurization by Absorbent Prepared from Coal Fly Ash	4B-113
Results of Spray Dryer/Pulse-Jet Fabric Filter Pilot Unit Tests at EPRI High Sulfur Test Center	4B-125

Results of Medium- and High-Sulfur Coal Tests on the TVA 10-MW SD/ESP Pilot Plant	4B-151
Evolution of the B&W Durajet™ Atomizer	4B-173
Characterization of the Linear VGA Nozzle for Flue Gas Humidification	4B-189
High SO <sub>2</sub> Removal Dry FGD Systems	4B-205
 <b>Session 5A - Wet Full Scale FGD Operations</b>	
FGD System Retrofit for Dalhousie Station Units 1 & 2	5A-1
Zimmer FGD System: Design, Construction, Start-Up and Operation	5A-17
Results of an Investigation to Improve the Performance and Reliability of HL&P's Limestone Electric Generating Station FGD System	5A-37
Full-Scale Demonstration of EDTA and Sulfur Addition to Control Sulfitic Oxidation	5A-59
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	5A-81
Organic Acid Buffer Testing at Michigan South Central Power Agency's Endicott Station	5A-101
Stack Gas Cleaning Optimization Via German Retrofit Wet FGD Operating Experience	5A-127
Operation of a Compact FGD Plant Using CT-121 Process	5A-143

### VOLUME 3

#### **Session 5B - Combined SO<sub>x</sub>/NO<sub>x</sub> Technologies**

Simultaneous SO <sub>x</sub> /NO <sub>x</sub> Removal Employing Absorbent Prepared from Fly Ash	5B-1
Furnace Slurry Injection for Simultaneous SO <sub>2</sub> /NO <sub>x</sub> Removal	5B-21
Combined SO <sub>2</sub> /NO <sub>x</sub> Abatement by Sodium Bicarbonate Dry Injection	5B-41

SO <sub>2</sub> and NO <sub>x</sub> Control by Combined Dry Injection of Hydrated Lime and Sodium Bicarbonate	5B-67
Engineering Evaluation of Combined NO <sub>x</sub> /SO <sub>2</sub> Controls for Utility Application	5B-79
Advanced Flue Gas Treatment Using Activated Char Process Combined with FBC	5B-101
Combined SO <sub>2</sub> /NO <sub>x</sub> Control using Ferrous•EDTA and a Secondary Additive in a Lime-Based Aqueous Scrubber System	5B-125
Recent Developments in the Parsons FGC Process for Simultaneous Removal of SO <sub>x</sub> and NO <sub>x</sub>	5B-141
 <b>Session 6A - Wet FGD Operating Issues</b>	
Pilot-Scale Evaluation of Sorbent Injection to Remove SO <sub>3</sub> and HCl	6A-1
Control of Acid Mist Emissions from FGD Systems	6A-27
Managing Air Toxics: Status of EPRI PISCES Project	6A-47
Results of Mist Eliminator System Testing in an Air-Water Pilot Facility	6A-73
CEMS Vendor and Utility Survey Databases	6A-95
Determination of Continuous Emissions Monitoring Requirements at Electric Energy, Inc.	6A-117
Improving Performance of Flushless Mechanical Seals in Wet FGD Plants through Field and Laboratory Testing	6A-139
Sulcis FGD Demonstration Plant Limestone-Gypsum Process: Performance, Materials, Waste Water Treatment	6A-163
 <b>Session 6B - Clean Coal Demonstrations</b>	
Recovery Scrubber - Cement Application Operating Results	6B-1
The NOXSO Clean Coal Technology Demonstration Project	6B-17

Economic Comparison of Coolside Sorbent Injection and Wet Limestone FGD Processes	6B-33
Ohio Edison Clean Coal Projects Circa: 1991	6B-55
Sanitech's 2.5-MWe Magnesia Dry-Scrubbing Demonstration Project	6B-79
Application of DOW Chemical's Regenerable Flue Gas Desulfurization Technology to Coal-Fired Power Plants	6B-93
Pilot Testing of the Cansolv® System FGD Process	6B-105
Dry Desulphurization Technologies Involving Humidification for Enhanced SO <sub>2</sub> Removal	6B-119

#### VOLUME 4

#### **Session 7 - Poster Papers**

Summary of Guidelines for the Use of FRP in Utility FGD Systems	7-1
Development and Evaluation of High-Surface-Area Hydrated Lime for SO <sub>2</sub> Control	7-13
Effect of Spray Nozzle Design and Measurement Techniques on Reported Drop Size Data	7-29
High SO <sub>2</sub> Removals with a New Duct Injection Process	7-51
Combined SO <sub>x</sub> /NO <sub>x</sub> Control Via Soxal™, A Regenerative Sodium Based Scrubbing System	7-61
The Healy Clean Coal Project Air Quality Control System	7-77
Lime/Lime Stone Scrubbing Producing Usable By-Products	7-93
Modeling of Furnace Sorbent Injection Processes	7-105
Dry FGD Process Using Calcium Sorbents	7-127
Clean Coal Technology Optimization Model	7-145
SNRB Catalytic Baghouse Process Development and Demonstration	7-157
Reaction of Moist Calcium Silicate Reagents with Sulfur Dioxide in Humidified Flue Gas	7-181

Commercial Application of Dry FGD using High Surface Area Hydrated Lime	7-199
Initial Operating Experience of the SNOX Process	7-221
Progress Report of the NIPSCO - Pure Air - DOE Clean Coal II Project	7-241
Development of a Post Combustion Dry SO <sub>2</sub> Control Reactor for Small Scale Combustion Systems	7-253
Scrubber Reagent Additives for Oxidation Inhibited Scrubbing	7-269
Recovery of Sulfur from Calcium Sulfitite and Sulfate Scrubber Sludges	7-277
Magnesite and Dolomite FGD Technologies	7-285
SO <sub>2</sub> and Particulate Emissions Reduction in a Pulverized Coal Utility Boiler through Natural Gas Cofiring	7-293
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	7-321

## VOLUME 5

### Session 8A - Commercial FGD Designs

Mitsui-BF Dry Desulfurization and Denitrification Process Using Activated Coke	8A-1
High Efficiency, Dry Flue Gas SO <sub>x</sub> , and Combined SO <sub>x</sub> /NO <sub>x</sub> Removal Experience with Lurgi Circulating Fluid Bed Dry Scrubber - A New, Economical Retrofit Option for U.S. Utilities for Acid Rain Remediation	8A-21
Incorporating Full-Scale Experience into Advanced Limestone Wet FGD Designs	8A-43
Design and Operation of Single Train Spray Tower FGD Systems	8A-69
Selecting the FGD Process and Six Years of Operating Experience in Unit 5 of the Altbach-Deizisau Neckarwerke Power Station	8A-93
Development and Operating Experience of FGD-Technique at the Vœlkingen Power Station	8A-121
Advantages of the CT-121 Process as a Throwaway FGD System	8A-135

**Session 8B - By-Product Utilization**

German Experience of FGD By-Product Disposal and Utilization	8B-1
The Elimination of Pollutants from FGD Wastewaters	8B-25
The Influence of FGD Variables on FGD Performance and By-Product Gypsum Properties	8B-47
Quality of FGD Gypsum	8B-69
Chemical Analysis and Flowability of By-Product Gypsums	8B-91
Evaluation of Disposal Methods for Oxidized FGD Sludge	8B-113
Commercial Aggregate Production from FGD Waste	8B-127

## PREFACE

The 1991 SO<sub>2</sub> 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 (SO<sub>2</sub>) 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 <sub>x</sub> /NO <sub>x</sub> Technologies
6A	Wet FGD Operating Issues
6B	Clean Coal Demonstrations/Emerging Technologies
7	Poster Session - papers on all aspects of SO <sub>2</sub> 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 SO<sub>2</sub> 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 Engineerir Co.
- 2-8            IPL Petersburg 1 & 2 CAAA Retrofit FGDs, C.P. Wedig, Stone & Webster Engineering Corp.
- 2-9            Evaluation of SO<sub>2</sub> 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 SO<sub>2</sub> 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           FGDPRIISM, 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 SO<sub>2</sub> Control by Dry Sorbent Injection, P.J. Smith, The University of Utah
- 3B-2 Studies of the Initial Stage of the High Temperature CaO-SO<sub>2</sub> 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 Sparing 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 SO<sub>2</sub> 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<sub>x</sub>/NO<sub>x</sub> Technologies**

**Session Chair:** Mildred E. Perry - DOE

- 5B-1            Simultaneous SO<sub>x</sub>/NO<sub>x</sub> Removal Employing Absorbent Prepared from Fly Ash, H. Tsuchiai, The Hokkaido Electric Power Co.
- 5B-2            Furnace Slurry Injection for Simultaneous SO<sub>2</sub>/NO<sub>x</sub> Removal, B.K. Gullett, U.S. EPA
- 5B-3            Combined SO<sub>2</sub>/NO<sub>x</sub> Abatement by Sodium Bicarbonate Dry Injection, J. Verlaeten, Solvay Technologies, Inc. (124)
- 5B-4            SO<sub>2</sub> and NO<sub>x</sub> Control by Combined Dry Injection of Hydrated Lime and Sodium Bicarbonate, D. Helfritsch, R-C Environmental Services & Technologies
- 5B-5            Engineering Evaluation of Combined NO<sub>x</sub>/SO<sub>2</sub> 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            SO<sub>2</sub>/NO<sub>x</sub> 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<sub>x</sub> and NO<sub>x</sub>, 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 SO<sub>3</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub> Removals with a New Duct Injection Process, S.G. Nelson, Jr. Sanitech, Inc.
- 7-5 Combined SO<sub>x</sub>/NO<sub>x</sub> 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.
- 7-14 Initial Operating Experience of the SNOX Process, D.J. Collins, ABB Environmental System
- 7-15 Progress Report of the NIPSCO - Pure Air - DOE Clean Coal II Project, S. Satrom, Pure Air
- 7-16 Development of a Post Combustion Dry SO<sub>2</sub> Control Reactor for Small Scale Combustion Systems, J.C. Balsavich, Tecogen Inc.

- 7-17        Scrubber Reagent Additives for Oxidation Inhibited Scrubbing, J. Thompson, Process Calx, Inc.
- 7-18        Recovery of Sulfur from Calcium Sulfitite and Sulfate Scrubber Sludges, J. Thompson, Process Calx, Inc.
- 7-19        Magnesite & Dolomite FGD Technologies, D. Najmr, Ore Research Institute
- 7-20        SO<sub>x</sub> and Particulate Emissions Reduction in a Pulverized Coal Utility Boiler through natural Gas Cofiring, K.J. Clark Aptech Engineering Services
- 7-21        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, H. Kropfitsch, Voitsberg

**Session 8A - Commercial FGD Designs**

**Session Chair:** Robert E. Moser - EPRI

- 8A-1        Mitsui-BF Dry Desulfurization and Utility Compliance Strategies, K. Tsuji, Mitsui Mining Company Ltd.
- 8A-2        High Efficiency Dry Flue Gas SO<sub>x</sub> and Combined SO<sub>x</sub>/NO<sub>x</sub> Removal Experience with Lurgi Circulating Fluid Bed Dry Scrubber; A New Economical Retrofit Option for Utilities for Acid Rain Remediation, J. G. Toher, Environmental Elements Corp.
- 8A-3        Incorporating Full-Scale Experience into Advanced Limestone Wet FGD Designs, P.C. Rader, ABB Environmental Systems
- 8A-4        Design and Operation of Single Train Spray Tower FGD Systems, A. Saleem, GE Environmental Systems
- 8A-5        Selecting the FGD Process and Six Years of Operating Experience in Unit 5 FGD of the Altbach-Deizisau Neckawerke Power Station, R. Maule, Noell Inc.
- 8A-6        Development and Operating Experience of FGD Technique at the Völkingen Power Station, H. Petzel, SHU-Technik
- 8A-7        Advantages of the CT-121 Process as a Throwaway FGD System, M.J. Krasnopoler, Bechtel Corp.

**Session 8B - By-Product Utilization**

**Session Chair:** Charles E. Schmidt - DOE

- 8B-1 German Experience of FGD By-Product Disposal and Utilization, J. Demnich, Noell Inc.
- 8B-2 The Elimination of Pollutants from FGD Wastewaters, M.K. Mierzejewski, Infilco Degremont Inc.
- 8B-3 The Influence of FGD Variables on FGD Performance and By-Product Gypsum Properties, F. Theodore, Consolidation Coal Co.
- 8B-4 Quality of FGD Gypsum, F.W. van der Bruggen, N.V. Kema
- 8B-5 Chemical Analysis and Flowability of By-Product Gypsums, L. Kilpeck, Centerior
- 8B-6 Evaluation of Disposal Methods Stabilized FGD & Oxidized FGD Sludge & Fly Ash, W. Yu, Conversion Systems, Inc.
- 8B-7 Commercial Aggregate Production from FGD Waste, C.L. Smith, Conversion Systems, Inc.

## Session 8A

### COMMERCIAL FGD DESIGNS

#### MITSUI-BF DRY DESULFURIZATION AND DENITRIFICATION PROCESS USING ACTIVATED COKE

K. Tsuji

Mitsui Mining Company, Limited  
2-1-1 Nihonbashi Muromachi  
Chuo Ward, Tokyo, Japan 103

I. Shiraishi

Mitsui Mining Company, Limited  
1-3 Hibikimachi, Wakamatsu Ward  
Kitakyushu City, Fukuoka, Japan 808

#### ABSTRACT

The problem of acid rain has been a growing concern in recent years. In this paper, Mitsui-BF dry DeSO<sub>x</sub>/DeNO<sub>x</sub> process is introduced as an effective process for reduction of SO<sub>x</sub> and NO<sub>x</sub> from flue gas. This process can achieve 100% removal of SO<sub>x</sub> and over 80% removal of NO<sub>x</sub> by contacting flue gas with activated coke and injecting NH<sub>3</sub> for DeNO<sub>x</sub> at temperature range of about 100-200° C (212-392°F).

The dry desulfurization and denitrification process using activated coke (AC) was originally researched and developed during the sixties by Bergbau Forschung (BF)<sup>1)</sup>, now called Deutsche Montan Technologies. Mitsui Mining Company (MMC) concluded a licensing agreement with BF to investigate, test and adapt the system to the facilities in Japan where the regulations are stricter towards SO<sub>x</sub>/NO<sub>x</sub> pollutants, as well as dust emissions from the utility industry, oil refineries and other industries. There are four commercial plants of this process installed to coal fired boilers and FCC units. These plants were constructed by MMC in Japan and Uhde GmbH in Germany.

MMC also developed a technology to produce activated coke, used in dry DeSO<sub>x</sub>/DeNO<sub>x</sub> process, based on our own metallurgical coke manufacturing technology.

This paper provides the information on the details of MMC's activated coke used in the dry DeSO<sub>x</sub>/DeNO<sub>x</sub> process in the former section and of the dry DeSO<sub>x</sub>/DeNO<sub>x</sub> process using activated coke in the latter section.

## MMC'S ACTIVATED COKE FOR DRY DESOX/DENOX PROCESS

Activated coke (AC) is a formed carbonaceous material designed for dry DESOX/DENOX process of flue gas cleaning. For this purpose, AC is able to remove SO<sub>x</sub> and NO<sub>x</sub>, has high mechanical strength against abrasion and crush during circulation and handling in the process. There is a stable supply of AC and the price is reasonable.

### Research and Development of Activated Coke Production in MMC

Laboratory tests of AC have been conducted since 1980 and the following information has been obtained.<sup>2)</sup>

- Selection of suitable raw materials from bituminous coals and the technology of their pretreatment. ( It was recently found that lignites and petroleum coke are suitable starting materials.)
- Blending ratio of pretreated starting material and binders produce high mechanical strength in activated coke. (Roga index was introduced to represent proper blending ratio.)
- Briquetting process and briquetts' size.
- Heating program and atmosphere for carbonization and activation process ( A high mechanical strength of AC is obtained with a controlled carbonization condition and a proper micro-porous structure of AC is grown with a controlled chemical activation condition.)
- Chemical treatment technologies of AC micro-porous surface have increased the ability to remove SO<sub>x</sub> and NO<sub>x</sub>.

Based on the results of laboratory tests, in 1982 MMC constructed and operated a pilot plant, which had a capacity of 0.5 tons/day AC production.

Table 1 summarizes MMC's activities for AC production and supply in chronologic order since the pilot test. AC produced at this pilot plant was tested on DeSOX/DENOX pilot plant at Tochigi and the demonstration plant at Ohmuta. Each of these extended more than 4,000 hours and 16,000 hours, respectively. This confirms the excellent performance of MMC's AC on the desulfurization and denitrification efficiencies and on the mechanical strength against abrasion during circulation in large scale plants.

In October 1986, a commercial plant with the capacity of 3,000 tons/year AC production began operation at MMC's Kitakyushu Works. Since 1987, AC has been supplied to the DeSOx/DeNox unit at Idemitsu Aichi Oil Refinery. MMC's AC is also supplied to the DeSox unit of an iron ore sintering plant at Nippon Steel Co., Nagoya Works, as well as several other customers.

#### Characterization of MMC's Activated Coke

Table 2 shows the characteristics of MMC's activated coke compared to activated carbon using criteria such as gas recovering process and deodorizing process. BET surface area of activated coke is less than one third of activated carbon. BET surface area of these carbon materials represent their micro-porous structure, which becomes larger as chemical activation condition is severe in manufacturing. As the activation becomes more severe the yield of the product decreases and the mechanical strength of the product falls. A decrease in yield results in increased product cost and a decrease in mechanical strength causes greater material loss during the process. As a result, MMC's activated coke processed with a temperate activation condition is one fourth to one third in price and has a high mechanical strength compared with activated carbon.

Activated coke also has advantages in the abilities to remove SOx and NOx as compared with activated carbon or a metallic catalyst. The following are some characteristic features of activated coke in desulfurization and denitrification found in laboratory studies.

#### Desulfurization with Activated Coke.

Figure 1 shows SO<sub>2</sub> adsorption capacities of activated coke and activated carbon with fresh one and used one. With fresh one, SO<sub>2</sub> adsorption capacity becomes higher as BET surface area of adsorbent increases. On the other hand, with the used one, which has experienced several cycles of SO<sub>2</sub> adsorption and thermal desorption, the BET surface area of materials generally tends to increase. SO<sub>2</sub> adsorption capacity of the used one of activated carbon decreases drastically, while those of activated coke, having a smaller BET surface area and still less micro-porous than activated carbon, are less influenced. The decrease of SO<sub>2</sub> adsorption capacity on activated carbon may be caused by a chemical modification of its micro-porous surface through SO<sub>2</sub> adsorption and desorption.

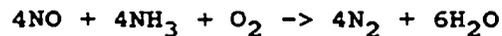
As SO<sub>2</sub> removal efficiency in DeSOx process is approximately estimated with the SO<sub>2</sub> adsorption capacity, it is supposed that activated coke keeps a stable DeSOx performance during the process and it has been confirmed through pilot and demonstration tests mentioned later in this paper.

### Denitrification with Activated Coke

Catalytic activities of carbon catalysts (activated coke and activated carbon) for denitrification do not always depend on their BET surface area. It is also true that their activities are raised by the chemical modification of their micro-porous surface through SO<sub>2</sub> adsorption and desorption, (called SO<sub>x</sub> treatment). With both fresh and used one, (after SO<sub>x</sub> treatment), the catalytic activity of activated coke is superior to that of activated carbon. It should be noted that the chemical surface structure of carbon catalysts is a dominant factor for controlling the rate of denitrification over the physical micro-pore structure.

In the DeSO<sub>x</sub>/DeNO<sub>x</sub> process, the catalytic activity of activated coke for denitrification is enhanced<sup>3)</sup> by SO<sub>x</sub> treatment joining with NH<sub>3</sub> treatment forming oxides groups and nitrogen-species on its micro-porous surface, which also has been confirmed with pilot and demonstration tests as mentioned later in this paper.

Figure 2 shows the catalytic activities of activated coke and vanadium/titania catalyst for denitrification (called selective catalytic reduction: SCR) in each working temperature range. The SCR reaction occurs on these two catalysts with the same mechanism :



The catalytic active sites of these catalysts for SCR reaction are mainly surface oxides, which are bonded to carbon in activated coke and is doubly bonded to metal in vanadium catalyst. It is undesirable that the surface oxide on vanadium is also active for oxidation of SO<sub>2</sub> to SO<sub>3</sub> at the working temperature for SCR ( about 350° C) because of forming ammonium bisulphate deposition at down stream of flue gas flow. On the other hand, it is an advantage that the surface oxide on activated coke works in a relatively lower temperature range and it catches SO<sub>3</sub> effectively.

## MITSUI-BF DRY SIMULTANEOUS DESOX/DENOX PROCESS DESCRIPTION

A schematic of the Mitsui-BF DeSOx/DeNOx process is provided in Figure 3. This process consists of three sections; adsorption, AC regeneration and by-product recovery.

### Adsorption Section

Adsorption section consists of two stages in simultaneous DeSOx/DeNOx process.

Activated coke (AC) moves from top to bottom through adsorbers continuously. First, AC enters in the top of the 2nd stage, where NOx reduction, with addition of NH<sub>3</sub> occurs. The discharged AC from bottom of 2nd stage enters in top of 1st stage, where SOx adsorption occurs. AC adsorbed SOx up to its designed capacity is discharged from bottom of 1st stage, and sent to regeneration section by bucket conveyer.

If only DeSOx or only DeNOx (in case of no SOx in flue gas) is required, a one stage process can be designed.

### SOx Removal by Adsorption at 1st Stage

Flue gas, ranging from 100 to 200°C, passes through the 1st stage. During this stage, SOx (SO<sub>2</sub> and SO<sub>3</sub>) is removed mainly by adsorption. AC acts as an adsorbent for SOx at this stage, SOx is adsorbed and held as sulfuric acid (partially as ammonium salts) in micro-porous structure of AC. Chemistry of SOx removal is listed in Table 3-1.

### NOx Removal by Selective Catalytic Reduction at 2nd Stage.

When NH<sub>3</sub> is added while SO<sub>2</sub> concentration is high, the NH<sub>3</sub> is consumed by SOx forming ammonium salts and effective denitrification is not achieved. Hence, the optimum performance is achieved by injection of NH<sub>3</sub> at a location where less concentrated SO<sub>2</sub> exists. This approach would provide a greater denitrification rate at a lesser NH<sub>3</sub> consumption. Then, the flue gas, which has had almost all of the SOx removed at the 1st stage, is introduced in the 2nd stage.

During the 2nd stage, mainly NOx (NO and NO<sub>2</sub>) is decomposed into N<sub>2</sub> and H<sub>2</sub>O catalytically with the addition of NH<sub>3</sub> as a reductant. Surface oxides and nitrogen-species in micro-porous structure of AC act as the catalytic active sites for NOx-NH<sub>3</sub>-O<sub>2</sub> (SCR) reaction. Chemistry of NOx removal is listed in Table 3-2.

### Removal of Dust by Filtration at Adsorber.

Moving bed of AC acts as granular filter for removal of dust in flue gas. It is the third function of the AC dry process. MMC designed a special louver for effective removal and discharge of dust.

### Removal of Trace Elements

Halogen compounds and trace elements such as mercury vapor and dioxines contained in flue gas are also removable by chemical or physical adsorption into AC.

### AC Regeneration Section

AC discharged from 1st stage is sent to regeneration section, where sulfuric acid and its ammonium salts adsorbed into AC are thermally decomposed and generate SO<sub>2</sub> concentrated gas. It is called SO<sub>2</sub> rich gas (SRG), which is sent to by-product section. Chemistry of regeneration section is listed in Table 3-3.

After cooling, the regenerated AC is sieved out fine dusts (AC fine powder generated by abrasion plus fly-ash in flue gas caught by AC) through vibration screen, then recycled back to the adsorber.

The lost AC by mechanical abrasion on circulation in the process (called mechanical loss, depends on AC moving velocity and distance) and by chemical consumption of SO<sub>2</sub> adsorption and desorption, (called chemical loss, depends on SO<sub>x</sub> load of AC) is made up of fresh AC after this section.

### By-Product Section

SRG, generated in AC regeneration section, contains approximately 20-25% SO<sub>2</sub>. It can be converted into either elemental sulfur, sulfuric acid or liquid SO<sub>2</sub>.

### ADVANTAGES OF MITSUI-BF PROCESS

Two process flows for flue gas desulfurization and denitrification of a power plant are compared as an example in Figure 4. Mitsui-BF process using activated coke is the upper one in the diagram. The lower one is a combination of two separate processes before and after air preheater. These processes are ; a catalytic denitrification process using vanadium/titania catalyst at about 350° C before air preheater and a wet scrubbing desulfurization process using lime milk after air preheater.

Mitsui-BF process has the following advantages compared with the lower one in Figure 4.

### Simultaneous SOx/NOx Removal Process

It is one of the advantages of Mitsui-BF process that both desulfurization and denitrification are performed in a single process. Dedusting and removal of trace elements from flue gas are also achieved additionally.

### Dry Process

Contact of flue gas with activated coke bed under dry condition has been able to simplify the process flow and save the installation space. No large scale waste water treatment, no SO<sub>3</sub> mist-seperator, and no reheater of treated flue gas are necessary in Mitsui-BF process.

### Low Temperature Process

High removal efficiencies of SOx and NOx from flue gas are achieved at temperature ranging from 100 to 200° C in Mitsui-BF process. Removal efficiency for SOx becomes higher with lowering flue gas temperature in this range. High removal efficiency of SO<sub>3</sub> is also an advantage of this dry process. On the other hand, removal efficiency for NOx becomes higher with raising flue gas temperature in this range. These two relationships are opposite. Therefore, suitable gas temperatures need to be designed for each flue gas condition and expected removal efficiencies. Usually, flue gas after recovering its waste heat through heat exchanger(just before stack) is suitable for Mitsui-BF process.

### Optional By-Product

Either elemental sulfur, sulfuric acid or liquid SO<sub>2</sub> can be made optionally from SRG generating in AC regeneration section.

### DEVELOPMENT OF MITSUI-BF PROCESS

Table 1 also summarizes MMC's activities for dry DeSOx/DeNOx process development and plant construction in chronologic order.

### Process Development

MMC concluded a licensing agreement with Bergbau Forschung (now called Deutsche Montan Technologies:DMT) for the dry DeSOx/DeNOx process in 1980.

### Pilot Test

During the years 1981-1983, MMC operated a pilot plant of DeSOx/DeNOx process treating 1,000 Nm<sup>3</sup>/Hr flue gas at Tochigi, Japan.<sup>4)</sup> Main purposes of this plant were as follows.

- To obtain basic performance data of this process such as:
  - (1) correlation of SOx removal efficiencies versus flue gas temperature, space velocity, AC retention time in adsorber and other factors.
  - (2) correlation of NOx removal efficiencies versus flue gas temperature, space velocity, NH<sub>3</sub> injection volume, and other factors.
- To obtain working knowledge of the engineering and operation of this process.
- To improve original process aiming at minimization of process running cost and maximization of process performance.
- To confirm the performance of MMC's activated coke (AC) for this process.

### Demonstration Test

In 1984, MMC constructed a dry DESOx/DeNOx plant treating 30,000 Nm<sup>3</sup>/Hr flue gas from coal-fired boiler of Mitsui Coal Mining Company at Ohmuta, Japan. Two-stage adsorbers, in which MMC's activated coke is filled up and circulating, performed 100% of SOx removal and over 80% of NOx removal efficiencies. Figure 5 shows the correlation of SO<sub>2</sub> removal efficiency with ranges of 700-1250 ppm of inlet SO<sub>2</sub> concentration, when NH<sub>3</sub> was not injected. This is one of the parameter test runs done during the demonstration operation. Perfect removal and 87% removal of SO<sub>2</sub> was achieved till approximately 1,000 ppm and at 1,250ppm of SO<sub>2</sub> concentration, respectively, with designed AC retention time for this demonstration plant. The removal efficiency of SO<sub>2</sub> can be kept at a high level by controlling AC retention time to treat higher concentration of SO<sub>2</sub> containing flue gas.

Although NH<sub>3</sub> was not injected in this test run, 16-22 % of NOx removal efficiency was achieved. This may occur by a direct reaction of NOx and carbon and/or a reaction with nitrogen-species on the microporous surface of AC, which seemed to be formed through SOx and NH<sub>3</sub> treatments of AC in the DeSOx/DeNOx process as mentioned in former section.

This demonstration test operation has extended over 16,000 hours. Through this long term operation, stability and reliability of the system has been confirmed.

Elemental sulfur was recovered from SRG in the process combined reduction-reactor with metallurgical coke as reductant ( $\text{SO}_2 \rightarrow \text{H}_2\text{S}$ ) and Claus-unit ( $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$ ).

During this test, activated coke circulating in the plant was sampled periodically and analysed. Figure 6 shows the characteristics of sampled AC in accordance with plant operation time.

- BET surface area of sampled AC increased with operation in the early period. It suggests that AC micro-porous structure expanded with SOx adsorption and desorption in turn in the process. The reaction of carbon to  $\text{SO}_3$ , which formed through thermal decomposition of  $\text{H}_2\text{SO}_4$  in the AC regeneration section, is the chemistry for surface area expansion.
- $\text{SO}_2$  adsorption capacity of sampled AC was almost constant, though AC microporous structure was expanding. It means that SOx removal efficiency depends on not only micro-porous structure, but also the chemical structure of AC in practice.
- Strength index of sampled AC against abrasion was almost constant. It means that mechanical strength of AC doesn't go down in practice.
- AC chemical structure, which are represented by O/C and N/C also increased with operation in the early period. It suggests that oxide groups and nitrogen species on AC microporous surface were formed by contacting with oxygen containing gas (SOx, NOx,  $\text{O}_2$ ) and nitrogen containing gas ( $\text{NH}_3$ , NOx) in the process. In accordance with an increasing amount of oxides and nitrogen-species on AC chemical structure, NOx removal efficiency of AC increased as shown in Figure 7.

#### PROCESS APPLICATION

In 1987, Mitsui-BF DeSOx/DENox commercial plant started operation at Idemitsu Kosan, Aichi Oil Refinery. This plant has been treating flue gas (236,000  $\text{Nm}^3/\text{Hr}$  designed) from catalyst regeneration section of Residue Fluid Catalytic Cracking Unit (RFCC). Performance of this DeSOx/DeNOx plant has been very successful. 100% of SOx ( $\text{SO}_2 + \text{SO}_3$ ) removal efficiency and over 80% of NOx removal efficiency has been achieved constantly at approximately 180° C. This plant is easy to operate and experienced almost no trouble.

In 1990, MMC constructed AC DENox pilot plant, which has been commissioned to EPDC by the Japanese government. This pilot plant was designed for treating 10,000  $\text{Nm}^3/\text{Hr}$  flue gas at 140° C from a fluidized bed combustion boiler.

In Germany, Uhde GmbH, which is also a licensee of BF, constructed two dry DeSOx/DeNOx commercial plants. One started operating in 1987 for treating flue gas (totally 1,110,000 Nm<sup>3</sup>/Hr designed) from lignite fired power plant at EVO's Arzberg power station. Another began operation in 1989 for treating flue gas (323,000 Nm<sup>3</sup>/Hr designed) from hard coal fired boiler of Hoechst AG at Frankfurt. MMC cooperated with Uhde in the engineering of these two plants.

Mitsui-BF process is applicable to a broad range of flue gas cleaning as follows:

- boilers
- furnaces for sintering and heating
- incinerators for trash and refuse
- regenerator of catalysts such as FCC
- chemical plants such as sulfuric acid plant and others.

#### MITSUI-BF PROCESS ECONOMICS

##### Simultaneous DeSOx/DeNOx Process

Capital cost : US\$ 220 - 240/KW

This is estimated based on the following conditions :

- 500 MW (250 MW x 2 units, 25% allowance for our system included)
- SO<sub>2</sub> 2000 ppm, NOx 326 ppm
- DeSOx efficiency : more than 90%
- DeNOx efficiency : more than 80%
- Civil, foundation works are excluded
- Including by-product equipment (elemental sulfur or sulfuric acid)

##### DeSOx Only Process

Capital cost: US\$ 140 - 160/KW

This is estimated based on the same conditions as above except DeNOx efficiency.

### DeNOx Only Process

Capital cost : US\$ 70 -80/KW

This is estimated based on conditions as follows.

- 350 MW
- NOx 250 ppm, SOx less than 50 ppm
- DeNOx efficiency: more than 80%
- Civil, foundation works are excluded

Remarks : If the flue gas has no SOx, no dust like LNG boiler, we can introduce fixed bed AC for DeNOx. Thus, our capital cost might decrease further.

### CONCLUSION

Mitsui-BF dry DeSOx/DeNOx technology, it's history of research, development and commercialization has been provided in this paper with both aspects of the activated coke used in this process and the DeSOx/DeNOx process using activated coke. There are four commercial installations of this process for cleaning flue gas from coal fired boilers and oil refinery in Japan and Germany. Air, water and land are essential for life, but they are no longer infinite resources. We believe that the Mitsui-BF system is an important contribution to emission control technology and an effective method to keep our atmosphere clean.

### REFERENCES

1. K. Knoblauch, E. Richter and H. Juntgen. " Application of active coke in processes of SOx and NOx removal from flue gases. " Fuel, September, Vol. 60, 1981, p. 832.
2. Y. Komatsubara, M. Yano, I. Shiraishi and S. Ida. " Preparation of active coke for the removal of SOx and NOx in the flue gases." In Proceedings of 16th Biennial Conference on Carbon, 1983, p. 325.
3. I. Mochida, M.Ogaki, H. Fujitsu, Y. Komatsubara and S. Ida. " Catalytic Activity of coke activated with sulfuric acid for the reduction of nitric oxide." Fuel, July 1983, Volume 62, p. 867.
4. S.M. Dalton. " Current status of dry NOx-SOx emission control processes." In Proceedings of the 1982 Joint Symposium on Stationary Combustion NOx Control , 1982, p. 32-1.

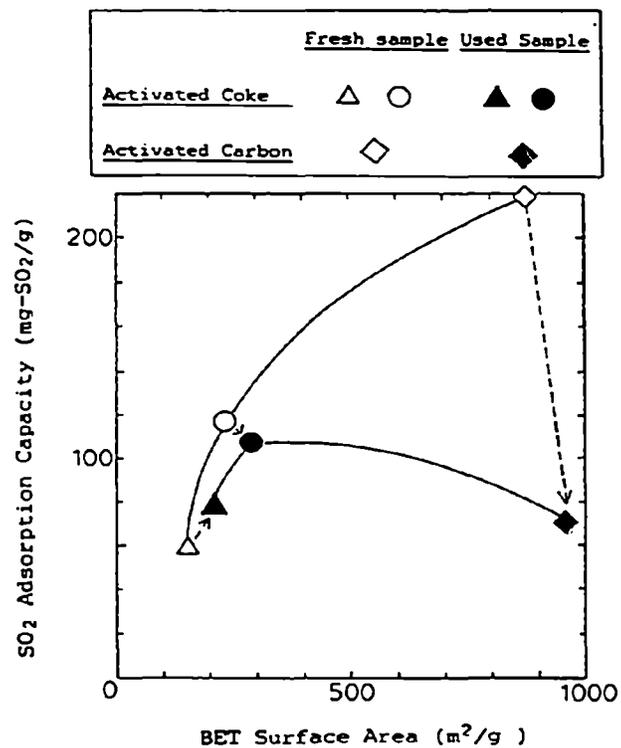


Figure 1 The SO<sub>2</sub> adsorption capacities of Activated coke and Activated carbon

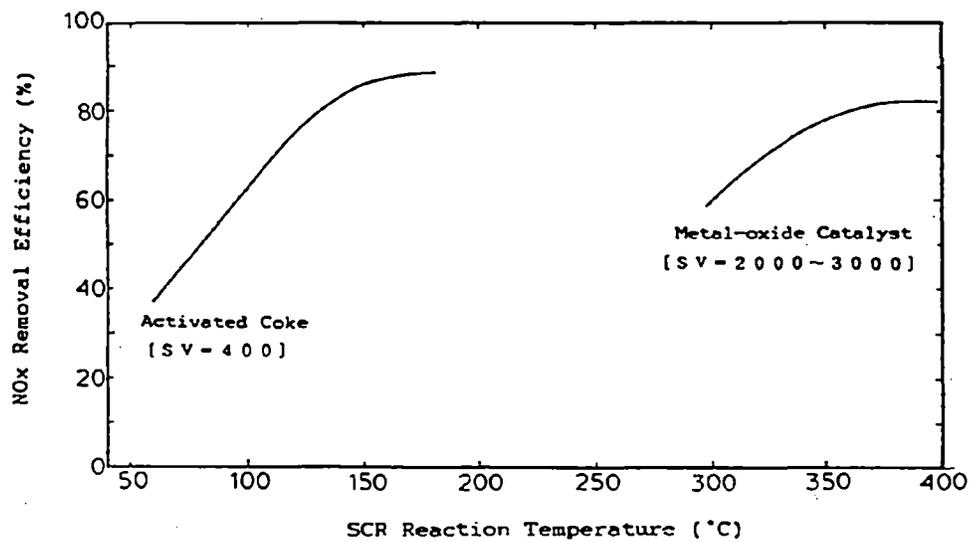
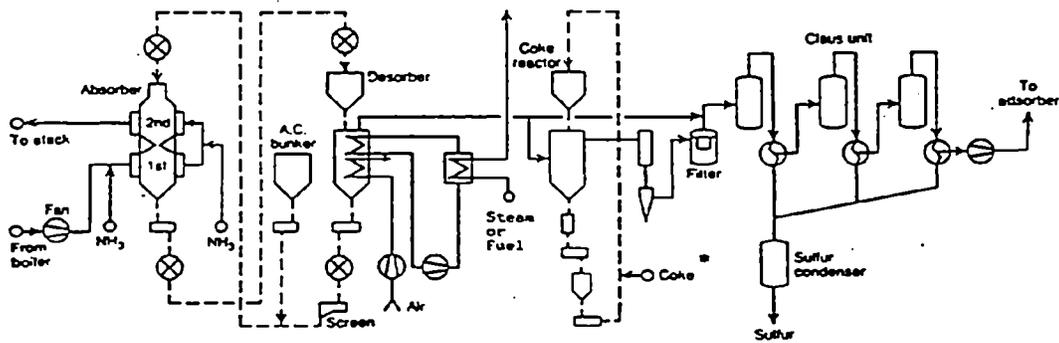


Figure 2 The catalytic activities of Activated coke and Metal-oxide catalyst for SCR reaction



\* Metallurgical coke breeze was used in the coke-reactor(Sulfur recovery)

Figure 3 Mitsui-BF dry DESOx/DENox process with Sulfur recovery

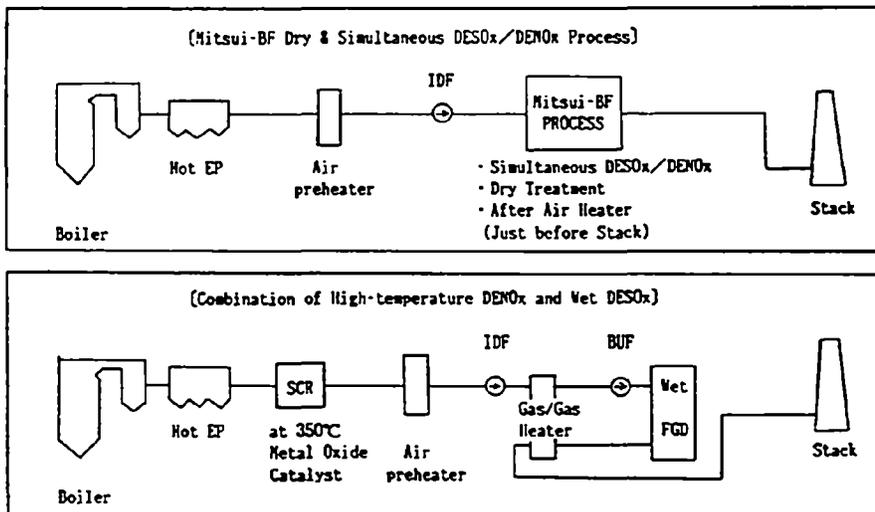


Figure 4 Advantages of Mitsui-BF process for flue gas DESOx/DENox

- \* Electrostatic precipitator(EP) also can be located after air-preheater.
- \* Wet EP also can be additionally arranged after Wet FGD to remove mists.

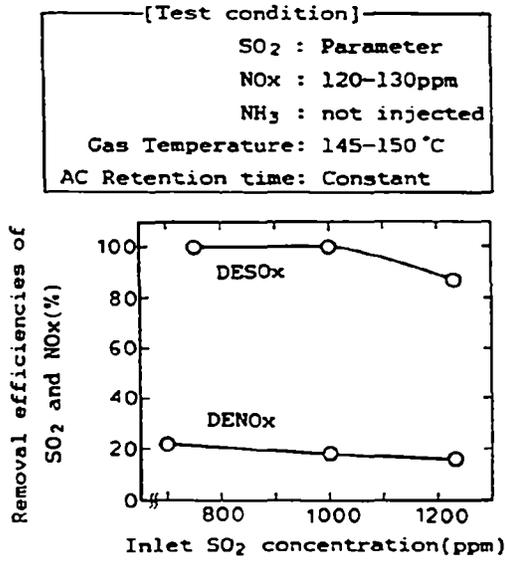


Figure 5 Correlation of SO<sub>2</sub> removal efficiency with inlet SO<sub>2</sub> concentration [Demonstration test at Ohmuta, Japan]

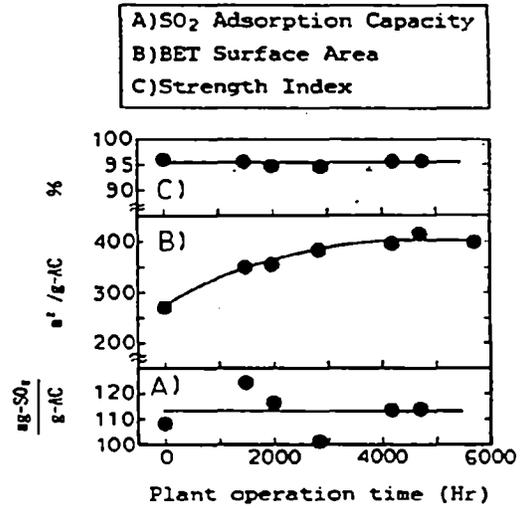


Figure 6 Characteristics of sampled AC in accordance with plant operation time [Demonstration test at Ohmuta, Japan]

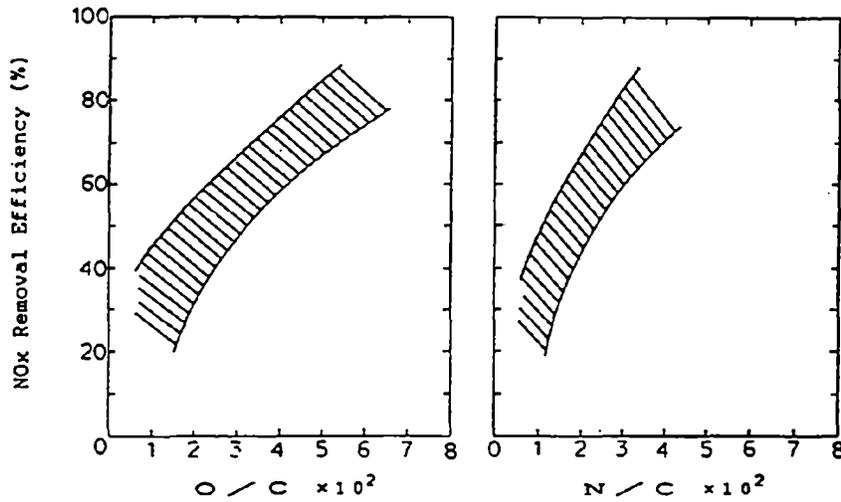


Figure 7 Correlation of NO<sub>x</sub> removal ability of AC with elemental ratio of AC surface

Table 1

SUMMARY OF MMC'S ACTIVITIES FOR AC PRODUCTION AND DRY DESOx/DENOx PROCESS

<u>Year</u>	<u>AC Production and Supply</u>	<u>Mitsui-BF Dry DESOx/DENOx Process</u>
1982	<ul style="list-style-type: none"> <li>● Pilot plant(0.5Ton/Day)</li> <li>● AC supply(10Ton) for Tochigi</li> </ul>	<ul style="list-style-type: none"> <li>● DESOx/DENOx pilot plant (1,000Nm<sup>3</sup>/Hr) test operation at Tochigi [from Feb.1981 to Oct.1983]</li> </ul>
1984	<ul style="list-style-type: none"> <li>● AC supply for Ohmuta</li> </ul>	<ul style="list-style-type: none"> <li>● DESOx/DENOx plant(30,000Nm<sup>3</sup>/Hr)starts to operate at Mitsui Coal Mining,Ohmuta</li> </ul>
1985	<ul style="list-style-type: none"> <li>● AC supply for Matsushima power station of EPDC</li> </ul>	
1986	<ul style="list-style-type: none"> <li>● Commercial AC production (3,000Ton/Year)start to operate at Kitakyusyu</li> </ul>	
1987	<ul style="list-style-type: none"> <li>● Start to supply of AC for Idemitsu-Aichi Refinery</li> </ul>	<ul style="list-style-type: none"> <li>● DESOx/DENOx plant(236,000Nm<sup>3</sup>/Hr)starts to operate at Idemitsu-Aichi Refinery</li> <li>● DESOx/DENOx plant(1,110,000Nm<sup>3</sup>/Hr)starts to operate at Arzberg power station of EVO,Germany #1)</li> </ul>
1988	<ul style="list-style-type: none"> <li>● Start to supply of AC for Nippon Steel-Nagoya Works</li> </ul>	
1989	<ul style="list-style-type: none"> <li>● AC supply for Hoechst,Germany</li> </ul>	<ul style="list-style-type: none"> <li>● DESOx/DENOx plant(323,000Nm<sup>3</sup>/Hr)starts to operate at Hoechst,Frankfurt,Germany #1)</li> </ul>
1990	<ul style="list-style-type: none"> <li>● AC supply for Wakamatsu Research Center of EPDC</li> </ul>	<ul style="list-style-type: none"> <li>● Low-Temperature DENOx pilot plant (10,000Nm<sup>3</sup>/Hr) at Wakamatsu of EPDC #2)</li> </ul>

#1) These plants were constructed by Uhde GmbH,Germany.  
MMC cooperated in engineering.

#2) Commissioned to Electric Power Development Company(EPDC)  
by Japanese government

Table 2

## CHARACTERISTICS OF MMC'S ACTIVATED COKE COMPARED WITH ACTIVATED CARBON

Items	MMC's Activated Coke	Activated Carbon
BET Surface Area (m <sup>2</sup> /g) #1)	150 - 250	850
Mechanical Strength (%) #2)	95	85
SO <sub>2</sub> Adsorption Capacity #3) (mg-SO <sub>2</sub> /g)	60 - 120	220(with fresh one) 70(with used one)
NO <sub>x</sub> Removal Efficiency #4) (%)	80 - 85	60 - 70
Price Ratio (-)	1/4 - 1/3	1

#1) Measured by CO<sub>2</sub> adsorption at 199K

#2) Defined as the yield of powder after 1,000 revolution in the drum tester

#3) SO<sub>2</sub> amount adsorbed under following conditions:

Adsorption : 100 °C × 3Hr

Contacting gas composition: SO<sub>2</sub>=2%, O<sub>2</sub>=5%, H<sub>2</sub>O=10%, N<sub>2</sub>=Balance

#4) Measured with fixed bed flow reactor under following conditions:

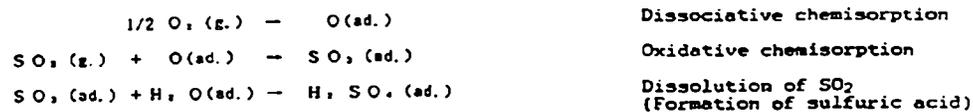
Samples amount:300cc, Temperature: 140 °C, Space velocity: 400Hr<sup>-1</sup>

Contacting gas composition: NO=NH<sub>3</sub>=200PPM, O<sub>2</sub>=5%, H<sub>2</sub>O=10%, N<sub>2</sub>=Balance

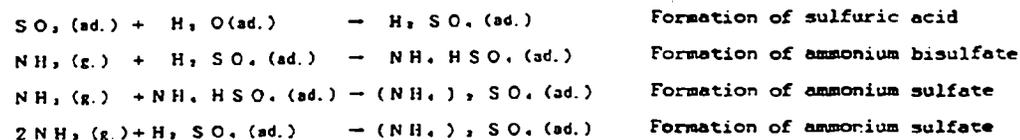
Table 3-1

CHEMISTRY OF SO<sub>x</sub> REMOVAL IN ADSORPTION SECTION

[Desulfurization into micro-porous structure of AC without NH<sub>3</sub>  
: mainly proceeds in 1st-stage adsorber]

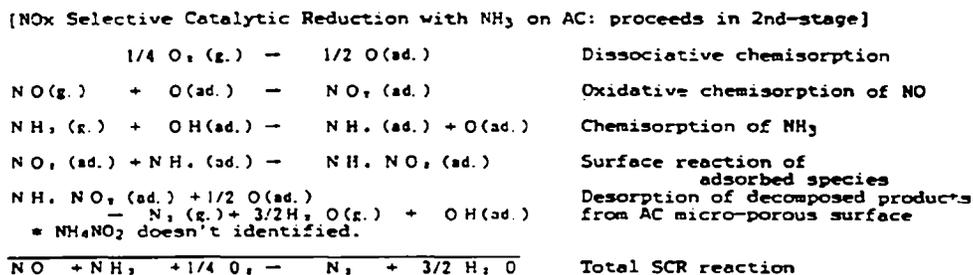


[Desulfurization into micro-porous structure of AC with NH<sub>3</sub>  
: mainly proceeds in 2nd-stage adsorber]

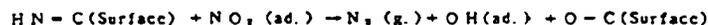


s(ad.):adsorbed state    \*(g.):gas phase

Table 3-2  
CHEMISTRY OF NO<sub>x</sub> REMOVAL IN ADSORPTION SECTION



[NO<sub>x</sub> reduction with nitrogen-species on micro-porous surface of AC]



\* Nitrogen-species doesn't identified.

[NO<sub>x</sub> direct reduction by carbon of AC]

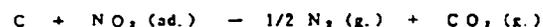
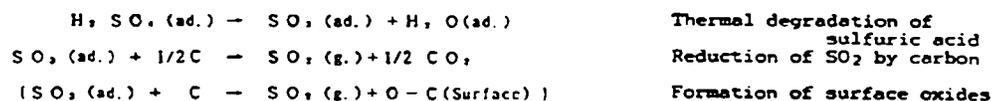
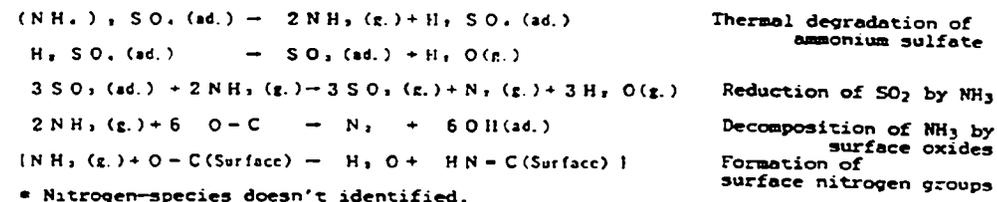


Table 3-3  
CHEMISTRY OF AC REGENERATION

[Regeneration of AC: case without NH<sub>3</sub>]



[Regeneration of AC: case with NH<sub>3</sub>]



\* Nitrogen-species doesn't identified.

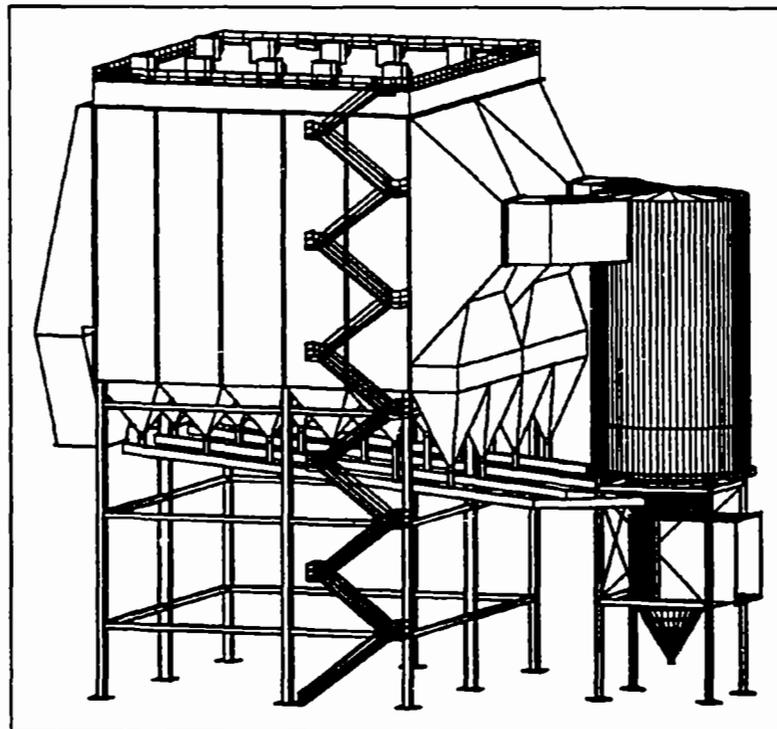


**HIGH EFFICIENCY, DRY FLUE GAS SO<sub>x</sub>, AND COMBINED SO<sub>x</sub>/NO<sub>x</sub> REMOVAL  
EXPERIENCE WITH THE LURGI CIRCULATING FLUID BED DRY SCRUBBER—  
A NEW, ECONOMICAL RETROFIT OPTION FOR U.S. UTILITIES  
FOR ACID RAIN REMEDIATION**

J.G. Toher  
Environmental Elements Corporation  
3700 Koppers Street  
Baltimore, Maryland 21227

G.D. Lanois  
Environmental Elements Corporation  
3700 Koppers Street  
Baltimore, Maryland 21227

Harald Sauer  
Lurgi GmbH  
Frankfurt am Main, Germany





## **ABSTRACT**

The Lurgi dry flue gas desulfurization Circulating Fluid Bed (CFB) process has been in commercial operation on five coal-fired utility boilers in Germany since 1987. The process has consistently demonstrated SO<sub>2</sub> removal efficiencies up to 97% since its introduction in 1984. Several U.S. utilities are now seriously considering the CFB in their Phase I acid rain remediation planning.

Currently, the CFB is being further developed for combined SO<sub>x</sub>/NO<sub>x</sub> removal. Pilot study results indicate removal efficiencies of 95%/85%, respectively.

The presentation covers:

- Operating data and experience from five plants
- Process design data
- Performance data (i.e., 97% SO<sub>2</sub> removal on 6% sulfur coal)
- Economics showing favorable capital and O&M costs compared to wet flue gas desulfurization processes and spray dryers
- Retrofit strategies with little or no footprint which provide options for plants with limited space availability
- Description of advanced, combined SO<sub>x</sub>/NO<sub>x</sub> CFB process and performance results

## THE CFB DRY FGD TECHNOLOGY CONCEPT

### Process Overview

The circulating fluid bed FGD process provides a viable, proven alternative to wet limestone scrubbing (LSFO). The process uses a dry reagent and precludes the liquid phase absorption mechanism used in LSFO and in lime spray dryer absorbers (LSD). The system is less complicated to operate and easier to maintain because it does not require high maintenance mechanical equipment such as grinding mills, abrasion resistant slurry pumps, agitators, rotary atomizers, and sludge dewatering devices. The CFB's reagent flow is independent from water balance around the reactor vessel.

In general, process operation begins with calcium oxide (pebble lime) hydrated on site and injected dry into the flue gas on the cold side of the air preheater. A fluid bed of lime develops in the reactor, providing the contact medium between gaseous sulfur oxides and the hydrated lime. Dry recirculation of material from the downstream particulate collector is used to optimize fresh lime consumption.

### Reactor Operation

Gas enters the scrubber vessel at the bottom and flows vertically upward through a venturi section. The venturi is designed to achieve the proper flow distribution throughout the operating range of the vessel. Inside the venturi, the gas is first accelerated, then decelerated before entering the upper cylindrical vessel. The upper vessel's height is designed to accommodate the mass of bed material required for the desired Ca and S contact time. The vessel is designed with an internal gas velocity range of 6 to 20 feet per second. This range of gas velocities supports boiler loads from 30% to 100%.

The upper vessel's height is designed to accommodate the mass of bed material required for the desired Ca and S contact time. The vessel is designed with an internal gas velocity range of 6 to 20 feet per second. This range of gas velocities supports boiler loads from 30% to 100%.

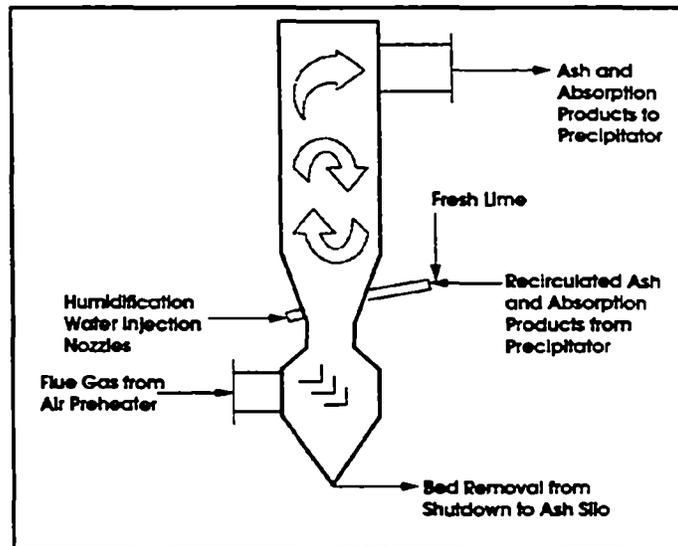


Figure 1. Details of CFB Reactor

All external inputs of recirculating material, fresh reagent and gas conditioning water are introduced to the gas on the diverging wall of the venturi. The vessel has no internal mechanical or structural components. When operating at a full load design pressure loss of 5 to 6 inches W.G., the gas residence time in the vessel is approximately 3 seconds.

## CFB PROCESS DESIGN

### Process

Gas from the boiler air preheater passes through the scrubber vessel, then through a particulate control device before being exhausted via a fan to the stack. The gas path material is carbon steel. The existing stack can be re-used, a feature usually possible with any "dry" technology. Flue gas entering the scrubber is evaporatively cooled to within 45°F of the adiabatic saturation temperature with a water spray. This process is relatively insensitive to the chemistry of the cooling water, therefore on-site waste waters may be consumed in the CFB.

The cooled gas passes up through the circulating bed of fresh reagent and recirculated material. Abrasion between particles in the fluid bed continuously removes the outer layer of absorption products and exposes the underlying surfaces of unused lime. The continuous contact between particles, combined with the evaporative cooling of the gases, optimize the overall consumption of fresh lime.

The gases are cleaned of dry dust in the downstream particulate collector. As much as 98% of the material collected is recirculated to the CFB to resupply the bed. This high recirculation ratio keeps unused calcium in the process for up to 1/2 hour and boosts the performance capability level up to 99% total sulfur capture. The vast particle surface area in the circulating bed permits successful capture of virtually all of the SO<sub>3</sub> in the gas, eliminating the possibility of gas path corrosion from condensed SO<sub>3</sub> aerosol mist. The disposal material from the process is moved to an ash silo for discharge and eventually transported to a landfill or mine.

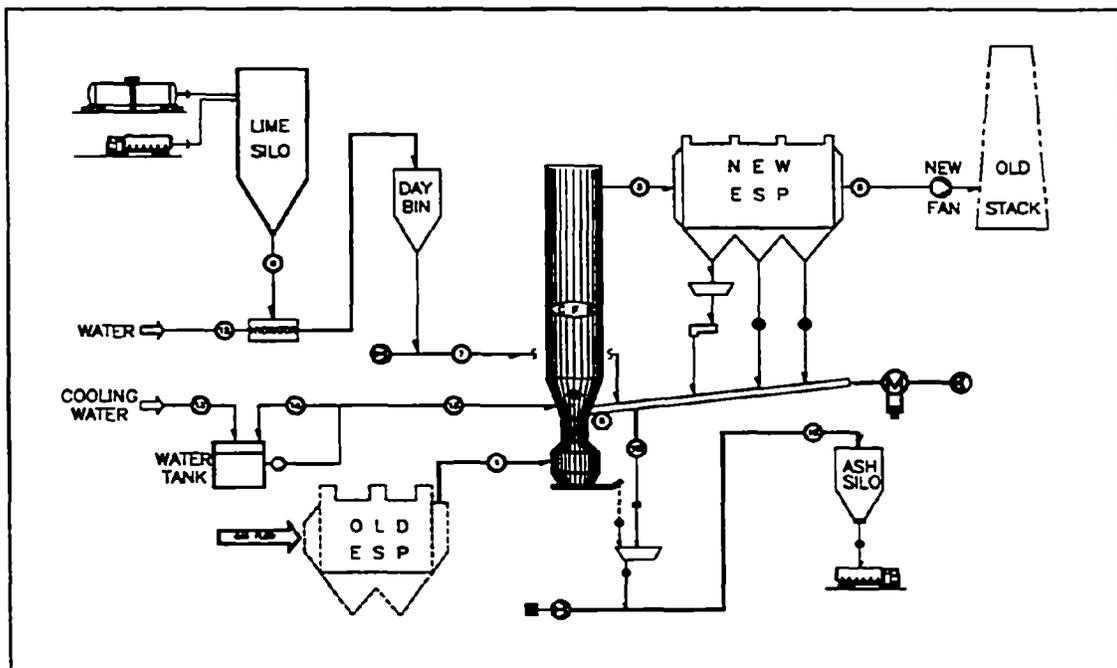


Figure 2. CFB Process Schematic

## Control System

The simplicity of the process and limited number of control loops allow the system to be operated either by the existing boiler control room DCS system or by a separate PLC based architecture. Only three continuous control parameters are used in the process:

1. The gas temperature exiting the CFB vessel is maintained by modulating the flow of water returning from the high pressure nozzles. Opening the return flow control valve reduces pressure at the nozzle tip, thus reducing the flow of water through the nozzle tip and into the gas.
2. The stack  $\text{SO}_2$  gas concentration is maintained by modulating the flow of fresh lime into the CFB lime transport line. Rapid response to changes in stack  $\text{SO}_2$  are possible due to close coupling of the CFB lime transport system to the CFB reactor.
3. The mass of the fluid bed is maintained by modulating the disposal of material in accordance with a pre-set differential pressure across the scrubber vessel. The pressure loss associated with fluidizing and suspending the mass of the bed will remain constant throughout the range of boiler load. This parameter is therefore used to regulate the discharge of material and to insure proper flow of recirculated material to replenish the bed.

All other control logic is discrete (yes/no) signals or typical particulate control logic.

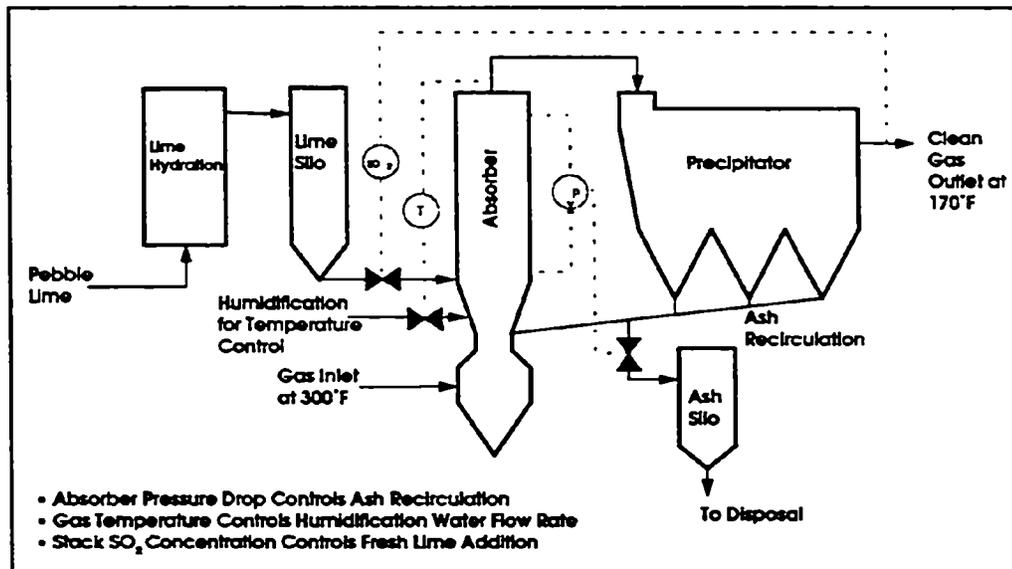


Figure 3. CFB Process Control

During start-up of the boiler, the circulating bed of material is established at 30% boiler load. Either the inventory of material in the surge bin or fresh lime can be used; the choice depends upon how long the system has been shutdown. When a preset pressure differential across the fluid bed is reached, a signal releases an interlock, allowing the flow of cooling water for humidification. The process is now fully functional and automatically follows the boiler up to full load.

## PERFORMANCE

### Operation and Maintenance

Figure 4 presents an overview of CFB scrubber operating experience in the power, process steam, and cement industries.

	Rated Capacity MW	Operational Time (YRS)	Capacity Factor (%)	Coal Sulfur (%)	Removal Efficiency (%)	Stoichiometry as tested
Schwandorff	50	1+	50	1.5	95	1.3
Borken	100	3+	<50	6.0	97	1.5
Siersdorf	2 @ 85	3+	70	1.0	93	1.2
Utervaz	50*	3+	80	1.5*	90	1.2
Opel	50*	1	70	1.0	92	1.3

\*Equivalent

Figure 4: CFB Installations

The experience base includes fuels with low to very high sulfur contents. Plant operations cover both peaking stations and base loaded high capacity stations. Current installations are demonstrating system availability of 99% or higher. Operating and maintenance costs have been in line with original design predictions.

A 1991 survey of power plant operations indicates that the CFB does not require a full-time person to operate and maintain it. Two of the facilities surveyed relied upon their existing staff to operate the newly installed CFB.

### Waste Characterization

The dry waste product from this process has characteristics similar to LSD waste, therefore, it can be transported and disposed of in the same manner. The product can be fixated with an optimum amount of water and will achieve yield strengths in excess of 2000 psi with permeability equivalent to clay ( $10^{-10}$  ft/sec). The material has compacted densities in the range of 80 lb/ft<sup>3</sup>.

Laboratory analysis of the material produced at Schwandorff show the following typical values after mixing with 30% water:

- Density: 80 lb/ft<sup>3</sup>
- Compressive Strength: 2,600 psi @ 56 days
- Permeability:  $12.2 \times 10^{-10}$  ft/sec @ 28 days

This product's ability to achieve lean concrete strength and clay like permeability make it a good source of material to stabilize spent mines or reclaim open quarries and landfills.

## **FGD PROCESS ECONOMICS COMPARISON**

This economic comparison evaluates current (1991) capital and O&M costs for dry Circulating Fluid Bed (CFB), Wet Limestone Scrubbing with Forced Oxidation (LSFO), and Lime Spray Drying (LSD) processes.

To make a fair and objective comparison of these three technologies, an established data base was used. The format and methodologies of the recent EPRI FGD Economics Studies were selected. Highlights of EPRI evaluation criteria are as follows:

### **Technical**

- 300 MW PC Boiler
- 2.6% coal @ 13,100 b/# HHV
- 65% capacity factor
- 90% SO<sub>2</sub> removal
- 1.276 retrofit factor
- (3) 50% absorbers
- Not included
  - Particulate removal equipment
  - Stack modifications
  - Boiler modifications

### **Economic**

- 1/90 dollars
- 15 yr. plant life
- Labor \$20/hr.
- Reagent
  - Lime \$55/ton
  - Limestone \$15/ton
- Disposal \$8.15/ton
- 5% annual inflation
- 0.3% annual inflation (power & steam)
- Levelized constant/current dollar factors, and process/project contingencies all as per 1991 EPRI FGD report

Certain adjustments to the EPRI report criteria and cost assumptions have been made to develop a comparison that reflects FGD process economics that are currently being considered for actual Phase I Acid Rain remediation projects. These adjustments are tabulated along with explanatory comments as follows:

	CFB	LSFO	LSD
Number of Absorber Modules	1	1	1
Total Process Capital	70 \$/KW	124 \$/KW	80 \$/KW
Particulate Equipment	ESP added	(None)*	ESP added
Ca/S Ratio	(1.15)*	(1.1)*	1.25
Operating Labor	One Man Year	(4-5 man years)*	(3-4 man years)*
Maintenance Labor		(4.8% TPC)*	(4.4% TPC)*
Solids Disposal Cost	Flyash excluded	(Flyash excluded)*	Flyash excluded

\* Items in parentheses denote no change from the EPRI study

Figure 5. Adjustments to EPRI Study

Notes to Figure 5

- **Absorber Modules/Total Process Capital** - Single 100% capacity modules are considered, thus the total process capital (TPC) was adjusted for CFB and LSD based on current estimates. The LSFO TPC was adjusted based on the stated EPRI report cost reduction.
- **Particulate Equipment** - The EPRI study assumes there is existing particulate equipment in place and no new particulate additions are needed. Current experience indicates additional particulate equipment is usually needed for the CFB and LSD. A new full size ESP is now included in the TPC at approximately 20-25 \$/KW.
- **Ca/S Ratio** - The LSD Ca/S Ratio is set at 1.25 and thus the CFB and LSD are approximately in the same range of +/- 10%.
- **O&M Labor** - Actual costs are included based on 1991 studies of data obtained from three operating CFB systems at utility plants.
- **Solids** - Assuming particulate equipment is in place and operational, the waste disposal costs for the CFB and LSD are subtracted from the waste volume stated in the EPRI study.

Figure 6 displays fixed and variable operating costs, fixed charges, and total cost comparisons for CFB, LSFO, and LSD. Levelized current dollars and levelized constant dollars are calculated based upon a 15 year life cycle.

	First Year Cost			Levelized Constant Dollars			Levelized Current Dollars		
	CFB	LSFO	LSD	CFB	LSFO	LSD	CFB	LSFO	LSD
<b>Fixed O &amp; M Costs</b> (Operating Labor, Maintenance Labor & Materials, Admin. & Support)	\$ 0.51	\$ 2.05	\$ 1.59	\$ 0.51	\$ 2.05	\$ 1.59	\$ 0.70	\$ 2.81	\$ 2.18
<b>Variable Operating Costs</b> (Reagent, Solids Disp., Water & Power)	1.93	2.11	1.99	1.94	2.14	2.03	2.64	2.93	2.71
<b>Fixed Charges</b> (Debt/Equity Return, Income Taxes, Deprec., Property Tax & Insurance)	4.96	7.81	5.57	2.81	4.42	3.15	3.88	6.11	4.35
<b>Total Costs</b>	<b>\$ 7.40</b>	<b>\$ 11.97</b>	<b>\$ 9.15</b>	<b>\$ 5.26</b>	<b>\$ 8.61</b>	<b>\$ 6.77</b>	<b>\$ 7.22</b>	<b>\$ 11.85</b>	<b>\$ 9.24</b>

Comparison (MILLS/KWH)

Figure 6. FGD Process Economics

### Economics Conclusions

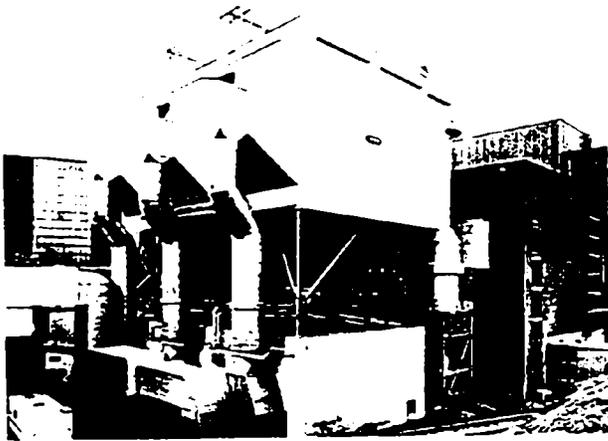
- CFB fixed O&M costs are significantly less than LSFO and LSD due the system's simplicity (minimum components) and very low O&M labor requirements.
- Variable operating costs for both dry systems (CFB and LSD) are comparable to LSFO at 65% capacity factor and are sensitive as capacity factor changes.
- The fixed charge for the CFB (including particulate equipment) is the lowest of the systems compared.
- While the LSFO capital cost could vary downward, additional costs not included but typically required for LSFO (new stack, reheat, etc.) would tend to increase the fixed charge component.
- While LSD is included in this study, it is generally not considered to be a practical option for acid rain retrofits due to its significant plant space requirements.
- Total O&M and fixed charge costs indicate that the CFB is a viable economic choice for FGD retrofit applications when compared to LSFO, even allowing for significant reduction in LSFO capital costs and/or capacity factor increases.

## **CFB OPERATING HISTORY**

The CFB dry scrubbing technology emerged from fluosolids processes used in the 1950s and '60s for calcining, roasting and coal burning. During the 1970s, CFB dry scrubbers were installed to control HF emissions from aluminum potlines, typically handling multi-million ACFM at each installation. In the early 1980s the CFB was installed on incinerators for controlling HF, HCl, and SO<sub>2</sub>.

The first CFB installation on a coal-fired boiler was in 1984 on a 50 MW demonstration plant. CFB systems were installed for commercial operation on utility power plants in 1987, 1988 and 1990. The most recent CFB system is planned for start-up in 1993. Additional proposed projects are expected to be finalized in the next several months. The number of developing CFB projects suggests that the European and American power generating industry now regard the CFB as a viable system for efficient FGD.

Current operating CFB installations are:



**Figure 7**

**Company: VAW Bonn**

**Location: Schwandorff, Germany**

**Start-Up: 1982**

**Application: Incinerator**

**Boiler Type: Traveling Grate**

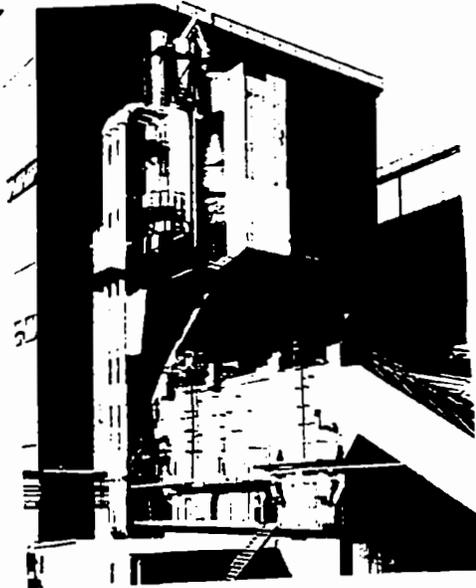
**Fuel: Municipal Waste**

**Inlet SO<sub>2</sub> (PPM): 175**

**SO<sub>2</sub> Removal Efficiency: 60%**

**Particulate Outlet (GR/SCF): .031**

**Gas Volume (ACFM): 3 x 111,300**



**Figure 8**

**Company:** Bayernwerk  
**Location:** Schwandorff, Germany  
**Start-Up:** 1984  
**Application:** Utility Power  
**Capacity:** 50 MW  
**Boiler Type:** PC  
**% Sulfur:** 2-3.5  
**% Ash:** 8-10  
**Fuel:** Lignite  
**Inlet SO<sub>2</sub> (PPM):** 1,490  
**SO<sub>2</sub> Removal Efficiency:** 95%  
**Particulate Outlet (GR/SCF):** .062  
**Gas Volume (ACFM):** 231,400

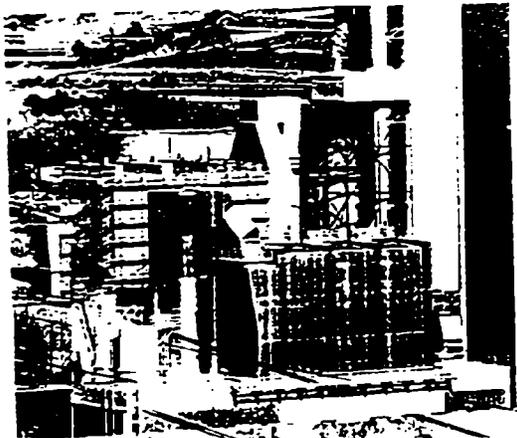


**Figure 9**

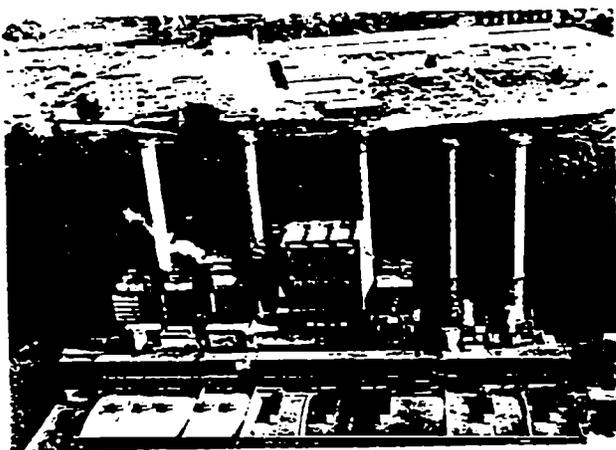
**Company:** Prussia Electric  
**Location:** Borken, Germany  
**Start-Up:** 1987  
**Application:** Utility Power  
**Capacity:** 100 MW  
**Boiler Type:** PC  
**% Sulfur:** 3-6.5  
**% Ash:** 20-24  
**Fuel:** Lignite  
**Inlet SO<sub>2</sub> (PPM):** 4,450  
**SO<sub>2</sub> Removal Efficiency:** 97%  
**Particulate Outlet (GR/SCF):** .033  
**Gas Volume (ACFM):** 585,600



**Figure 10**  
**Company:** EBV  
**Location:** Siersdorf, Germany  
**Start-Up:** 1988  
**Application:** Utility Power  
**Capacity:** 2 x 85 MW  
**Boiler Type:** PC  
 % Sulfur: .8-1.6  
 % Ash: 23-30  
**Fuel:** Bituminous Coal  
**Inlet SO<sub>2</sub> (PPM):** 945  
**SO<sub>2</sub> Removal Efficiency:** 93%  
**Particulate Outlet (GR/SCF):** .02  
**Gas Volume (ACFM):** 2 x 315,000



**Figure 11**  
**Company:** Buendner Cement  
**Location:** Untervaz, Switzerland  
**Start-Up:** 1988  
**Application:** Raw Mill  
**Fuel:** Bituminous Coal  
**Inlet SO<sub>2</sub> (PPM):** 1,260  
**SO<sub>2</sub> Removal Efficiency:** 90%  
**Particulate Outlet (GR/SCF):** .02  
**Gas Volume (ACFM):** 236,000  
**Note:** Sulfur source is from raw material



**Figure 12**  
**Company:** Adam Opel AG  
**Location:** Russelsheim, Germany  
**Start-Up:** 1990  
**Application:** Industrial Power  
**Capacity:** 33 MW  
**Boiler Type:** PC  
 % Sulfur: .6-1.3  
 % Ash: 6-8  
**Fuel:** Bituminous Coal  
**Inlet SO<sub>2</sub> (PPM):** 945  
**SO<sub>2</sub> Removal Efficiency:** 92%  
**Particulate Outlet (GR/SCF):** .012  
**Gas Volume (ACFM):** 2 x 82,300

### CFB RETROFIT OPTIONS

The CFB offers several plant layout options and can be installed on plants with limited space. Typically, these plants cannot be retrofit with LSFO or LSD systems.

In addition to its adaptable layout plans, the CFB conserves plant space because its reactor is compact and close-coupled to the precipitator. The system frequently uses the existing stack, and its support equipment can be conveniently located in available plant space.

In situations where existing particulate equipment requires upgrading, the CFB is more economical than LSFO systems because the CFB includes new particulate control equipment as an integral component. In such cases, the CFB requires less plant space.

Options for CFB arrangements are as follows:

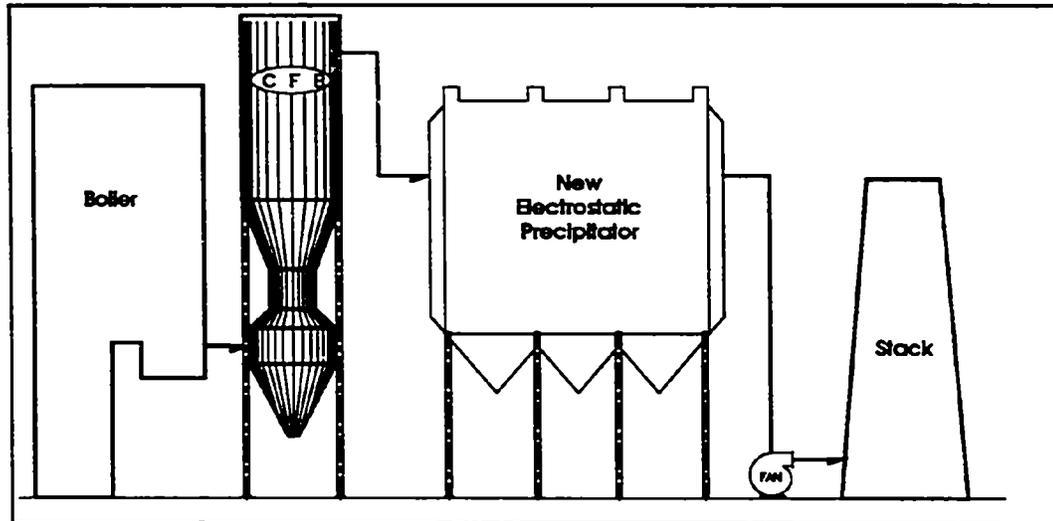


Figure 13. Replacement of Existing ESP with CFB and New ESP

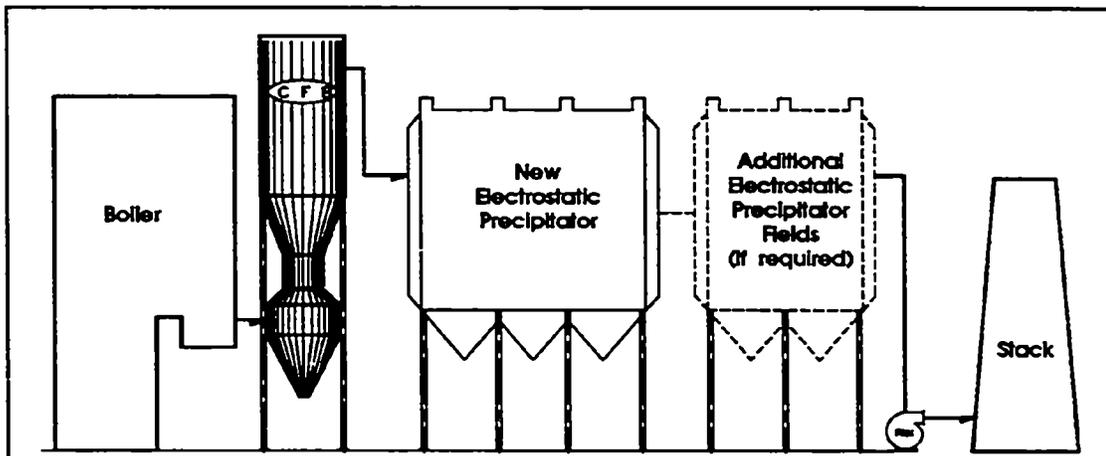


Figure 14. CFB Installed Upstream of Existing ESP

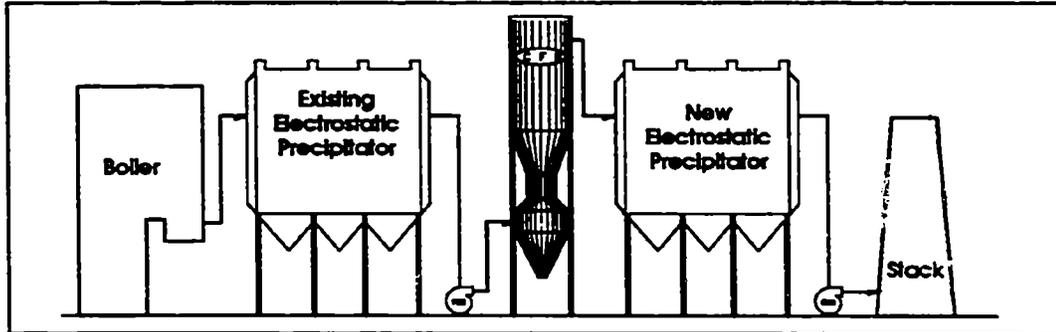


Figure 15. CFB Installed before Existing Stack and Downstream of Existing ESP

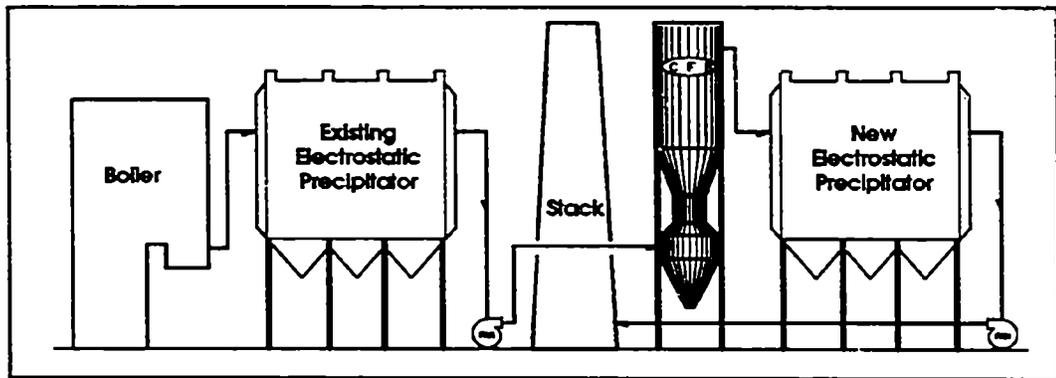


Figure 16. CFB Installed After Existing Stack Downstream of Existing ESP

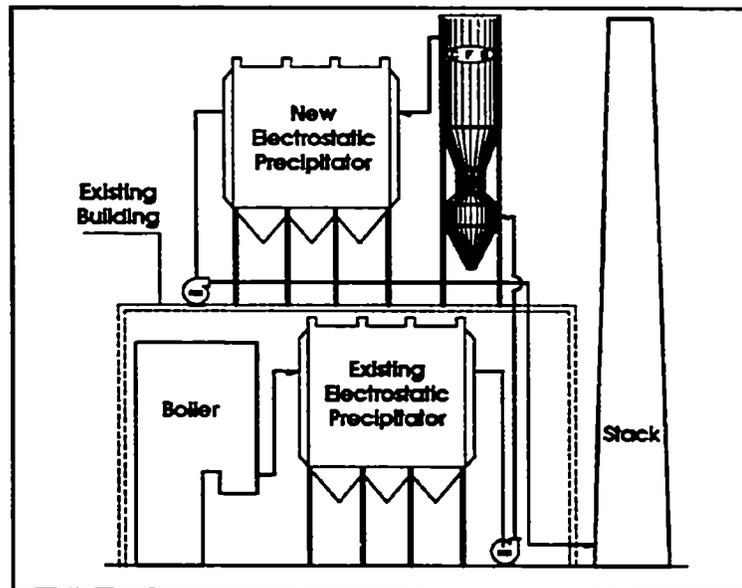


Figure 17. CFB Installed and New ESP Elevated above Existing Boiler and ESP

## COMBINED DeSO<sub>x</sub>/DeNO<sub>x</sub> PROCESS

A combined DeSO<sub>x</sub>/DeNO<sub>x</sub> process which uses one circulating fluid bed is currently being developed. This process can also be used as a single process for either desulfurization or NO<sub>x</sub> reduction.

In the combined process, the CFB reactor is located upstream of the boiler and operates at approximately 725°F. Hydrated lime is used as the sorbent for sulfur oxides and water is not required for this process. The absorption products are mainly CaSO<sub>4</sub> (anhydrate) and approximately 10% CaSO<sub>3</sub>. This is a result of SO<sub>2</sub> oxidation during the NO<sub>x</sub> reduction. Usually, this side reaction would be minimized in DeNO<sub>x</sub> systems because it creates corrosion problems. However, in the combined DeSO<sub>x</sub>/DeNO<sub>x</sub> process, this side reaction is responsible for the desulfurization process.

The DeNO<sub>x</sub> reaction is a selective catalytic reduction which uses ammonia as the reducing agent and a catalyst. The catalyst is a fine powder of the active compound, FeSO<sub>4</sub> x 7 H<sub>2</sub>O, without a supporting carrier. This catalyst was chosen based upon investigations conducted in the laboratory and at a pilot plant.

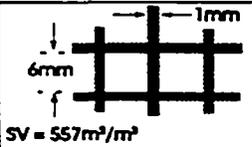
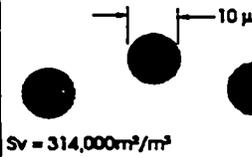
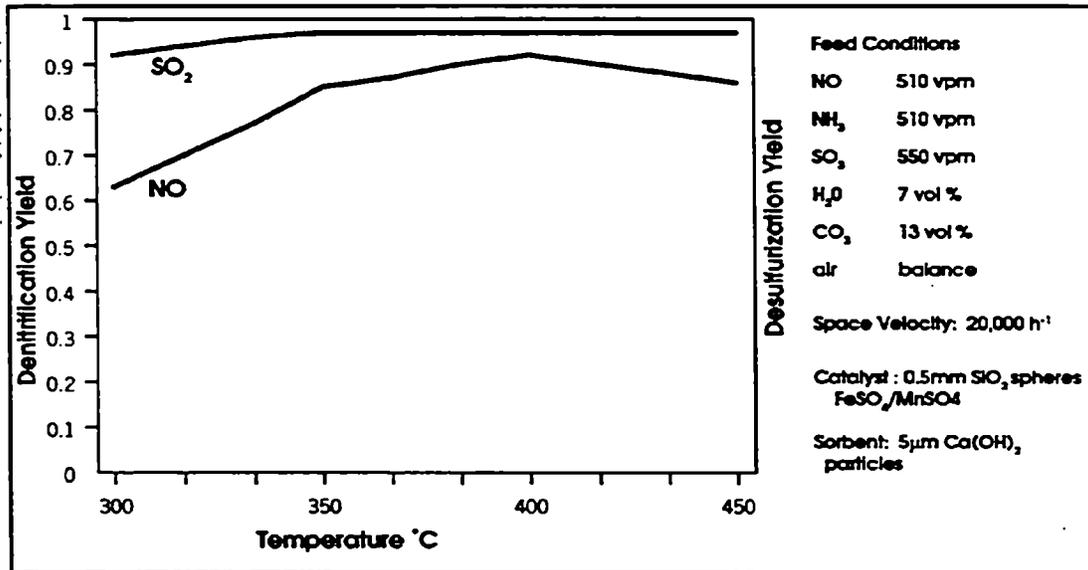
Selective Catalyst Reduction		
$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \xrightarrow{\text{CAT}} 4\text{N}_2 + 6\text{H}_2\text{O}$ $4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \xrightarrow{\text{CAT}} 3\text{N}_2 + 6\text{H}_2\text{O}$		
Catalyst	Support	Active Compounds
 <p>SV = 557m<sup>2</sup>/m<sup>3</sup></p>	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub> MoO <sub>3</sub> WO <sub>3</sub>
 <p>SV = 314,000m<sup>2</sup>/m<sup>3</sup></p>	—	FeO/FeSO <sub>4</sub> MnO/MnSO <sub>4</sub>

Figure 18. Catalyst Comparison

Initial laboratory tests of the combined process were done at the University of Karlsruhe and at Chemtall, a subsidiary of Metallgesellschaft AG and Lurgi AG (2,3,4). Figure 19 shows the results obtained from the laboratory CFB. This CFB used a catalyst with 0.5mm SiO<sub>2</sub> carrier particles at a space velocity of 20,000 h<sup>-1</sup>.



**Figure 19. Test Results from a Laboratory CFB Performing Simultaneous SO<sub>2</sub> and NO<sub>x</sub> Removal**

The pilot CFB system was built at the Rheinisch Westfälische Elektrizitätswerke power station in Dettingen, Germany. Initially, the catalyst used here had a silica or alumina support of 0.5mm (0.0197 inch) and the active compound on the surface of the support. However, during the plant's eighteen month operating period, the active compound without a supporting carrier proved to be the most effective and economical catalyst.

The results from the pilot plant show that fine grained particles offer an advantage over honey-comb catalysts because the particles provide a larger physical surface area. Very thin honey-comb walls with a thickness of 1mm and a pitch of 6mm provide a catalyst surface area of 557 m<sup>2</sup>/m<sup>3</sup>. At an average particle diameter of 10 microns, the fine powdered catalyst obtains a physical surface area of more than 300,000 m<sup>2</sup>/m<sup>3</sup>. If comparable course particles of 50 microns are used, the physical surface area is still 68,000 m<sup>2</sup>/m<sup>3</sup>.

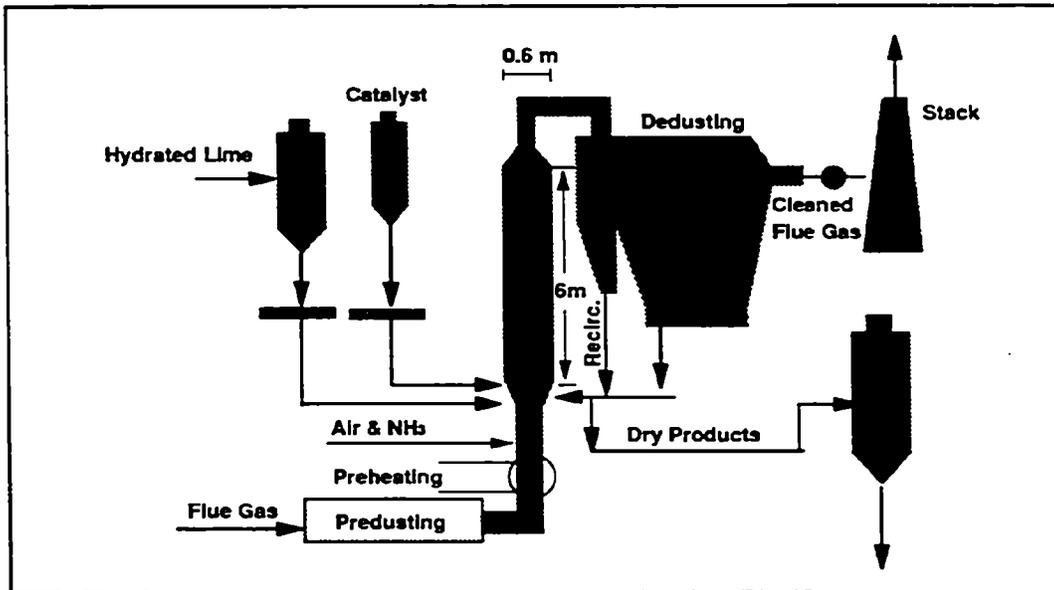


Figure 20. Flow Diagram of DeSO<sub>x</sub>/DeNO<sub>x</sub> Pilot Plant

Figure 20 shows the simplified flow diagram of the pilot plant. The absorber is 600 mm (1.96 ft.) in diameter and 6 m (19.7 ft.) in height. Downstream of the absorber is a two-field electrostatic precipitator for dust collection.

SO<sub>2</sub> concentrations at the pilot plant varied between 450-630 ppm. NO<sub>x</sub> concentrations varied between 170 - 320 ppm (calculated as NO<sub>2</sub>). At a Ca/S-mole ratio of 1.6 to 1.8, 97% desulfurization could be achieved. A NO<sub>x</sub>-reduction rate up to 88% was achieved at a mole ratio of NH<sub>3</sub>:NO = 0.7 to 1. At higher NO raw gas concentrations up to 750 ppm, a DeNO<sub>x</sub> cleaning efficiency of 94% was obtained.

N<sub>2</sub>O could not be detected in the clean gas from the combined DeSO<sub>x</sub>/DeNO<sub>x</sub> process. Ammonia slip values were less than 5 ppm.

Tests conducted at this plant proved that the fly ash loading of the flue gas does not obstruct NO<sub>x</sub>-reduction or desulfurization.

In summary, the features of the CFB process are:

for DeNO<sub>x</sub>:

- the NO<sub>x</sub> removal is higher than 90% at 400°C
- a small particle sized catalyst with simple geometry,
- simple components,
- renewable during operation,
- environmentally acceptable (Fe/Mn),
- constant activity,
- resistant against -SO<sub>2</sub>
- SO<sub>2</sub>- oxidation is a positive additional effect,
- easy handling,
- and lower N<sub>2</sub>O-formation

for desulfurization:

- the SO<sub>2</sub>-removal is higher than 95% at 400°C,
- a small particle sized CaOH<sub>2</sub> sorbent,
- no water injection,
- total SO<sub>3</sub>-removal,
- and no interference between DeNO<sub>x</sub> and DeSO<sub>x</sub> reactions.

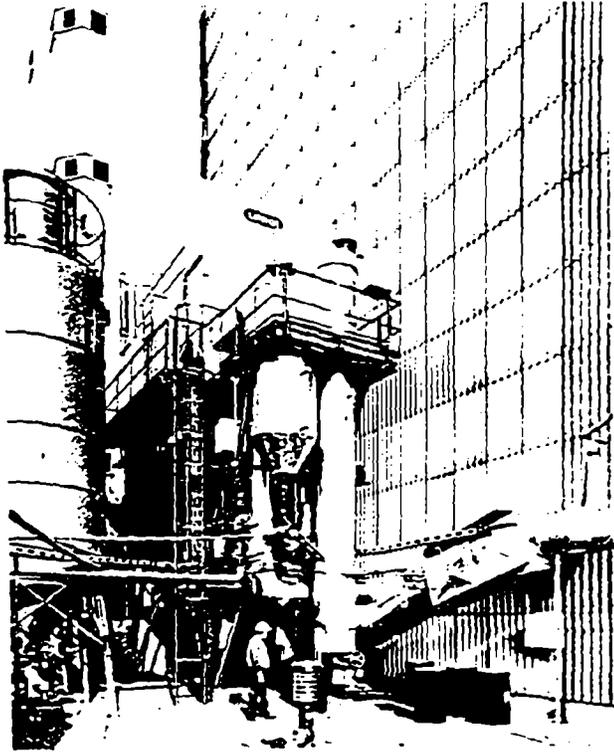


Figure 21. Plant equipped with continuous measuring and recording of raw and clear gas concentrations of NO, SO<sub>2</sub>, CO, O<sub>2</sub>, and NH<sub>3</sub>-slip and continuous feed control for the NH<sub>3</sub>.

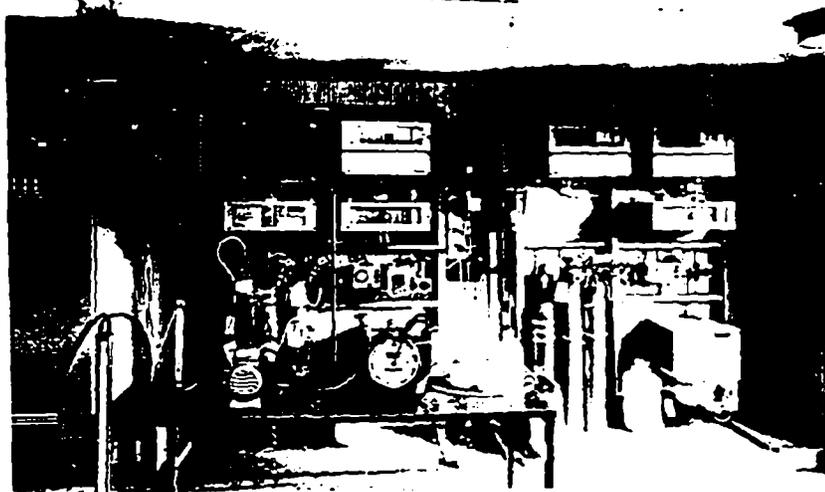


Figure 22. Details of all the additional measuring and control equipment.

## REFERENCES

1. H. Sauer, J.D. Riley, G.Haug. "Operating Experience with a Dry FGD-Plant using a Circulating Fluid Bed at the Lignite-Fired Power Station of PREAG in Borken, F.R.G." Paper presented at the First Combined FGD and Dry SO<sub>2</sub> Control Symposium in St. Louis, MO/USA .October 25 -28, 1988
2. W. Weisweiler. "Umweltfreundliche Entstickungs-Katalysatoren auf Basis Eisen/Mangan Oxid/Sulfat DECHEMA-Jahrestagung 1989 Frankfurt/Main June 01 - 02, 1989
3. H. Sauer, W.Weisweiler, J.D.Riley. "Simultaneous SO<sub>2</sub>- and NO<sub>x</sub>-Removal in the Circulating Fluid Bed" Paper presented at The First International Power Technology Conference, Chicago, Ill, October 31 November 2, 1989
4. W.Weisweiler, E. Herrman, J. Zimmer, H.Sauer. "Der zirkulierende Wirbelschicht Reaktor zur simultaneous trockenen Reinigung von NO<sub>x</sub> and SO<sub>x</sub>-haltigen Feuerungsgasen" Proceedings GVC/VDI-Jahrestreffen
5. R.J. Keeth, P.A. Ireland, P.T. Radcliffe."1990 Update of FGD Economic Evaluations."
6. EPRI Report 1991, Project 1610-6, "Economic Evaluations of Flue Gas Desulfurization Systems."



# **Incorporating Full-Scale Experience Into Advanced Limestone Wet FGD Designs**

**P. C. Rader  
E. Bakke**

**ABB Environmental Systems**



## Introduction

Utilities choosing flue gas desulfurization as a strategy for compliance with Phase 1 of the 1990 Clean Air Act Amendments will largely turn to limestone wet scrubbing as the most cost-effective, least-risk option. It has also become increasingly apparent that employing high efficiency scrubbers on larger, newer plants is the favored alternative for implementing FGD.

The special demands of retrofitting scrubbers into plants affected by acid rain legislation can be effectively met through the use of advanced limestone FGD technology. State-of-the-art single absorber wet scrubbing systems can be designed to achieve:

- SO<sub>2</sub> removal efficiencies in excess of 95%,
- System availabilities in excess of 98%, and
- Byproducts which can be marketed or landfilled.

Further, these objectives can be accomplished at levelized costs which compare favorably to other clean air compliance options.

As a result of varying fuel characteristics, site considerations, and owner preferences, FGD plants for large central power stations are typically custom-designed. In order to avoid the risks associated with new, first-of-a-kind technologies,

utilities have preferred to purchase FGD systems from suppliers with proven utility experience and reference plants as close as possible to the design envisioned. This tendency favors suppliers with broad, diverse experience bases.

Further, as the market for FGD systems is regulatory driven, the demand has shifted geographically in response to national environmental policies. Although limestone wet scrubbing has emerged as the overwhelming choice for SO<sub>2</sub> emission control in coal-fired power stations, the technology has evolved and been adapted to suit local and regional technical and economic situations. Global suppliers are able to benefit from experience and technological advances in the world market.

ABB is a leading supplier of wet FGD systems worldwide having contracted for over 23,000 MW of coal-fired utility capacity (Table 1). With market units in the U.S., Denmark, Italy, Sweden, and Germany active in the design and supply of wet FGD plants, ABB has a unique ability to incorporate knowledge and experience gained throughout the industrialized world to acid rain retrofit projects in the U.S.

This paper describes the design of advanced limestone wet scrubbing systems for application to acid rain retrofits. Specifically, the evolution of advanced design concepts from a global experience base is discussed.

## Designing for High Efficiency

### Design Criteria

Unlike previous SO<sub>2</sub> emission regulations which provided no incentive to scrub beyond the legally permitted level, the 1990 Clean Air Act Amendments have created a system of allowances and credits which can be used to offset emissions at other stations, banked, or sold. Hence, the economics of FGD system design depend on the relationship between the marginal cost of additional scrubbing capacity, the value of emission allowances, and a utility's future needs for these allowances.

While there is considerable speculation concerning the various economic tradeoffs a clear pattern of increasing SO<sub>2</sub> removal efficiencies is emerging. Whereas plants purchased under the NSPS provisions of the 1979 Clean Air Act Amendments rarely required removal efficiencies in excess of 90%, acid rain retrofit plants are typically designed for a minimum of 95%. This upward pressure on SO<sub>2</sub> removal efficiencies has challenged designers to develop approaches to maximize efficiency while minimizing operating costs. At the same time, reliability cannot be sacrificed.

### High Efficiency Spray Tower Absorbers

The single loop, countercurrent spray tower has been proven to be the most cost effective and reliable device for removal of sulfur dioxide from coal-fired utility flue gases. This is demonstrated by the fact that spray tower absorbers have predominated in FGD markets throughout the world. In fact, since early 1990 about 80% of world-wide wet FGD orders (totalling 22,500 MW) have been awarded to spray towers. Advances in process design, control systems, materials of construction, and operating philosophies have enabled countercurrent spray towers to maintain their competitive edge over competing technologies such as packed or tray towers which tend to increase operational risks in exchange for potential marginal reductions in operating cost.

Although many aspects are weighed in the design of spray tower absorbers for high efficiency acid rain retrofits, three very critical considerations are L/G selection, gas/liquid contact, and power consumption. The following paragraphs will discuss these issues in more detail.

### L/G Selection

The ratio of the quantity of slurry used to

treat a given quantity of flue gas is arguably the single most significant design parameter in limestone wet scrubbing. L/G impacts capital costs due to its relationship to spray system design and operating cost due to its effect on energy consumed by the recycle pumps.

Table 2 outlines the effect of a number of design parameters on the liquid-to-gas ratio selection for both high and low sulfur applications. The relationship between many of these parameters and the L/G is straightforward and easily understood. For example, there is little doubt that increasing the design removal efficiency will result in a higher L/G requirement, or that lowering the pH of the spray slurry will require a higher L/G. The effects of droplet size, bank spacing, and tower height are commonly misunderstood and deserve further discussion.

### Droplet Size

The relationship of spray droplet size to removal efficiency or L/G depends on the SO<sub>2</sub> concentration in the flue gas. At high concentrations, the overall absorption process is limited by the availability of liquid phase alkalinity to neutralize the absorbed SO<sub>2</sub>. Thus, factors such as the slurry pH, the presence of buffer additives, or the limestone grind are relatively more important in determining the overall absorption rate.

At lower gas phase SO<sub>2</sub> concentrations, more than sufficient alkalinity is generally present to neutralize the absorbed SO<sub>2</sub> and, consequently, the limiting step in the absorption process becomes the interfacial area available for SO<sub>2</sub> transfer. Hence, droplet size has a relatively larger effect on removal efficiency and L/G selection in low sulfur applications.

In advanced limestone systems, the nozzle design and operating pressure are selected to provide the optimum droplet size for the design sulfur dioxide regime. While most acid rain retrofit applications call for nozzles with capacities of 250-400 gpm, ABB has commercial experience with nozzles ranging from 125 to 850 gpm.

Improved hollow cone nozzle designs are capable of providing the required atomization and spray pattern characteristics at pressures as low as 7-8 psi. Consideration may be given to utilizing two or more nozzle configurations in high sulfur

applications. For example, low energy nozzles may be employed in the lower stages where droplet size is less critical due to the higher sulfur concentrations, and higher pressure nozzles with smaller droplets in the upper stages where the SO<sub>2</sub> concentration is lower.

#### *Tower Height/Bank Spacing*

There currently exists significant confusion concerning the effect of tower height and spray bank spacing on SO<sub>2</sub> removal efficiency and L/G selection. Some investigators have conducted experiments which have led them to conclude that a strong dependency exists between overall tower height and removal efficiency. Were this to be true, it would suggest that greater spacing between spray banks and, hence, taller towers are preferable.

In general, the conclusion that tower height exhibits a strong effect on efficiency resulted from experiments in which single spray banks at different elevations were placed in service. The removal efficiency was then recorded with different elevations in operation. Significantly improved performance was noted with higher elevations in service. Neglected in this analysis is the fact that gas/liquid contact conditions in the upper elevations are more favorable due to development of more uniform gas flow distribution.

Figure 1 depicts actually operating data from full-scale ABB installations in which multiple elevations were in operation. In this scenario, which attenuates non-uniformities in gas flow distribution and more correctly simulates actual operation, the effect of tower height can be seen to be minimal.

Hence, spray tower absorbers in advanced limestone scrubbing systems can be quite compact in size. In addition to the obvious capital cost savings associated with compact towers, retrofitability is enhanced. ABB spray towers are designed for 5-6 feet spacing between spray elevations depending on physical constraints of the header and support systems.

#### *Gas/Liquid Contact*

The demand for SO<sub>2</sub> removal efficiencies in excess of 95% requires very effective contact between the flue gas and the spray slurry. Sneakage or under-treatment of even a small percentage of the gas can cause removal efficiencies to fall below the anticipated level. Figure 2 demonstrates the effect of non-ideal gas/liquid contact. In Case A, the curve indicates that despite large increases in L/G no

further improvement in removal efficiency occurs. Simplistically, about 5% of the flue gas is not being treated properly in this example. In Case B where gas/liquid contact was improved by utilizing different nozzles it can be seen that extremely high efficiencies can be obtained at reasonable liquid-to-gas ratios with spray tower absorbers in limestone FGD systems without the use of buffer additives.

Key factors related to efficient gas/liquid contacting in spray tower absorbers include gas inlet design and spray system design.

#### *Gas Inlet Design*

The two principal process considerations for proper gas inlet design are:

- Uniformity of gas distribution at the absorber inlet flange, and
- Sufficient flue gas momentum entering the quench zone.

Uniform gas distribution at the absorber inlet flange is clearly important to obtaining the desired uniformity in the spray zone. Of particular importance are side-to-side variations which would result in higher gas velocities on one side of the tower than the other. ABB experience has demonstrated that variations in excess of 15% RMS are detrimental to tower performance. The required uniformity is obtained by the placement of turning vanes and perforated plates in the inlet duct and confirmed by gas flow modelling.

ABB also employs a sweep bottom design to improve performance and minimize inlet duct deposition. The sweep bottom inlet is designed to divert a slightly higher fraction of the incoming flue gas to the inlet duct bottom at a velocity which is higher than the mean. By doing so, splash back of slurry and gas recirculation which could lead to solids deposition in the wet/dry interface area are minimized. Further, this design assists in obtain good front-to-back gas distribution in the tower.

In addition to uniform distribution entering the tower, it is important that the flue gas have sufficient momentum to insure turbulent contacting and penetration of the incoming gas into the quench zone. Both commercial experience and wet flow modelling studies have indicated that high efficiency spray towers should have inlet gas velocities of 2700-3000 fpm. This feature along with the deflector baffle (rain hood) over the inlet prevent build up of

deposits which could adversely affect performance or service life of materials.

#### *Spray System Design*

Selection and placement of spray nozzles is of critical importance in high efficiency spray towers. To assist designers in laying out spray systems, ABB has developed a computer model which analyzes and provides a pictorial representation of spray flux and pattern overlap. Given the spray nozzle characteristics (e.g. spray angle, radial spray distribution, etc.) and the header arrangement, the model determines the degree and number of overlaps at a predetermined distance from the nozzle tip.

Figure 3 is a typical example of the spray coverage achieved by ABB designs. Generally, overlaps on the order of 600-700% at a distance of 3 feet are achieved with 250-400 gpm hollow cone nozzles.

Having achieved the desired spray coverage from a single spray elevation, the overall gas/liquid contact in the tower is further improved by staggering the headers on adjacent elevations (Figure 4). Staggering the headers insures full development of the spray pattern from the nozzles and prevents the formation of passages for flue gas sneakage.

The impact of spray system design is graphically demonstrated by Figure 2. The principal difference between the performance between Case A and Case B is an improvement in spray coverage. In Case A, poorly designed nozzles resulted in non-uniform spray pattern development and, consequently, substantial gas sneakage. When the nozzles were replaced in one of the absorbers, side-by-side comparisons showed substantial performance improvement as demonstrated by the curve for Case B.

Thus, ABB experience has shown that with proper inlet and spray system design SO<sub>2</sub> removals in excess of 98% are readily achievable without the use of buffer additives with limestone spray towers. This level of performance when coupled with the inherent simplicity and reliability of countercurrent spray towers are highly desirable in advanced wet scrubbing systems.

#### *Power Consumption*

Because of the inherently low gas-side pressure drop associated with spray tower absorbers, a typical breakdown of power consumption by component in an advanced FGD system on a 2-3%

sulfur application would be as follows:

<u>Component</u>	<u>Percent of Total Power</u>
Recycle (spray) pumps	50%
Booster fans	20%
Oxidation blowers	10%
Others	20%

For this reason considerable attention has been given to minimizing recycle pump power consumption in advanced limestone FGD systems.

The principal determinants of recycle pump power are L/G, tower height, and nozzle pressure. Concepts used to optimize these variables are discussed in the following paragraphs:

#### *Liquid-to-Gas Ratio*

Under typical U.S. utility purchasing practices, the owner and its consultants define the basis for system design. By specifying variables such as the fuel composition, required efficiency, and reagent type, the supplier is provided with the basic requirements of the process design.

Computer models based on full-scale, commercial experience are the principal tools used by ABB process engineers to select the proper L/G for a given application. With the merger of Flakt, Peabody Process Systems, and Combustion Engineering into ABB Environmental Systems, a single data base of performance and operating data unparalleled in the industry has been created. This data has been used to calibrate performance models which allow L/G to be selected and optimized as a function of inlet SO<sub>2</sub> concentration, removal efficiency, buffer additives, limestone characteristics, tower design, and liquid phase chemistry. Table 3 summarizes the breadth and depth of ABB commercial experience with variables affecting SO<sub>2</sub> absorption.

#### *Tower Height/Nozzle Pressure*

One important component in determining the total discharge head of the recycle pumps and, hence power consumption, is the height from the surface of the recycle tank slurry to the nozzle tip for a given spray elevation (dimension *h* in Figure 5). In ABB advanced limestone scrubbers this parameter is minimized by compact tower designs based on proven commercial experience. All aspects of the design including the inlet duct geometry and aspect ratio,

height of the first spray elevation above the top of the inlet, and the spacing between spray elevations have been confirmed by full-scale operating experience. Typical values for key dimensions are shown in Figure 5.

Spray nozzle pressure drop is the other major contributor to recycle pump energy consumption. Process considerations which enter into nozzle selection include:

- Droplet size distribution
- Uniformity of spray distribution
- Uniformity of gas distribution
- Pluggage potential

ABB has determined that hollow cone nozzles operating at 7-8 psi provide the optimum balance between power consumption and atomization for most limestone scrubbing applications.

#### **Commercial Experience Base**

From the discussions above, it can be seen that the design of high efficiency absorbers for coal

-fired utility applications is a complex task involving numerous process and mechanical considerations. While theoretical models developed from mass transfer theory are very useful for predicting and extrapolating tower performance, it is absolutely critical that these models be rigorously calibrated with full-scale, commercial operating data.

Since ABB's first spray tower absorbers were placed in service in the U.S. in the late 1970's to present day, an extensive program of testing and performance characterization of commercial installations has been used to create a detail computerized database consisting of over 140 individual records. These tests have been conducted over a broad range of such key variables as sulfur dioxide inlet concentration, removal efficiency, L/G, spray tower configuration, nozzle type, gas velocity, chloride concentration, and limestone stoichiometry.

The data generated by these tests has been used to calibrate both internally developed design models and EPRI's FGD PRISM. The predictive capability afforded by these models allows ABB to produce highly optimized designs for its commercial offerings.

## Designing for High Availability

### Factors Affecting Availability

FGD availability is generally discussed in terms of the percentage of hours that the system is available for operation over a given period. Whereas first generation FGD plants often exhibited periods of very low availability, advances in design, materials, and operational philosophies have enabled more recently installed systems to achieve availability records which often exceed 98-99% on an annual basis. An ABB Flakt FGD system in Denmark at Elkraft's Amager Power Station Unit 3 (Figure 6) has recently completed a year's operation at 100% availability. This is even more remarkable considering that the 250 MW installation operates 8,000 hours per year at load factors as high as 80% with a single absorber train (i.e. no spare).

ABB has determined that FGD system reliability is primarily influenced by the following factors:

- Design and sparing philosophy (e.g. process design, oxidation, use of additives, materials of construction, component selection, etc.)
- Service conditions (e.g. fuel sulfur and chloride content, base vs. swing load, fly ash levels, etc.), and
- Operation and maintenance (e.g. control of key process parameters, preventive maintenance, etc.).

While a detailed discussion of factors affecting FGD system availability is beyond the scope of this paper, it is useful to consider several characteristics of advanced wet scrubbing systems and their relationship to availability. Of particular interest are issues such as the need for spare absorbers; operation in forced, natural, and inhibited oxidation modes; the use of chemical additives; and, process control and operation.

### Spare Absorber Vessels

The NSPS provisions of the 1979 Clean Air Act Amendments essentially mandated that FGD systems be equipped with spare absorber modules. While the cost associated with spare absorber modules is significant, considerable operational flexibility is achieved. FGD system operators have

developed effective operation and maintenance procedures based on rotating absorbers into and out of service on a periodic basis. As a result of this and improvements in design and materials, U.S. owners of limestone wet scrubbers recorded availabilities at or near 100% on an annualized basis.

The 1990 Clean Air Act Amendments however provide no specific incentives for the purchase of spare absorbers. In both Europe and Japan where this has always been the case, single train FGD systems have been installed on steam generators as large as 700 MW. Although there has been some debate as to whether this technology is directly translatable to U.S. high sulfur coal burning power stations with high load factors, ABB believes that single train systems will become the preferred choice for most applications in the U.S. as well. In the short term, some utilities are choosing an intermediate course in which multiple modules with no spare is specified. This permits partial load operation in the event of an emergency scrubber outage.

Economic studies including internal ABB analyses have confirmed that 10-20% reductions in Total Plant Cost (TPC) for a 500 MW acid rain retrofit can be realized by replacing 3 x 50% capacity trains with a single absorber. In addition to the obvious savings in absorber and flue gas handling system costs, substantial reductions and simplification in piping, controls, and electrical subsystems contribute heavily to the overall savings. Provided that availability of single absorber FGD systems is equal to or better than multiple module systems with spares, the economic benefits of the single train approach are clear.

Design of high reliability single train FGD systems requires superior design in several key areas. ABB advanced limestone FGD systems incorporate features such as the following to maximize availability:

- Absorber inlet ducts are constructed of highly corrosion resistant materials such as C-276 (solid plate or lining).
- Sweep bottom inlets with sufficient flue gas momentum to prevent recirculation are employed to eliminate deposition in the wet/dry interface area.

- Hollow cone nozzles with large free passage minimize the potential for pluggage.
- Proven multi-stage mist eliminator with top and bottom wash system capability are provided to minimize the need for manual cleaning.
- Alloy or rubber-lined spray zones insure low maintenance and excellent corrosion/erosion resistance.
- Spare absorber recycle pumps insure continued compliance with emissions regulations.

Features such as those described along with the owner's commitment to a comprehensive operation and maintenance program will permit advanced limestone FGD plants to achieve the high levels of availability required by modern power stations.

#### Oxidation Mode

FGD systems are operated in one of three modes with respect to oxidation.

- **Natural Oxidation** - Oxidation is uncontrolled. Some oxidation (typically 10-20% for medium to high sulfur coals) occurs due to the presence of oxygen in the flue gas. A mixture of calcium sulfite and calcium sulfate is formed in the slurry solids.
- **Forced Oxidation** - Air is injected into the absorber recycle tank to achieve oxidation percentages approaching 100%. High purity calcium sulfate dihydrate (gypsum) can be produced in such systems. Due to the production of large crystals, high capacity dewatering systems can be designed.
- **Inhibited Oxidation** - Oxidation inhibitors such as thiosulfate ion are used to minimize oxidation. Operation in this mode can result in the process operating subsaturated with respect to gypsum which has been shown to be beneficial from the standpoint of scaling and deposition. In addition, thiosulfate addition has been shown to improve dewatering characteristics of the slurry solids in comparison to natural oxidation

processes.

ABB experience with wet FGD systems producing gypsum is summarized in Table 4.

Although operation in any of these three modes is possible, ABB recommends that advanced limestone FGD systems be designed for either forced or inhibited oxidation. Experience has shown that fewer problems with scaling and deposition particularly in the mist eliminator area occur when oxidation is either forced or inhibited.

From an overall cost standpoint, studies have shown that forced oxidation is generally more cost-effective than natural oxidation. However, the margin is small enough that the choice between forced and inhibited oxidation is primarily dictated by waste product considerations. Gypsum production from forced oxidation systems offers considerable flexibility in that the product can be either sold or landfilled. Although disposal options are limited to landfill with inhibited oxidation, simplicity of operation, extremely clean operation, and the ability to co-dispose flyash make inhibited oxidation with byproduct fixation an alternative.

#### Use of Additives

Several types of chemical additives have been employed in advanced limestone scrubbers. Organic buffers are used to enhance SO<sub>2</sub> removal performance and oxidation inhibitors are used to minimize gypsum scaling potential. In addition, crystal growth modifiers and corrosion inhibitors have been investigated.

ABB experience with performance additives is summarized in Table 5. The roles of buffer additives and oxidation inhibitors in advanced limestone FGD systems are discussed in the following paragraphs.

#### *Buffer Additives*

The addition of modest amounts of organic acids such as formic, adipic, and dibasic acid cause substantial improvement in SO<sub>2</sub> removal efficiency. Figure 7 presents operating data from a full-scale installation at various DBA concentrations. The improvement in removal efficiency is due to the increased levels of soluble alkalinity caused by the dissociation of the DBA. Although the removal efficiency benefits are well documented both in terms of process design and economics, the reliability aspects of operation with buffer additives are often overlooked.

*First*, the addition of buffer additives allows the process to be operated at a lower pH than a corresponding non-buffered system. This has been shown to improve availability by promoting cleaner operation in the mist eliminator zone. Further, the presence of the buffer attenuates pH swings as a result of a mismatch between limestone feed rate and SO<sub>2</sub> absorption rate (e.g. during load changes or coal sulfur swings). Again, this tends to promote cleaner operation.

*Second*, use of buffer additives in systems designed for non-buffered operation may allow the desired removal efficiency to be achieved with fewer spray elevations in service. The corresponding benefits are reduced duty factors on spray pumps, headers, nozzles, etc. as well as increased operating flexibility.

*Third*, in closed loop operation with high concentrations of dissolved solids such as chlorides, the use of organic acid additives are extremely cost effective due to improved limestone solubility and reduced scaling potential as a result of low pH operation.

#### *Oxidation Inhibitors*

As described previously, thiosulfate ion either added as the sodium salt or generated in situ by elemental sulfur addition has been shown to dramatically reduce the oxidation of sulfite to sulfate in limestone scrubbers. If the level of oxidation and, hence, the rate of sulfate formation can be depressed sufficiently, the process can be operated subsaturated with respect to gypsum.

The principal benefit of this mode of operation is the elimination of gypsum scaling potential. Inhibited oxidation systems are therefore less subject to deposition and fouling of absorber internals as a result of process upsets. As the byproduct cannot be marketed, some loss in flexibility with respect to solid disposal results.

Advanced limestone FGD systems can be designed for operation with or without the use of chemical additives. The positive economics of organic buffer addition have been thoroughly documented. Taken to the fullest extent, substantial reductions in both capital and operating costs are possible. Currently, most systems are designed such that the required removal efficiency over the range of fuels is achievable without the use of organic buffers. The buffer additives are then employed primarily to

reduce operating costs and increase removal efficiency.

The cost benefit of oxidation inhibitors is more difficult to judge in the specification or design stage. The increase in availability resulting from subsaturated operation has not been sufficiently documented to enable reliable predictions to be made on a generic basis.

#### **Process Control and Operation**

Successful operation of single train limestone wet FGD systems has been widely demonstrated. As discussed previously, ABB's installation at the Amager Power Station in Denmark has achieved annual availabilities of up to 100%. A significant, if not the major, contributor to high FGD system availability relates to quality of the operation and maintenance. Production of wallboard quality gypsum which is the norm in European and Japanese installations requires close attention to process control in order to avoid product rejection. Hence, critical variables such as limestone stoichiometry, pH, chloride concentration, and slurry solids content are carefully monitored and controlled. In addition to minimizing the amount of off-spec gypsum produced, control of these variables contributes significantly to excellent availability generally observed in European FGD installations.

ABB believes the following O&M issues to be of key importance in achieving high availability in advanced limestone wet FGD systems:

- Control of pH, percent solids in the recycle tank, and chloride concentration are critical. Frequent calibration and redundant instrumentation are necessary. Control of chloride concentration to 30,000 ppm or less is desirable.
- Clean mist eliminator operation is achieved by operation at stoichiometries of less than 1.07 and by proper use and maintenance of washing systems.
- Prior to start-up, the recycle tank should be charged with gypsum seed crystals (except for inhibited oxidation systems) or stored slurry from previous operation. The recycle tank should be "lean" with respect to limestone concentration (i.e. limestone should not be overfed).

- Operability and maintainability must be seriously considered in the design stage. For example, sufficient access and lifting equipment to service all key components must be provided; key instruments which require frequent calibration should be easily accessible (at grade elevation where practical); automated flushing and draining of slurry piping systems should be provided, etc.
- Operator training programs with on-site support from the process supplier prior to commissioning and periodically thereafter are extremely important.

In recognition of the importance of O&M

issues to reliable operation, ABB sponsors FGD User's Conferences for owners of its systems. Operations and maintenance personnel from all U.S. and European FGD installations are invited to attend a three-day conference held every 12-18 months. Presentations and workshops related to reliability, O&M procedures/training, new technical developments, etc. are discussed in an open forum. These sessions have proved highly effective in providing a better understanding of O&M problems and issues to ABB engineers as well as a forum for exchange of ideas among the owner/operators of ABB systems. ABB is committed to continuing these conferences as a means of improving the design and reliability of its wet limestone scrubbing systems.

## Advanced Limestone FGD System Costs

### Advanced Technologies

The Total Plant Cost (TPC) for retrofitting FGD equipment on a coal-fired power station can reach \$200-250/KW according to a recent update of the Electric Power Research Institute's (EPRI) landmark economic study of FGD technologies. These figures underline the importance of cost in the selection of high efficiency wet scrubbing as a compliance option. Fortunately, however, advances in technology and a combination of economic and market conditions have caused FGD system costs to remain quite stable and, in fact, decline in recent years.

The following paragraphs summarize the results of an economic comparison among three alternative limestone WFGD designs. The alternatives are defined as follows:

*Conventional* refers to the limestone forced oxidation system used by EPRI in comparing costs of various FGD alternatives. The economics generated by EPRI for this technology serve as the benchmark for comparing advanced technologies.

*Advanced* refers to present day ABB designs featuring single absorber trains, high technology spray tower designs, and state-of-the-art materials. Costs are representative of current commercial offerings.

*Third Generation* refers to potential future advances in wet limestone FGD technologies. While still under development, the technology described as third generation represents possible future directions for performance improvement and cost reduction.

The plant design and economic evaluation criteria, process design, total plant investment, and operating costs for these alternatives are summarized in Tables 6, 7, 8, and 9 respectively and discussed in the following paragraphs.

### Plant Design and Economic Criteria

The plant design and economic criteria and methods (Table 6) used in this analysis are identical

to those used by EPRI for retrofit systems. These criteria were selected because they form the basis for a large body of work performed previously by EPRI and others. Hence, the figures generated in this analysis can be compared to other technologies in the EPRI database.

The analysis is based on a mid-west (Kenosha, WI) 300 MW power plant burning 2.6% sulfur fuel. The plant annual load capacity is assumed to be 65% and, being a retrofit on an existing power station, a plant life of 15 years is used in the analysis.

Capital and operating costs used by EPRI for the limestone forced oxidation process were used as the base (Conventional) case for this analysis. Cost estimates for the Advanced and 3rd Generation processes were generated on the basis of internal estimates. These costs were annualized on the basis of the economic criteria presented in Table 6.

All major operating costs are included on the basis of estimates for consumables and labor. The cost of consumables such as power, limestone, water, etc. are based on actual estimates of the performance and current costs. O&M labor costs were developed from estimates of the numbers of operations and maintenance personnel required on a per shift basis.

Other costs such as A/E fees, general facilities work, and project contingencies were also developed in accordance with the criteria and methods developed in the EPRI study.

### Design Comparison

The base (Conventional) case assumes a limestone forced oxidation system designed to remove 90% of the incoming sulfur dioxide (Table 7) using 3 x 50% capacity absorbers (i.e. 2 operating/1 spare). The process uses thickeners and vacuum filtration to produce gypsum for sale or disposal. The technology described in the Conventional case is typical of that offered in the late 1980's.

The principal differences between the Conventional and Advanced design are as follows:

- The advanced design employs a single absorber train.
- Improvements in spray tower technology (i.e. lower power consumption, compact

design, etc.) have been included.

- Removal efficiency has been increased to 95%.

The Advanced design is considered typical of current offerings in the industry.

The 3rd Generation design extrapolates current designs to project potential cost savings due to further improvements in absorber/mist eliminator design. These improvements which are still under development are expected to produce savings in the design of Phase 2 acid rain retrofits and new plant applications. In addition, the 3rd Generation system is designed to take full advantage of the use of chemical additives to enhance performance.

#### Economic Comparison

A comparison of the Total Plant Investment (TPI) for the three processes is presented in Table 8. As can be noted, Total Process Capital (TPC) reductions in the range of 15-20% are achieved by the Advanced technology when compared to the Conventional. These savings are primarily due to the impact of utilizing a single absorber train in the Advanced process. Savings are realized in absorbers, ductwork, piping, control, and electrical subsystems. Further savings are realized in the 3rd Generation system as a result of more compact absorber design and reduced spray system costs associated with the

use of organic acid buffers to enhance SO<sub>2</sub> removal. The TPC cost savings are reflected in proportional reductions in General Facilities, Contingencies, etc.

The cost reductions noted in the Advanced and 3rd Generation technologies occur despite the increase in design SO<sub>2</sub> removal efficiency (i.e. 95% and 98% vs. 90% for the Conventional process). In actual, practice ABB feels that the observed savings may not be quite as dramatic as indicated by this analysis. The costs attributed to the Conventional technology are probably somewhat higher than the market price due to conservatism in the original estimate and the presence of competitive market pressures.

A similar comparison of Operating Costs was performed and is presented in Table 9. Again, substantial savings are seen in the Advanced and 3rd Generation cases when compared to the Conventional. Annual O&M Cost savings result primarily from reductions in power consumption. Improvements in spray tower technology and, in the 3rd Generation case, the use of organic acid buffers contribute to substantially lower energy consumption in the pumping systems. Total Operating Cost savings in the Advanced and 3rd Generation result from the Annual O&M Costs savings as well as reduced Fixed Charges. Again, these savings result despite the improved SO<sub>2</sub> removal efficiencies offered by the Advanced and 3rd Generation technologies.

## Summary

Although modern wet limestone scrubbing has been in existence for nearly 30 years, evolution of the technology continues. The earliest utility FGD systems were based on designs adapted from wet dust collector technology and the chemical process industry. Often these systems attempted to remove SO<sub>2</sub>, calcined limestone, and fly ash in a packed or tray tower. A lack of understanding of the process and mechanical design requirements resulted in poor component performance; selection of unsuitable materials of construction; scaling/plugging of absorber internals and piping; and, numerous other O&M problems. These problems understandably lead to poor performance and availability of FGD equipment.

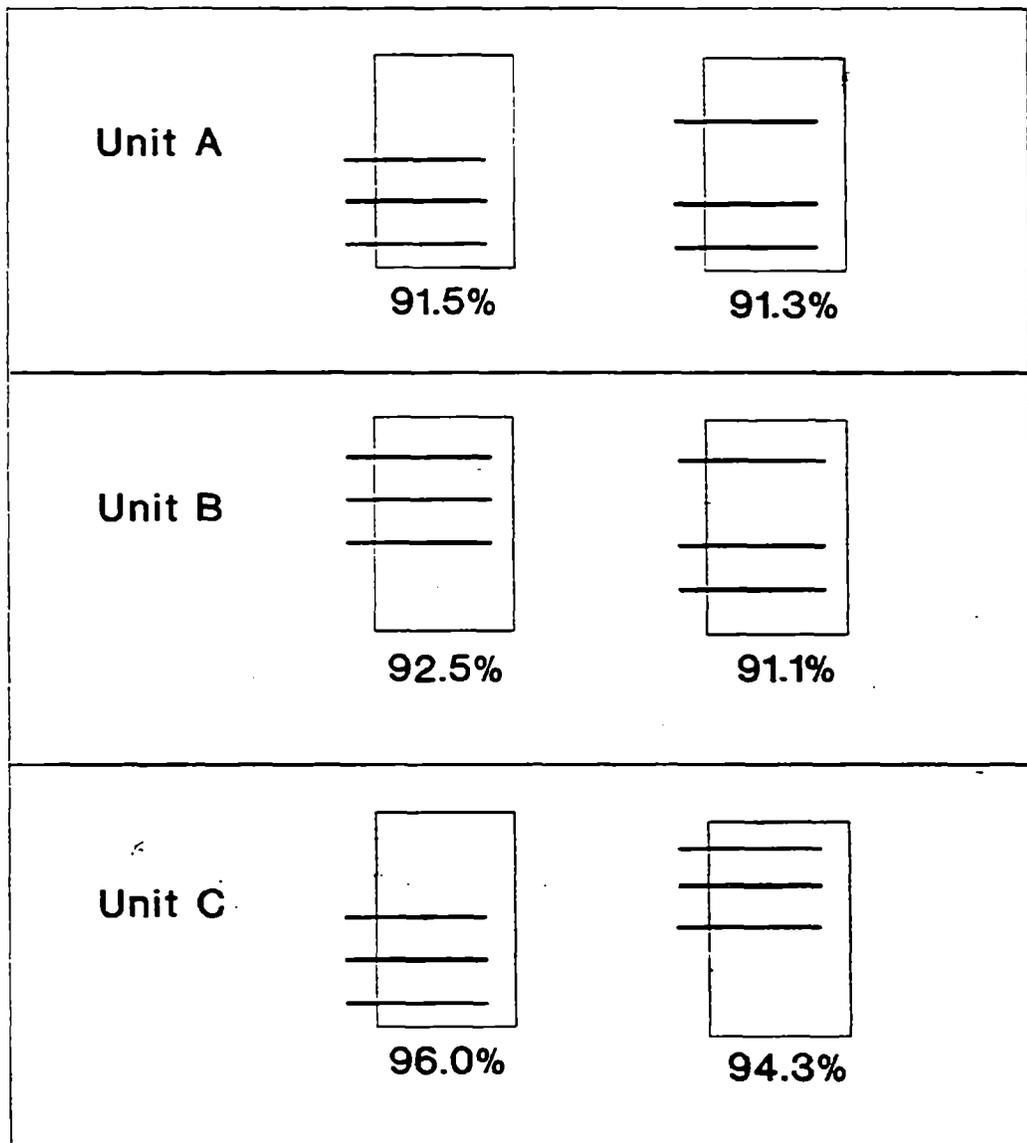
During the early and mid 1970's, experience with commercial installations coupled with R&D programs conducted by suppliers and organizations such as EPA and EPRI contributed significantly to improved performance and reliability in limestone wet scrubbers. Among other advances, the spray tower was adopted as the preferred absorber design due to its inherently low pluggage potential and low power consumption. Improved materials of construction and additional application experience reduced the incidence of corrosion, erosion, and general failures. The availability of more accurate

and reliable instrumentation permitted better process control. Plant operations and maintenance personnel developed O&M experience bases which allowed the development of standard policies and procedures aimed at high availability operation.

As utility wet scrubber technology prepares to enter its 25th year it continues to evolve in response to industry needs, technological advances, and competitive pressure. In the U.S., the concept of high efficiency, single train, multi-bank spray towers treating high sulfur flue gases while producing either marketable or landfill gypsum is expected to be the preferred choice for many acid rain retrofit projects. In Europe where many of these particular design features are already commonplace, concentrated efforts are underway to reduce capital and operating costs to achieve competitiveness in local and world markets.

Because of its global presence, ABB is active in both of these areas. Through regularly scheduled internal technical meetings, standardization of process and mechanical design, and an overall commitment to the world FGD market, ABB is able to benefit from knowledge and experience gained throughout the industrialized world. This unparalleled capability is applied to produce reliable, cost-effective wet limestone FGD designs for U.S. acid rain projects.

**Figure 1**  
**Effect of Tower Height**

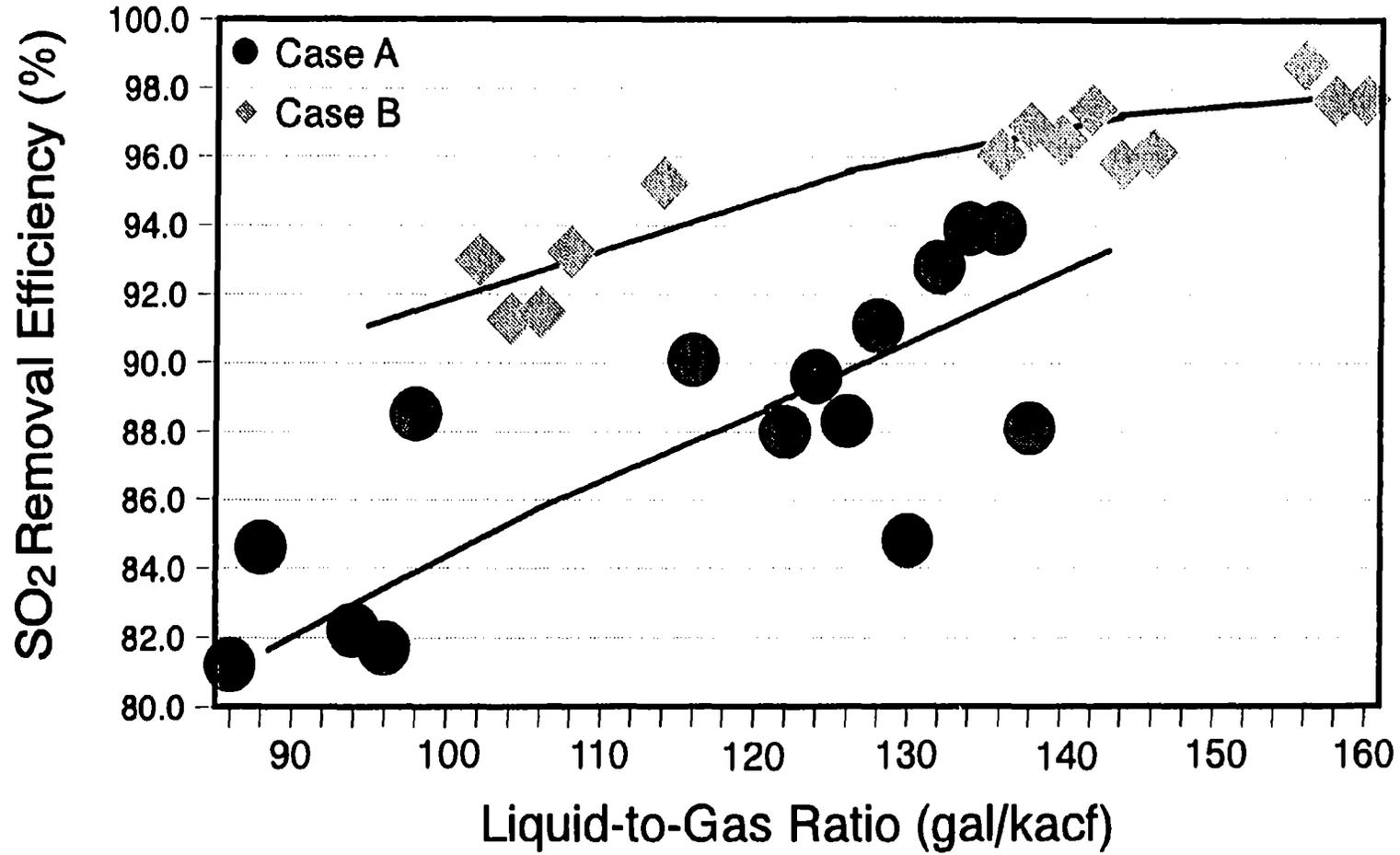


Spray Level in Service  
Spray Level Not in Service

Figure 2

# Gas Liquid Contact

8A-56



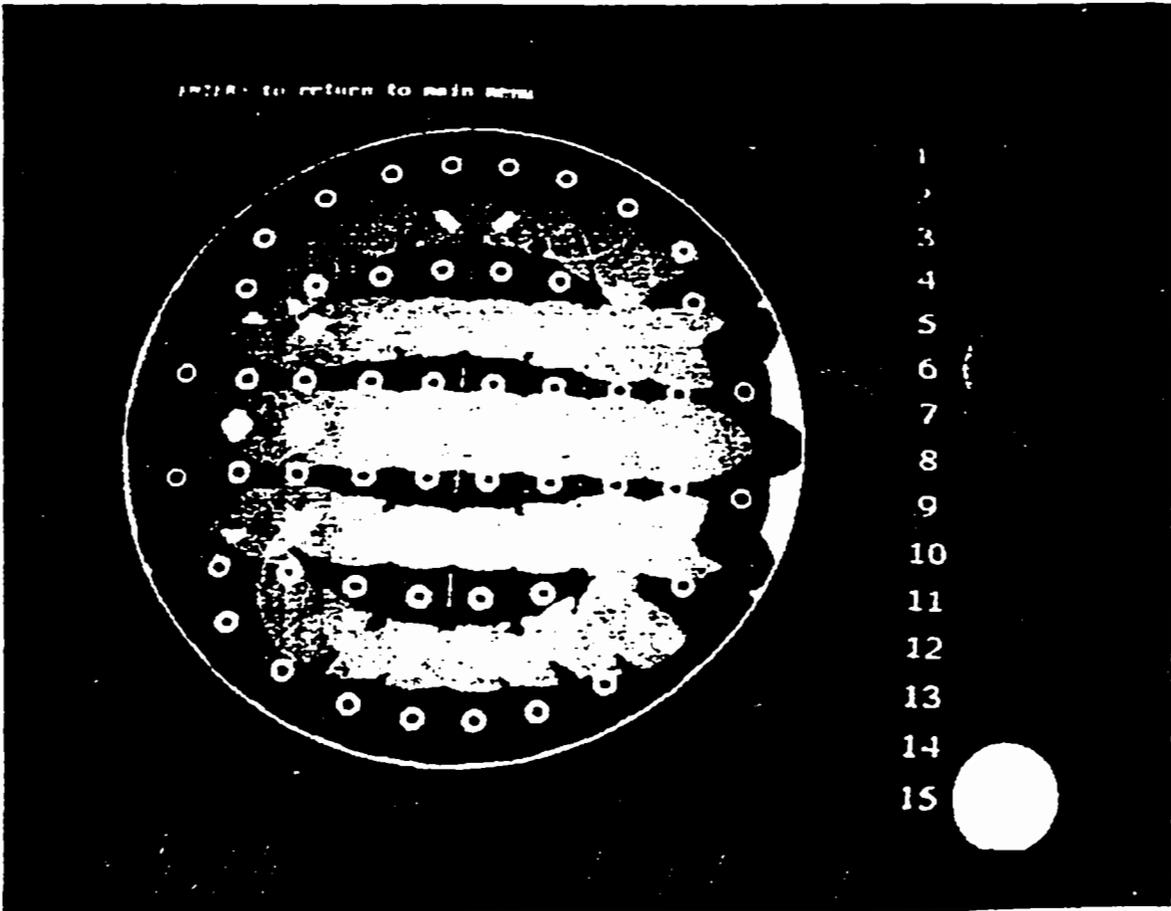


Figure 3  
Computer Simulation of  
Absorber Spray Pattern

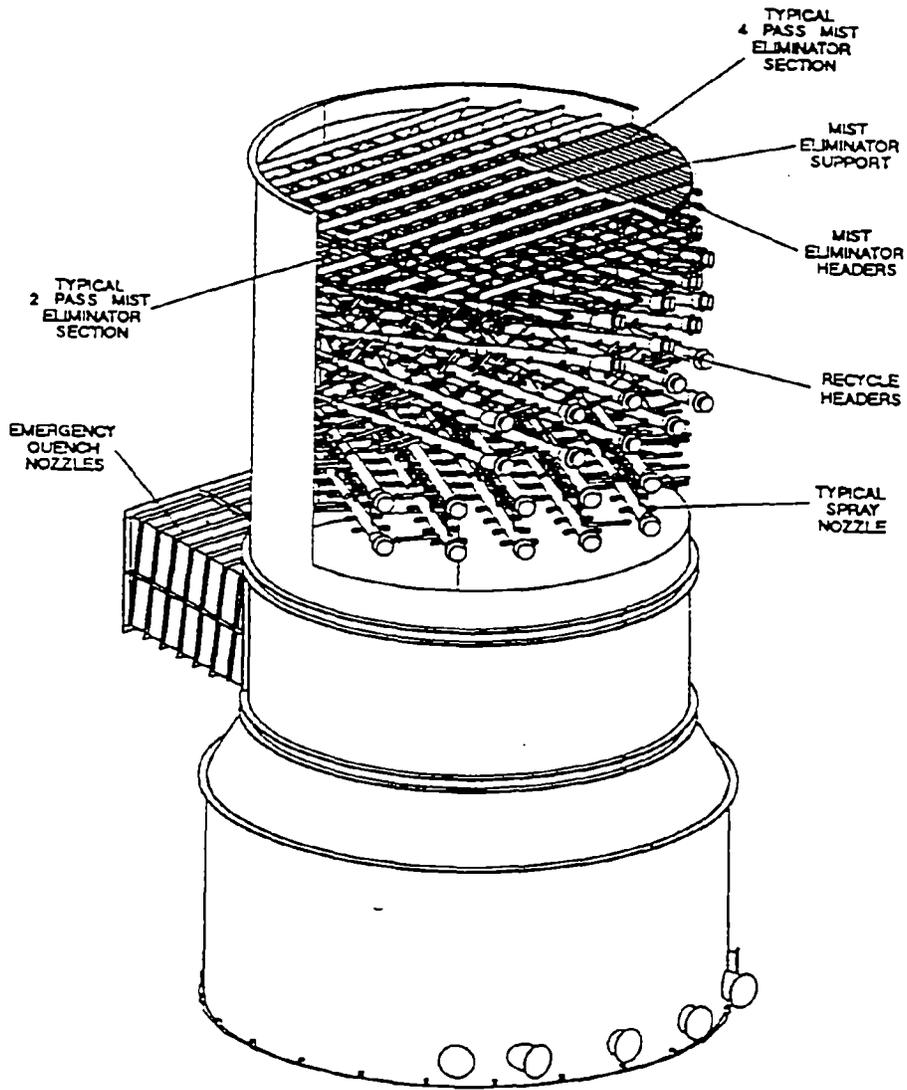
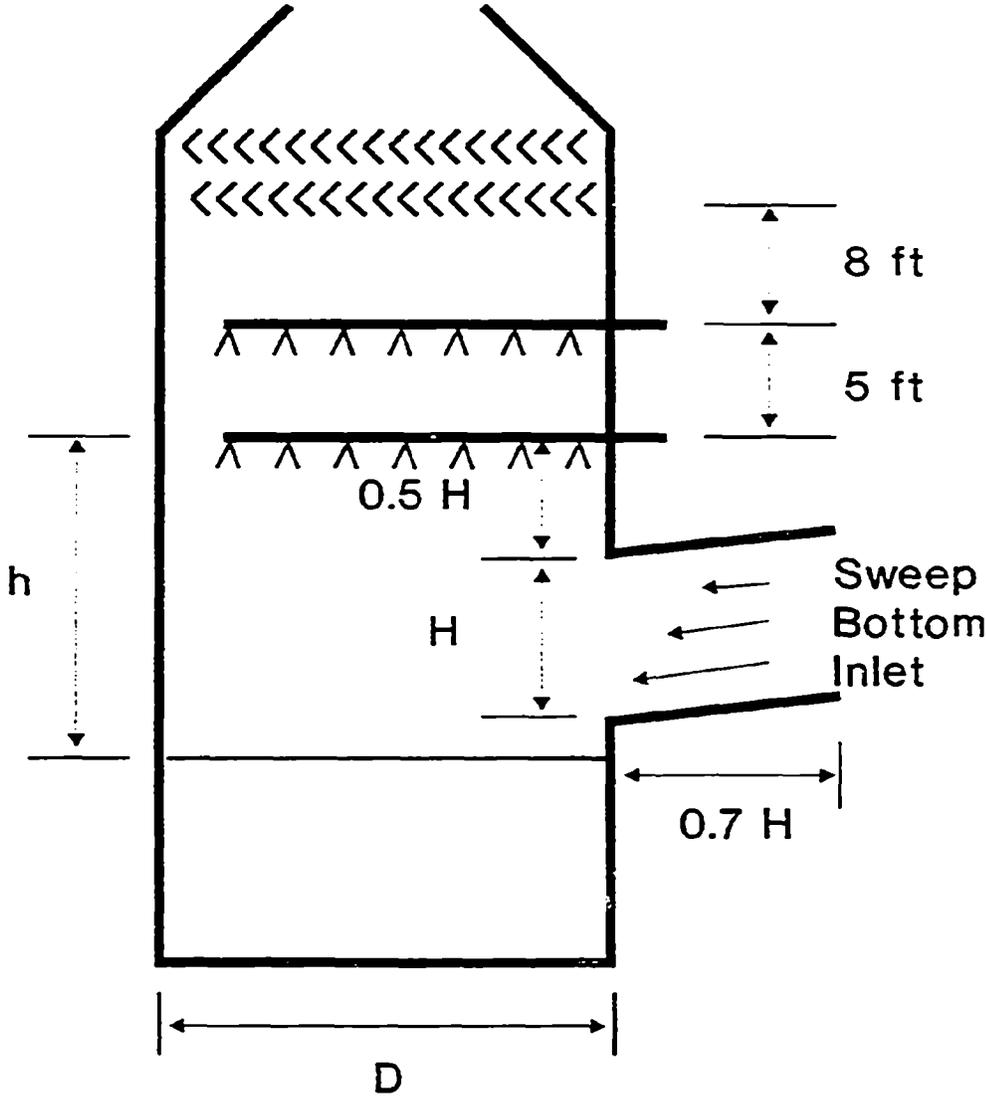


Figure 4  
 ABB Spray Tower Design

Figure 5  
Key Spray Tower Dimensions



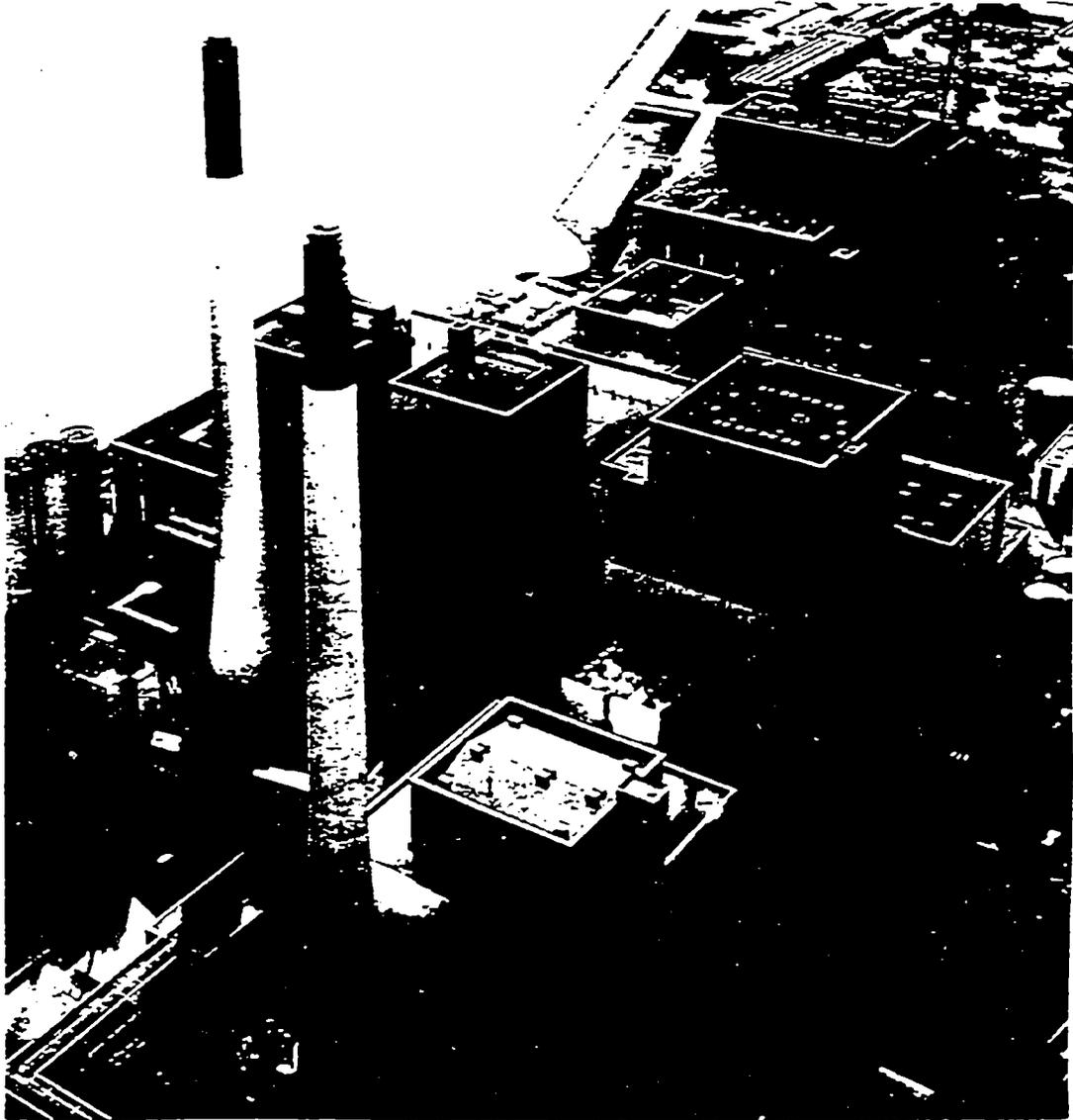
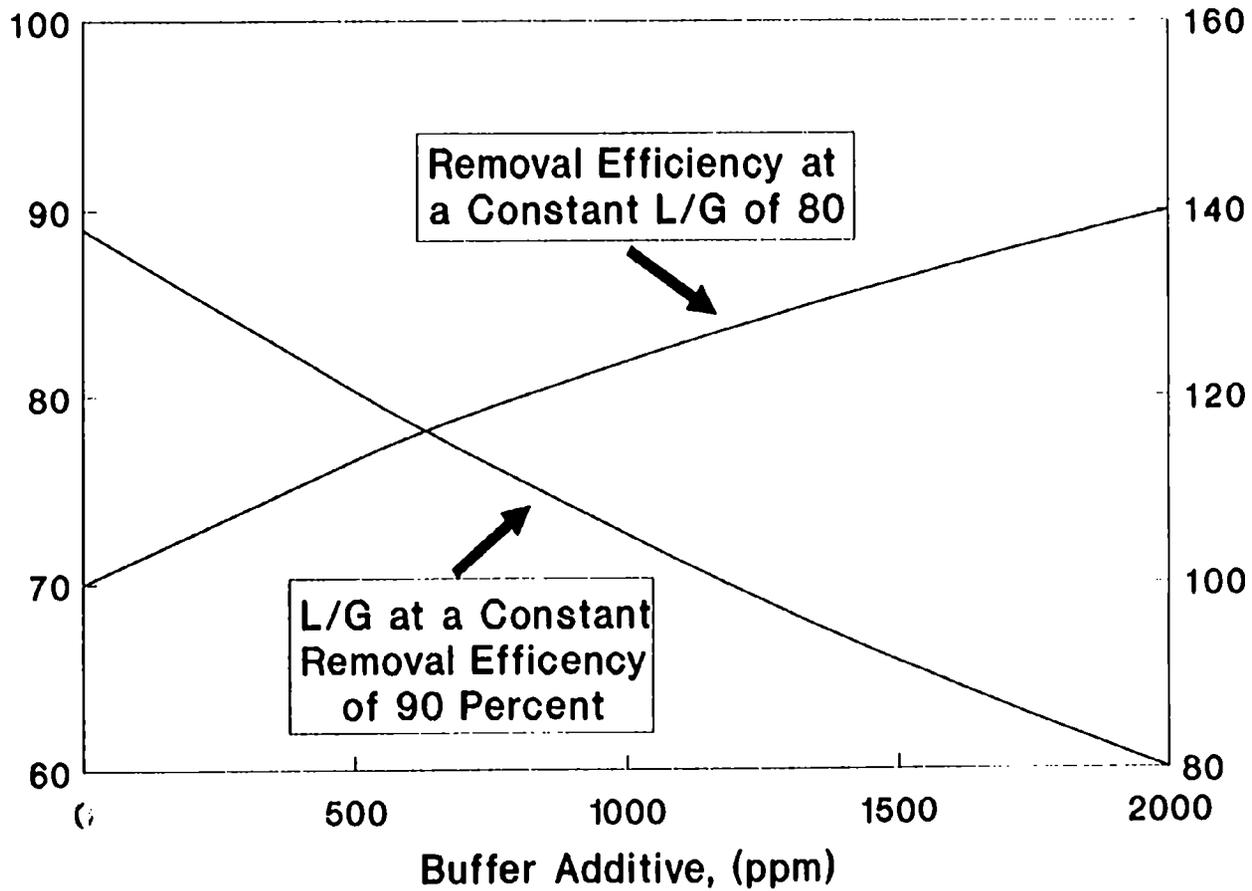


Figure 6  
Elkraft Amager Power Station  
*(ABB FGD Building in Foreground)*

Figure 7 - Influence of Buffer Additives  
3500 ppm SO<sub>2</sub>



8A-61

**TABLE 1**

**ABB WET FGD EXPERIENCE**

**WORLDWIDE**

---

U.S.	20,250 MW
Italy	1,960 MW
Denmark	900 MW
Taiwan	700 MW
<b>Total</b>	<b>23,810 MW</b>

**TABLE 2  
RELATIVE INFLUENCE OF KEY  
PARAMETERS EFFECTING L/G**

INCREASE IN PARAMETER	HIGH SULFUR	LOW SULFUR
SO2 Removal Efficiency	Strong/Increase	Strong/Increase
Droplet Size	Weak/Increase	Minimal Effect
Spray Bank Spacing	Minimal Effect	Minimal Effect
Tower Height	Minimal Effect	Minimal Effect
pH	Strong/Decrease	Strong/Decrease
Buffer Additive Concentration	Strong/Decrease	Weak/Decrease
Chloride Concentration	Strong/Increase	Strong/Increase
Spray Flux	Minimal Effect	Minimal Effect
Absorber Gas Velocity	Weak/Decrease	Weak/Decrease

**TABLE 3  
COMMERCIAL EXPERIENCE BASE**

Parameter	Minimum	Maximum
Inlet SO2 Concentration (ppm)	310	2,860
Removal Efficiency (%)	40.6	99.6
L/G (gal/kcf)	15	189
No. of Spray Elevations	1	5
Spray Flux (gpm/sq ft)	10	30
Spray Zone Height (ft)	13	38
Absorber Gas Velocity (fps)	6	15
Spray Droplet Size (micron)	1,320	2,950
pH	5.1	6.4
Buffer Additive Concentration (ppm)	0	3,030
Chloride Concentration (ppm)	200	20,000

**Table 4**  
**ABB Wet FGD Systems Producing Gypsum**

Utility	Unit	Type	Start Up	Capacity (MW)
Northern States Power	Sherburne 1	Disposal	1976	740
Northern States Power	Sherburne 2	Disposal	1977	740
Texas Utilities	Sandow 4	Disposal	1980	545
Tennessee Valley Authority	Widow's Creek 7	Disposal	1981	575
Lower Colorado River Authority	Fayette 3	Disposal	1988	435
Elkraft	Amager 3	Commercial	1988	250
Louisville Gas & Electric	Trimble County 1	Disposal	1990	500
Taiwan Power	Linkou 1	Commercial	1992	350
Taiwan Power	Linkou 2	Commercial	1992	350
ENEL	Giulia Tauro 1	Commercial	1994	660
ENEL	Giulia Tauro 2	Commercial	1994	660
Isefjordverket	Asnaes 5	Commercial	1993	650
			Total	6,455

**Table 5**  
**ABB Experience with Performance Additives**

Utility	Unit	Capacity (MW)
<b>DBA/Adipic Acid</b>		
Seminole Electric	Seminole 1	620
Seminole Electric	Seminole 2	620
Houston Lighting & Power	Limestone 1	750
Houston Lighting & Power	Limestone 2	750
Orlando Utilities	Stanton 1	450
Plains Electric	Escalante 1	235
<b>Oxidation Inhibitors</b>		
Louisville Gas & Electric	Mill Creek 1	360
Louisville Gas & Electric	Mill Creek 2	360
Texas Municipal Power Authority	Gibbon's Creek 1	445
Seminole Electric	Seminole 1	620
Seminole Electric	Seminole 2	620
New York State E & G	Somerset 1	635
Houston Lighting & Power	Limestone 1	750
Houston Lighting & Power	Limestone 2	750
South Carolina Public Service	Cross 2	500

**Table 6**  
**Plant Design and Economic Criteria**

Plant Size ( MW elec.)	300
Coal Heating Value (Btu/lb)	13,100
Coal Firing Rate (tph)	111
Max. Sulfur (%)	2.60
Max. Chlorine Content (%)	0.12
Ash Content (%)	9.10
Inlet Gas Flow (acfm nominal)	685,000
Inlet Temp. (deg. F)	300
Current Annual Load Factor (%)	65
Current Full load oper. (hrs/yr)	5,694
Plant Life (yr)	15
Discount Rate (%)	11.5%
Fixed Charge Rate, 15 yr (%)	19.2%
Power Cost (\$/MW-hr)	50
Limestone Cost (\$/Ton)	15
Dibasic Acid Cost (\$/lb)	0.18

**Table 7**  
**Process Design Comparison**

	Conventional	Advanced LS System	3rd Generation
SO <sub>2</sub> Removal (%)	90	95	98
L/G (gpm/kacfm)	140	125	100
No. of Operating Modules	2	1	1
No. of Spare Modules	1	0	0
Absorber Velocity (ft/sec)	10	10	15
Absorber Diameter (ft.)	29.8	42.2	34.4
Number of Operating Headers	5	4	3
Absorber Pressure Drop (in.W.G.)	5.00	5.00	6.50
Recycle Spray Nozzle Pres. (psi)	15.0	10.0	8.0
Avg. Net Header Elev. (ft)	50.0	47.0	43.0
Recycle Slurry Solids Conc. (%)	15.0	15.0	20.0
Solids Residence Time (hrs)	25.0	18.0	15.0
S.R. (mole alk./mole SO <sub>2</sub> abs.)	1.10	1.05	1.03
Organic Acid Conc. (ppm)	0	0	500
Oxidation Air Stoichiometry (O/SO <sub>2</sub> )	6.0	3.0	1.5

**Table 8**  
**Total Plant Investment Comparison (\$000)**

	Conventional	Advanced LS System	3rd Generation
Reagent Storage and Prep.	11,010	10,460	10,460
FGD Area	21,300	17,040	15,336
Flue Gas Handling	7,200	2,880	2,880
Waste Disposal	2,010	2,010	2,010
Other	1,770	1,770	1,770
<b>TOTAL PROCESS CAPITAL (TPrC)</b>	<b>43,290</b>	<b>34,160</b>	<b>32,456</b>
General Facilities @ 10% TPrC	4,329	3,416	3,246
Engineering & Home Office Fees @ 10% TPrC	4,329	3,416	3,246
Project Contingency @ 12.5% TPC	7,507	5,924	5,628
Process Contingency @ 1.5% TPC	901	711	675
<b>TOTAL PLANT COST</b>	<b>60,055</b>	<b>47,389</b>	<b>45,025</b>
Interest during Construction	3,003	2,369	2,251
<b>TOTAL PLANT INVESTMENT</b>	<b>63,058</b>	<b>49,758</b>	<b>47,276</b>
Delta	Base	(13,300)	(15,782)
<b>TOTAL PLANT INVESTMENT (\$/KW)</b>	<b>210</b>	<b>166</b>	<b>158</b>

**Table 9**  
**First Year Annualized Operating Cost Comparison (\$000)**

	Conventional	Advanced LS System	3rd Generation
Power	1,519	1,144	949
Reagent	788	794	803
Organic Acid	0	0	24
Waste Disposal inc. flyash	114	116	118
Waste Water Treatment	3	3	3
Maintenance	649	512	487
Manpower (5 shifts)	2,500	1,500	1,500
Byproduct Sale	(156)	(160)	(163)
<b>ANNUAL O&amp;M COST</b>	<b>5,418</b>	<b>3,909</b>	<b>3,721</b>
Delta	Base	(1,509)	(1,698)
Fixed Charges	12,107	9,554	9,077
<b>TOTAL OPERATING COST</b>	<b>17,525</b>	<b>13,463</b>	<b>12,798</b>
<b>TOTAL OPERATING COST (\$/MW-hr)</b>	<b>10.26</b>	<b>7.88</b>	<b>7.49</b>

**Design and Operation of Single Train Spray Tower FGD  
Systems**



A. Saleem  
General Electric Environmental Services, Inc.  
200 North Seventh Street  
Lebanon, PA 17042

**ABSTRACT**

This paper describes advances made over the past 20 years in the design of open spray towers to achieve dramatic results in performance, reliability and cost reduction. Today open spray towers are serving more than 25,000 MW of FGD systems dealing with flue gases from a wide variety of boilers burning low to high sulfur fuels. Desulfurization efficiencies of 90 to 99% are being achieved with reliability close to 100%. Of particular interest are the most advanced single train open spray tower FGD systems which have become the industry standard in Japan, Europe and now in the United States. Important design principles for achieving high reliability and performance will be presented along with operating experience of the single train spray tower FGD systems

Just as coal has come to dominate electric power generation, limestone has come to dominate flue gas desulfurization to meet the increasingly stringent regulations for reducing sulfur dioxide emissions. This preeminence of limestone reagent for sulfur dioxide control is dictated by cost, availability and logistics of material handling. A typical 500MW power plant, burning 3% sulfur bituminous coal, would generate about 15 tons per hour of sulfur dioxide. The quantities of various possible reagents that will be needed, and byproducts generated, per unit of sulfur dioxide removed from the flue gas are shown in Figure 1. Limestone is the most abundant naturally occurring reagent and has the lowest cost. Therefore, it is the most economic choice. This position is further reinforced when byproduct disposition is taken into consideration. Since the byproduct quantities are large, they need to be either sold or stored as environmentally safe solid waste to avoid secondary pollution problems. Byproducts of sulfur dioxide removal with limestone have low solubility in water. Therefore, they can be disposed of as landfill after proper treatment or converted into gypsum for which there is an outlet for wallboard and cement manufacture.

For reasons cited above, limestone (and to a lesser extent lime, which is derived from limestone) have come to dominate the field of flue gas desulfurization. However, the evolution of the limestone based processes has been fraught with difficulties, primarily due to plugging, scaling and inadequate performance. These difficulties can be traced back to a lack of understanding of fundamental chemical reactions and their implications on process and equipment designs.

### LIMESTONE FGD PROCESS REACTIONS

The most efficient means of removing sulfur dioxide with limestone (or lime) is the so called "wet" process in which an aqueous slurry of finely ground

limestone is contacted with the flue gas. Figure 2 shows a simplified block diagram of the wet FGD process. Flue gas leaving the fly ash collecting system is introduced into a suitable SO<sub>2</sub> absorber<sup>4</sup> in which SO<sub>2</sub> is removed by intimate contact with an aqueous suspension of limestone recycled from the absorber slurry tank. Fresh limestone slurry is continuously charged into the absorber tank for reaction with absorbed SO<sub>2</sub>. Reaction products are withdrawn and sent for dewatering and further processing. Figure 3 shows the basic chemical reactions of SO<sub>2</sub> absorption and reaction with limestone. Reaction (1) is common to all wet-scrubbing processes and shows the formation of sulfurous acid, which must be neutralized rapidly to enhance the SO<sub>2</sub> absorption. Reaction (2) shows the neutralization of sulfurous acid with limestone. The primary product of neutralization is calcium sulfite. Due to the presence of oxygen in the flue gas, the secondary oxidation reaction (3) takes place which converts a portion of the calcium sulfite to sulfate. Both calcium sulfate and sulfite have low solubility in water and result in precipitation as shown in reactions (4) and (5). Reaction (6) shows bisulfite formation, which is favored by decreasing pH.

The enormous quantities of SO<sub>2</sub> absorbed, reacted and precipitated from the absorbing solution create an environment in which scaling and plugging can readily take place. The development of proper safeguards against plugging and scaling is of paramount importance for reliability of the wet FGD system.

### PREVENTION OF PLUGGING AND SCALING

Process and absorber design go hand in hand in evolving an FGD system which is free from the debilitating effects of plugging and scaling. From a process point of view, the following criteria are essential:

**LARGE LIQUID-TO-GAS RATIO.** Both calcium sulfite and sulfate can form highly supersaturated solutions by virtue of their low solubility in water. Therefore, the liquid-to-gas ratio must be large enough to avoid any excessive instantaneous supersaturation which can cause uncontrolled precipitation. The minimum liquid-to-gas ratio can be estimated with a knowledge of the SO<sub>2</sub> content of flue gas and the expected amount of sulfite oxidation.

**SEED CRYSTALS.** A well-known technique for controlling scale uses a suspension of the crystals of the material being precipitated. These crystals not only enhance the precipitation rate, but also provide host sites where preferential precipitation takes place. Sufficient seed crystals of both calcium sulfite and sulfate must be maintained at all times in the SO<sub>2</sub> absorbing liquor<sup>1</sup>.

**DELAY TIME.** Because the process of precipitation proceeds at a finite rate, the SO<sub>2</sub>-absorbing liquor must be delayed in a tank after each pass through the absorber to allow time for the precipitation reactions. Failure to provide sufficient delay time increases the supersaturation, hence scaling. The exact delay time is a function of the degree of supersaturation that is allowed to take place during SO<sub>2</sub> absorption, as well as the delay tank design. Plug flow tanks are more efficient reactors than single backmixed tanks<sup>3</sup>.

**ABSORBER DESIGN.** From an absorber design point of view, Murphy's law must be taken into account, ie, if anything CAN go wrong, it WILL go wrong! During process upsets, such as loss of pH, loss of seed crystals, pump failures, etc. the system will experience conditions that could cause plugging and scaling. For this reason, an "open spray tower" is an ideal type of absorber for the wet limestone process. Because SO<sub>2</sub> absorption and reaction is carried out on freely moving droplets, there are no gas-flow-restricting devices, thus making the open spray tower virtually free from plugging and scaling problems even under upset conditions.

## **HISTORY OF SPRAY TOWER DEVELOPMENT**

The first formal development of a spray tower for SO<sub>2</sub> removal with limestone slurry was launched in 1970 at the Lakeview Generating Station of Ontario Hydro, on a 4,000 cubic foot per minute slipstream of a 300MW coal fired boiler. This pilot plant investigation clearly demonstrated the reliability and performance of the open spray tower. The effects of such variables as liquid-to-gas ratio, number of spray stages, nozzle size and pressure, limestone stoichiometry, gas velocity, etc. on the mass transfer coefficient (and hence performance) were investigated and correlated in an analytical model. The results of this pilot plant investigation were published in the Second International FGD Symposium in 1971.<sup>2</sup>

The first commercial application of the open spray tower took place in 1978 at the 750 MW lignite-fired Monticello Station of TUELECTRIC, Texas. Enlarging the spray tower from a mere 4,000 ACFM to 1,000,000 ACFM capacity was a daunting challenge. Additional pilot tests at Monticello Station were performed and coupled with 1/15 scale fluid dynamics model studies to point the way toward a confident scale-up. The Monticello FGD Station went into operation in January 1978 and its performance exceeded expectation with an SO<sub>2</sub> removal efficiency of over 95% and a reliability factor of over 99.5%. The operation and maintenance results of this landmark installation were published

in 1980 in the Sixth FGD Symposium in Houston, Texas.<sup>5</sup> Since then, over 90 open spray towers have been put into successful operation by GE and its licensees around the world. Many of these spray towers are single train including gigantic sizes of 700 MW. The single train spray towers have resulted in dramatic cost reductions. For instance, the 645MW Amercentrale #8 single train FGD system was contracted on a turnkey basis in July, 1985, at \$60/KW. After adding owner's costs for foundations, auxiliaries and interest during construction, the total cost of the FGD system amounted to \$84/KW with commercial operation commencing in March, 1988. The EPRI sponsored study completed in 1990 compared costs of multiple trains and a single train FGD system.<sup>8</sup> A single train system was found to be 28.5% less costly compared to a four 33% train system and 11.5% less costly compared to a two 50% train system.

#### IMPORTANT ASPECTS OF A SINGLE TRAIN FGD SYSTEM DESIGN

The single train system is defined as one in which the flue gas path has no spare absorber and the entire gas is treated by a single absorber. Such a system can be discussed in the context of two variations of the overall process depending on the byproduct of flue gas desulfurization. Figure 4 shows a system with no forced oxidation (NFO) in which the byproduct is a mixture of calcium sulfite hemihydrate and calcium sulfate dihydrate. Since this byproduct mixture is difficult to dewater, primary dewatering requires thickeners. The secondary dewatering is done with drum filters or continuous centrifuges. The final product, containing about 50 - 60% solids, is thixotropic in nature, thus requiring further drying by mixing with flyash and lime to make it suitable for disposal. It has little potential as a salable byproduct.

Figure 5 shows a system with insitu forced oxidation (IFO) in which the byproduct is calcium sulfate dihydrate, i.e. gypsum. Air is bubbled through the absorber slurry in the integral recycle tank which oxidizes all sulfite into sulfate. Since gypsum crystals are relatively large, the primary dewatering is accomplished by simple hydrocyclones followed by secondary dewatering in filters or centrifuges. The final product, containing about 90% solids, is easy to handle and may either be disposed of as landfill or sold as gypsum for wallboard or cement manufacture. Salable gypsum, however, requires gypsum washing during secondary dewatering to remove soluble salts such as chlorides, thus resulting in a water blowdown to purge these salts from the

system.<sup>9</sup> The water blowdown is treated in a waste water treatment system prior to disposal.

The reliability of a single train FGD system is first and foremost dependent on sound process design and design of the SO<sub>2</sub> absorber which is an integral part of the process. Avoiding plugging and scale is absolutely essential for reliability as discussed earlier. In this section important aspects of spray tower design, material of construction, process controls and equipment redundancy requirements are discussed.

#### OPEN SPRAY TOWER DESIGN:

The spray tower can be a very efficient mass transfer device. However, to achieve high performance requires a very intimate gas liquid contact so that no channelling of gas is possible. Since positive control can be exercised on liquid distribution through good hydraulic design, the key to achieving intimate gas liquid contact is through uniform liquid distribution. Each spray stage must have sufficient number of nozzles to cover the entire cross-section of the spray tower in a highly overlapping manner. A good design should provide a spray pattern overlap of over 150% within three feet from the tip of the spray nozzles. Such an intense overlapping spray pattern has a very beneficial effect on gas distribution as revealed by wet model tests.

#### GAS DISTRIBUTION:

An open spray tower does not need any gas distribution aids. The key to getting good gas distribution, however, is uniform liquid distribution across the cross-section of the tower as mentioned above. With uniform liquid distribution each spray stage becomes an effective screen, and the resistance created by dissipation of the enormous energy of liquid against the rising gas leads to good gas distribution. This beneficial effect of sprays on gas distribution was first confirmed in a 1/15 scale model study in 1974 before building the first commercial open spray tower.<sup>4</sup> Confirmation of this phenomenon has made it possible to confidently scale-up the open spray tower to gigantic sizes while achieving over 98% SO<sub>2</sub> removal efficiencies and extremely low liquid mist carryover. Recently, mist eliminator carryover tests at the 645 MW single train open spray tower at EPZ's Amercentrale #8 unit in The Netherlands were performed by the independent testing company, TÜV. Using a

single stage mist eliminator, the mist values obtained ranged between 1.1 to 4mg/NM<sup>3</sup> with an average value of 2.5 mg/NM<sup>3</sup> (~ 0.001 grains/SCFD). These extremely low values were measured at gas velocities of 10.7 to 12.1 feet/second. The high SO<sub>2</sub> removal efficiencies and low mist carryover values are clear indications that spray-induced gas distribution in a well designed open spray tower is sufficient for high performance.

Additional scale model tests were performed during 1990 and 1991 to study the effect of tower outlet geometry and a perforated tray on gas distribution. The results are summarized in Figure 6. With four spray banks in operation, the standard deviation of 67 velocity points across the lower face of the mist eliminator, (location "A"), ranged between 23.2% to 26.0% while gas outlet geometry was changed from completely open to 45° and 60° conical discharge to 90° side discharge. These results clearly demonstrate that the effect of sprays on gas distribution is very strong and practically unaffected by outlet geometry. This controlling influence of sprays is further illustrated by the results of installing a perforated tray with 46.6% open area above the first spray stage. The standard deviation with a tray in place was 23.1%, indicating no further improvement by a tray on spray-induced gas distribution of the open spray tower.

Tests were also performed to determine the gas distribution at locations "B" and "C", which are between the two stages of the mist eliminator system and on top of the second stage mist eliminator, respectively. A standard deviation of 25.1 is obtained at location "B", which is comparable to that at location "A". This is reasonable when considering that the first stage mist eliminator had 2.5 inch spaced continuous blades and a nominal resistance to gas flow of about 0.1 inch WC. Therefore, the prevailing gas distribution at location "A" was captured and displayed at location "B". As expected, some influence of the outlet geometry on gas distribution begins to show at location "C" which is above the second stage mist eliminator. The standard deviation at this location varied from 11.3% for a completely open discharge to 16.7% for a 90° side discharge. However, this variation is still small and within the norms of good gas distribution.

The above data clearly show that a well designed, open spray tower has excellent gas distribution and needs no gas distribution aids which can compromise its reliability. It further points out that the gas outlet geometry does not have a significant influence on gas distribution in the spray zone.

### MASS TRANSFER:

The open spray tower becomes a very efficient SO<sub>2</sub> absorber once proper liquid and gas distribution is achieved as discussed above. The mechanism of mass transfer can best be explained by the classical film theory which envisages very thin gas and liquid films on either side of the gas-liquid interface. Turbulence in these films dies out so that molecular diffusion is the only mechanism by which mass transfer occurs across the gas-liquid interface boundary. The resistance to mass transfer is inversely proportional to the film thicknesses. Since diffusion in gas is much faster than in liquid, efficient gas absorption can best be achieved by minimizing diffusion through liquid. In the case of SO<sub>2</sub> absorption in water, this means keeping the free SO<sub>2</sub> concentration at the liquid surface to a negligible level. Binding SO<sub>2</sub> with a chemical reaction at the interface is one sure way to achieve this. In a limestone slurry system, the reacting species are essentially calcium ions generated through dissolution of limestone. Since limestone has low solubility in water and also dissolves at a slow rate, it is necessary to have a large liquid-to-gas ratio as well as a large amount of limestone surface area to meet the demand for calcium ions at the gas-liquid interface for reaction with SO<sub>2</sub>. Failure to meet this demand can result in inefficient SO<sub>2</sub> absorption. The higher the SO<sub>2</sub> content, the higher the demand for calcium ions, hence, the higher the requirement for liquid-to-gas ratio as well as limestone surface area. For this reason, fine grinding of limestone becomes important for high sulfur coal applications.

Theoretical modeling of mass transfer in commercial absorbers is possible, but has little practical value, because of indeterminates such as gas and liquid film thicknesses and gas-liquid interface area. The mass transfer film thicknesses and gas-liquid interface area in a commercial absorber are impossible to measure directly, thus requiring gross assumptions to fit the experimental data and therefore making the theoretical models highly subjective. For this reason, it is customary to describe industrial gas absorption processes in analytical models based upon volumetric mass transfer coefficients, which embody the indeterminates peculiar to a given absorber. For an open spray tower, an analytical model was developed in 1970 which has

been refined and calibrated on numerous commercial spray towers. The model is briefly described here:

$$R = G (Y_1 - Y_2) = K_{ga} \cdot V \cdot (Y_1 - Y_2) / \ln \frac{Y_1}{Y_2} \quad (1)$$

**R** = Rate of SO<sub>2</sub> absorption (Moles/Hr)

**G** = Flue gas flow rate (Moles/Hr)

**Y<sub>1</sub>, Y<sub>2</sub>** = Absorber inlet and outlet SO<sub>2</sub> concentrations (Mole fraction)

$(Y_1 - Y_2) / \ln \frac{Y_1}{Y_2}$  = log mean driving force for mass transfer

**V** = effective volume of the absorber

**K<sub>ga</sub>** = overall volumetric mass transfer coefficient Moles/Hr. Ft<sup>3</sup>

Equation (1) above is analytical in nature and involves no assumptions, other than that the concentration of free SO<sub>2</sub> and therefore its back pressure at gas-liquid interface is negligible. This condition, of course, is a prerequisite for an efficient absorber design. Equation 1 can be rearranged to reflect efficiency (E) as follows:

$$K_{ga} = \frac{G}{V} \cdot \ln (1/1-E) \quad (2)$$

Equation 2 can be used to predict efficiency when the overall mass transfer coefficient for a given absorber is known. The overall mass transfer coefficient is a function of the absorber design and must be experimentally obtained from pilot and full size operations. For GE open spray towers, the mass transfer coefficient has been correlated to three most sensitive and important variables, namely...gas velocity, liquid density and inlet SO<sub>2</sub> concentration as follows

$$K_{ga} = C \cdot U^m \cdot L^n / Y_1^p \quad (3)$$

Where

**C** = proportionality constant

**U** = gas velocity in feet/sec

**L** = liquid spray density gpm/ft<sup>3</sup> of tower

**m, n, p** = correlation coefficients

Other variables such as pH and droplet size are not correlated. The pH cannot be used as a variable if condition of negligible SO<sub>2</sub> back pressure must be met for efficient absorption. Correlation with droplet size is not useful because of significant collision and agglomeration that occurs in the spray zone.

## MATERIALS OF CONSTRUCTION:

The WFGD process creates a very aggressive environment for corrosion and abrasion. The flue gas path from inlet of the absorber to stack discharge must be protected against acid attack due to adiabatic cooling and saturation of the gas. Equipment in the gas path includes isolation dampers, absorber inlet duct, absorber and its internals, outlet ducts, reheater system and stack. All slurry handling parts are subject to both corrosive and abrasive attack. These include absorber spray zones, tanks, agitators, pumps, pipes, valves and all dewatering equipment. The gas flow path presents the greatest challenge because of the large surfaces and weights involved. The choice is between carbon steel with protective linings or alloy materials. Alloy selection is further complicated by the presence of varying amounts of chlorides in the scrubbing liquor. Cost of the WFGD system is greatly influenced by the choice of materials.

Lined carbon steel results in the lowest cost. Industry experience with linings, however, has been a mixed bag of successes and failures. Lining carbon steel is both an art and a science. Careful attention must be paid to such details as material formulations, surface preparation, application technique, curing, temperature and humidity limitations, slurry impingement intensities, inspection and timely repairs. Therefore, it is not surprising to find widely varying industry experience on linings. Nonetheless, when linings are properly selected and applied, lined carbon steel does provide excellent service, as proven by more than 30,000 MW of GE design FGD systems. Figure 7 shows the history of various linings in GE FGD systems.

GE has also conducted extensive studies on corrosion of alloys in the simulated FGD environment.<sup>6</sup> Materials tested included 316 and 317 stainless steels, high nickel alloys such as Alloy G, Inconel 625 and Hastalloy G. Material samples were prepared to provide stressed conditions, welds and heat affected zones as well as base metals. These samples were exposed to slurry submergence, gas-liquid interface and saturated gas environment. The pH of the slurry was controlled by adjusting SO<sub>2</sub> injection and lime slurry additions. The dissolved chlorides were controlled at three levels of 10,000, 20,000 and 30,000 PPM. Figure 8 shows the results of a three month study. Although general corrosion rates of all materials were within tolerable limits, the pitting corrosion varied significantly and was greatly accelerated by increasing chloride levels. Only Inconel-625 shows resistance to pitting

corrosion. Therefore, when chlorides are present, Inconel or a similar alloy such as Hastalloy C would appear to be the only alloys which can be relied upon for long life. To reduce the cost of alloy construction, wallpapering of carbon steel with thin alloy sheets has recently been applied successfully, particularly in the outlet ducts where no abrasive environment exists. Successful application of alloys also requires very stringent quality assurance specifications and attention to such details as welding, prevention of surface contamination and careful post-installation handling to avoid damage. Since alloy wallpaper is not bonded to the carbon surface, any incursion of fluid through the wallpaper due to any localized pitting or cracks can cause widespread corrosion of carbon steel. Therefore, any wallpaper surface should be frequently inspected for early detection of damage and repair.

#### PROCESS CONTROLS SIMPLIFIED:

The critical process controls revolve around pH, slurry density and water balance. Optimum pH of the absorber slurry is essential to keeping SO<sub>2</sub> removal efficiency at peak performance. Absorber slurry density control keeps suspended solids at optimum level to prevent scaling and to provide crystal growth for maximum dewatering. Water balance control avoids any unnecessary blowdown and maximizes mist eliminator washing for trouble-free operations. These three process controls are fully automated, along with other operations, and yet are kept simple to allow easy integration with boiler operation. The Central Processing Unit (CPU) uses boiler load and absorber inlet SO<sub>2</sub> concentration signals to anticipate the demand for reagent feed and the need for product withdrawal. In both cases, the anticipatory feed forward and bleed signals are subservient to pH and density respectively. The master pH signal ultimately determines the amount of reagent fed to the absorber. Similarly, the master density control signal determines the ultimate amount of bleed to be withdrawn. The system can also be operated with pH and density controls only; however, feed forward helps minimize wide fluctuations in pH and density. Water balance is automatically controlled by total plant water inventory management. This is simply accomplished by the CPU with level signals from all storage tanks. Any change from the designed total water inventory determines the permissible make-up water additions. Since most of the makeup water is used for mist eliminator washing, the wash inventory signal is used to determine the frequency of mist eliminator washing, hence makeup water addition. Again the feed forward signal is used to determine washing frequency of the mist eliminator which is further adjusted by water inventory signals.

Since the quantity of makeup water is relatively small, the mist eliminator is sequentially washed in ten to twelve segments at a fixed intensity of about 1.5 gpm/ft<sup>2</sup> of cross-sectional area. The frequency of segmental wash, hence water input, is automatically adjusted by feed forward and water inventory signals. The bottom face of the mist eliminator which captures the bulk of the slurry droplets is washed in a cyclical fashion as frequently as permissible within the water balance constraints. The upper faces of the mist eliminator need less washing, therefore, only one segment is washed after each cycle of bottom face wash.

The simplified, automatic control of the above three critical process variables is readily integrated with boiler controls and ensures trouble-free peak performance of the FGD system.

#### **SPARING OF AUXILIARIES:**

All critical process operations must be secured through installed spares. An installed spare spray stage and recycle pump must be provided in the absorber to allow on-load isolation and maintenance of the recycle pumps without loss of SO<sub>2</sub> removal efficiency. This philosophy must be followed in other operations of the system. All pumping systems, such as bleed, reagent feed, reclaimed water, mist eliminator wash, filter feed, etc., must have an installed spare to allow on-load maintenance. Dewatering and reagent preparation operations can be secured by installed spares and/or through storage capacities. Certain critical process control instruments such as pH meters and density meters must also have installed spares. A warehouse inventory of spare parts must be kept up-to-date to facilitate timely maintenance.

#### **RELIABILITY OF THE SINGLE TRAIN SYSTEMS:**

With single absorber modules, the flue gas path is greatly simplified due to elimination of gas manifolds, most dampers and associated controls. When simplicity of the single train system is combined with design principles outlined in this paper, high reliability is readily achieved. These expectations are being clearly demonstrated by GE designed FGD systems. Figure 9 shows a list of single train FGD systems that GE and its licensees around the world have supplied. Although the single train design is a common practice overseas, the first commercial application of the single train system in the United States is slated for the Harrison Station of Allegheny Power Systems.

Each of the three 640 MW boilers at the Harrison Station will be equipped with a GE single train absorber to remove a minimum of 98% SO<sub>2</sub> removal while firing 4.5% sulfur coal and using high magnesium lime reagent. One of these absorbers will be built in the base of a 1,000 foot high chimney.

The performance record of some key single train FGD systems is shown in Figures 10 and 11. Sulfur dioxide removal efficiencies of 95-98% are being achieved using limestone reagent with both low and high sulfur coals while producing salable gypsum. Materials of construction are traditional carbon steel with rubber or flakeglass linings for absorber and ducts. The reliability factor, expressed as one minus ratio of forced outage hours over boiler operating hours, is close to 100%. This remarkable performance of the single train system is achieved while providing flue gas reheat. The reheat systems in the U.S. have been a particular source of problems. Recently, the trend in the U.S. is toward wet stacks which eliminate the troublesome reheat system. This further simplifies the single train systems and ensures reliability.

#### **CONCLUSION:**

The state-of-the-art of flue gas desulfurization has been greatly enhanced by the introduction of single train systems. The inherent simplicity of the open spray tower has made it possible to confidently scale-up FGD systems to large sizes. The dramatic cost savings coupled with excellent performance and high reliability has made the single train open spray tower FGD system the ideal choice for controlling sulfur dioxide emissions from power plants.

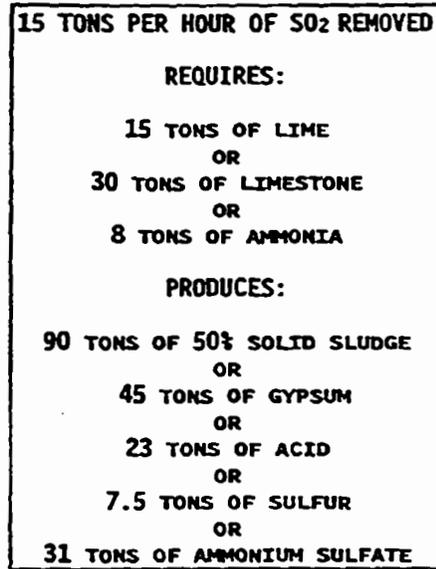
**ACKNOWLEDGMENTS:** Author is grateful to the following individuals and their organizations for providing the performance data on single train open spray tower FGD systems presented in this paper.

Mr. N.A. Doets, Director, EPZ, Geertruidenberg, The Netherlands  
Mr. P. Kneissle, Director, OKA, Riedersbach, Austria  
Mr. W. Schaller, Director, STEWEAG, Graz, Austria  
Mr. Sunao Sato, Director, Thermal Power Department, EPDC, Tokyo, Japan  
Mr. H. Weiler, Head of Dept. of Environmental Tech., STEAG, Essen, Germany  
Mr. R. Hewitt, Supervisor-Engineering, TUELECTRIC, Dallas, Texas, USA

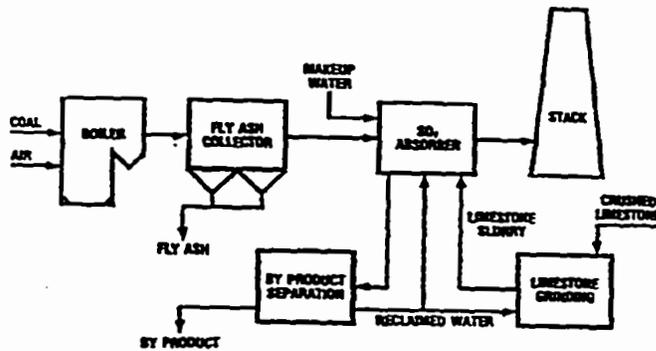
**REFERENCES:**

1. R. Lessing, "The development of a process of flue-gas washing without effluent", Journal of the Society of Chemical Industry, Transaction and Communications, November 1938
2. A. Saleem, D. Harrison, N. Sekhar, "SO<sub>2</sub> removal by limestone slurry in a spray tower", Proceedings of the Second International Lime/Limestone Wet-Scrubbing Symposium, November, 1971, New Orleans, Louisiana. Sponsored by the U.S. EPA.
3. R.H. Borgwardt, "Increasing limestone utilization in FGD scrubbers", 68th annual meeting of the American Institute of Chemical Engineers, Nov 16, 1975
4. A. Saleem, "Spray Tower: The Workhorse of Flue Gas Desulfurization", POWER, October 1980
5. R. Hewitt, A. Saleem, "Operating and Maintenance Experience of the World's Largest Spray Tower Scrubbers", 6th Symposium on Flue Gas Desulfurization, October 1980, Houston, Texas. Sponsored by the U.S. EPA
6. N.L. Koshkin and M.C. Chen, "Wet Flue Gas Desulfurization System Alloy Corrosion Test Program Test Results", presented at The 7th Symposium on Flue Gas Desulfurization, May, 1982, Hollywood, Florida. Sponsored by the U.S. EPA/EPRI.
7. W.H.P. Goossens and P.C. VanLoon, "First Year Operational Experience with the Largest Single Absorber FGD in Europe," Proceedings of the 8th World Clean Air Congress, 1989, The Hague, The Netherlands, 11-15 September 1989
8. S.M. Katzberger, C.E. Dene and R.J. Keeth, "FGD Retrofit Design Improvements" presented at 1990 SO<sub>2</sub> Control Symposium, May 8 - 11, 1990, New Orleans, Louisiana. Sponsored by EPRI/EPA/DOE
9. A. Saleem, "GE's Worldwide Experience with IFO Based Gypsum Producing FGD Systems", presented at The Second International Conference on FGD and Chemical Gypsum, May 12 - 15, 1991, Toronto, Canada. Sponsored by ORTECH of CANADA.

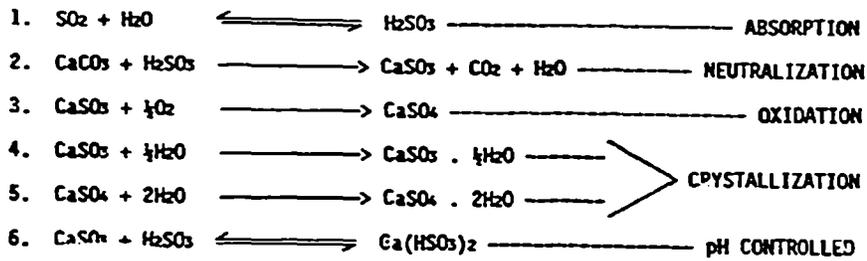
**FIGURE 1: LOGISTICS OF VARIOUS REAGENTS AND BYPRODUCTS  
FROM FLUE GAS DESULFURIZATION  
(500MWE, 3.0% SULFUR COAL 90% SO<sub>2</sub> REMOVED)**



**FIGURE 2: SIMPLIFIED BLOCK DIAGRAM  
OF THE WET LIMESTONE FGD PROCESS**



**FIGURE 3: BASIC CHEMICAL REACTIONS OF SO<sub>2</sub> ABSORPTION WITH LIMESTONE**



**FIGURE 4: GE NFO FLUE GAS DESULFURIZATION PROCESS**

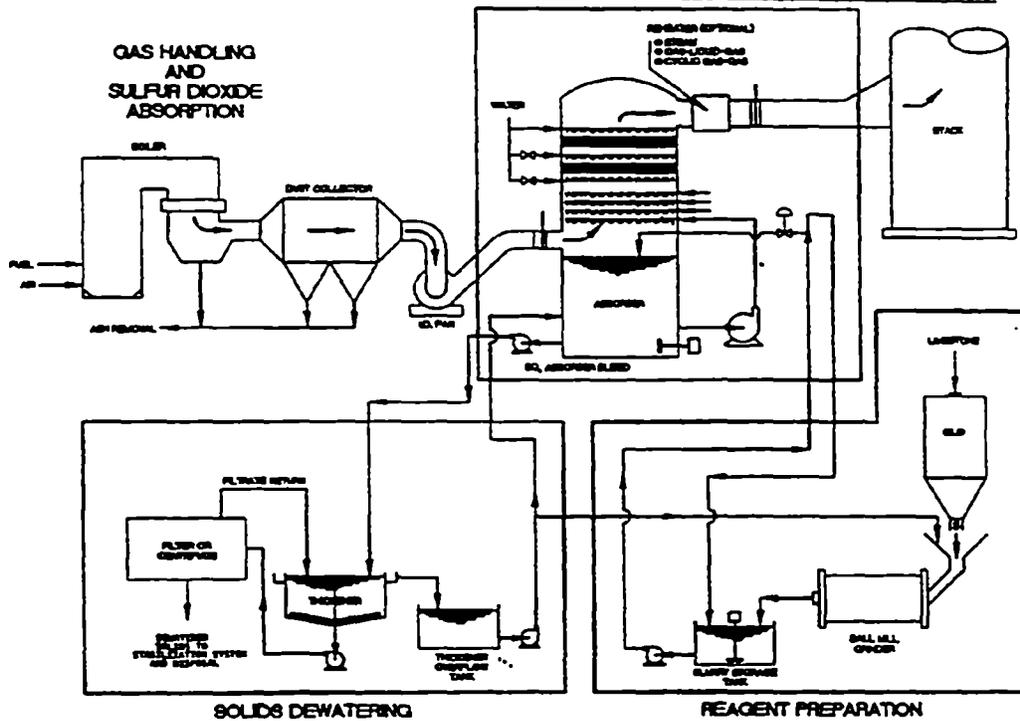


FIGURE 5: GE IFO FLUE GAS DESULFURIZATION PROCESS

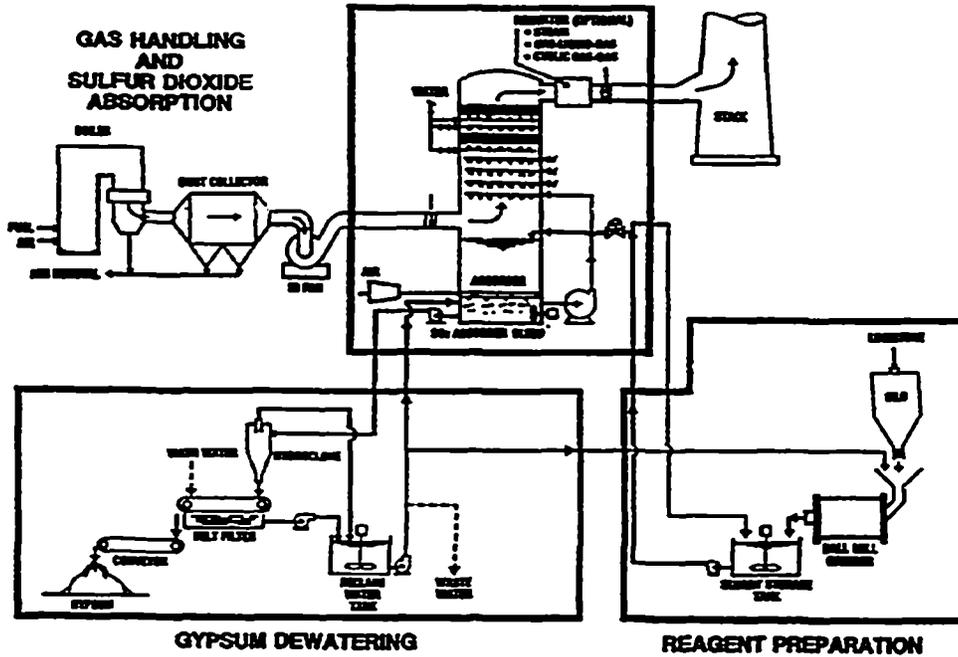


FIGURE 6: GAS VELOCITY DISTRIBUTION DATA EXPRESSED AS STANDARD DEVIATION  $\frac{1}{2}$  OF MEAN VELOCITY AT VARIOUS LOCATIONS IN THE SPRAY TOWER.

OUTLET GEOMETRY	Diagram 1	Diagram 2	Diagram 3	Diagram 4
LOCATION: A (67 VEL. POINTS)	23.3	26.7	24.6	23.6
LOCATION: A WITH 45.6% OPEN TRAY (67 VEL. POINTS)	—	—	—	23.1
LOCATION: B (68 VEL. POINTS)	—	—	—	25.1
LOCATION: C (60 VEL. POINTS)	11.3	11.2	12.6	16.7

FIGURE 7: GE EXPERIENCE WITH LININGS

AREA	MATERIAL	NUMBER OF MODULES	HW	SQ. FEET (X 1000)	YEARS IN SERVICE
1. SPRAY ZONE	• RUBBER LINING	39	9200	257	9
	• FLAKEGLASS PLASTIC	95	12000	325	17
2. ABOVE SPRAY ZONE	• RUBBER LINING	39	9200	141	9
	• FLAKEGLASS PLASTIC	95	12000	180	17
3. SUPPORT BEAMS	• RUBBER LINING	149	23000	30	17
4. RECYCLE TANK	• RUBBER LINING	30	9200	171	6
	• FLAKEGLASS PLASTIC	98	13000	195	17
5. INLET DUCT	• GLASS BLOCK	18	3000	25	5
	• FLAKEGLASS PLASTIC	22	4750	24	15
6. OUTLET DUCT	• GLASS BLOCK	15	2400	103	5
	• FLAKEGLASS PLASTIC	35	8000	240	15

FIGURE 8: GE STUDY ON CORROSION OF ALLOYS IN FGD ENVIRONMENT  
DATA ON PITTING OCCURENCE, DENSITY AND RATE\* AT PH 5.2

ALLOY	POSITION	C1 = 10,000 PPM			C1 = 20,000 PPM			C1 = 30,000 PPM		
		BM	W	HAZ	BM	W	HAZ	BM	W	HAZ
INCONEL 625	U	---	---	---	---	---	---	---	---	---
	M	---	---	---	---	---	---	---	---	---
	B	---	---	---	---	---	---	---	---	---
HASTALLOY G	U	---	---	---	---	0.28	---	0.20	0	---
	M	---	0.20	---	---	0.48	---	0	0.32	---
	B	---	---	---	---	---	---	---	---	---
ALLOY 904L	U	0	0.188	0.156	0.40	0	0	0	0.24	0
	M	0	0	0.20	0	---	---	0.48	0	0
	B	---	---	---	---	---	---	---	---	---
SS TYPE 317 LM	U	0	0.32	---	0	0.48	---	0.52	0	0
	M	0	---	0	0.20	0.20	---	0.80	0	0
	B	0.4	0	0	0.12	0.12	---	0.100	0	0
SS TYPE 316 L	U	0.200	0	0	0.200	0	0	0.116	---	---
	M	0.56	---	0	0	---	0.64	0.40	0	0
	B	0	---	0.8	0.24	---	0	---	---	0.4

COUPON POSITION  
U = ABOVE SLURRY  
M = AT SLURRY/VAPOR INTERFACES  
B = IMMERSION IN SLURRY

CONDITION  
W = WELD  
HAZ = HEAT AFFECTED ZONE  
BM = BASE METAL

PIT DENSITY  
0 = <10/SQ.IN.  
0 = 10-1000/SQ.IN.  
0 = >1000/SQ.IN.  
0 = LOCALLY >1000/SQ.IN.

\* NUMERICAL VALUES INDICATE ESTIMATED PITTING RATE IN MILS/YR BASED ON LINEAR PROJECTIONS FROM 90 DAYS TESTS

**FIGURE 9: INSTALLATIONS UTILIZING SINGLE TRAIN SPRAY TOWERS OF GE DESIGN**

<u>UTILITY</u>	<u>UNIT</u>	<u>SIZE MWE</u>	<u>% SULFUR COAL</u>	<u>%SO<sub>2</sub> REMOVAL</u>	<u>START UP</u>
<b>AUSTRIA</b>					
OKA	Riedersbach II	160	2.0 - 4.0	95 - 98	1986
STEWAG	Mellach	220	0.5	98 - 99	1986
VIENNA	Simmering	380	2.0 (oil)	97	1991
<b>JAPAN</b>					
EPDC	Matsushima #1	500	1.3	97 - 99	1980
EPDC	Takehara #3	700	1.0	96 - 98	1983
KEC	Minato	150	1.7		
CEPC	Shin Onoda #1	500	1.0	96 - 98	1985
CEPC	Shin Onoda #2	500	1.0	96 - 98	1985
EPDC	Ishikawa #1	156	1.0	96 - 98	1986
EPDC	Ishikawa #2	156	1.0	96 - 98	1987
HEC	Tsuruga	500	1.0	95	1991
<b>NETHERLANDS</b>					
EPZ	Amercentrale #8	645	1.5	90 - 94	1987
EPZ	Amercentrale #9	645	1.5	90	1992
AMSTERDAM	UNA 8	650	1.5	90	1992
<b>UNITED STATES</b>					
APS	Harrison #1	640	4.5	98	1995
APS	Harrison #2	640	4.5	98	1995
APS	Harrison #3	640	4.5	98	1995
<b>UNITED KINGDOM</b>					
POWERGEN	Ratcliffe #1	500	3.0	90	1994
POWERGEN	Ratcliffe #2	500	3.0	90	1994
POWERGEN	Ratcliffe #3	500	3.0	90	1995
POWERGEN	Ratcliffe #4	500	3.0	90	1995
<b>WEST GERMANY</b>					
RWE	Niederaussem	9x300	0.9	90	1987
STEAG	Herne IV	500	1.5	95.6	1989
STEAG	Charlottenburg	225	1.5	90	1987
BEWAG	Oberhavel	200	1.5	96	1988
HEW	Wedel	260	1.5	94	1987
<b>TAIWAN</b>					
TPC	Hsinta #1	500	1.2	90	1991
TPC	Hsinta #2	500	1.2	90	1992

ALL UNITS EXCEPT HARRISON USE LIMESTONE REAGENT AND PRODUCE GYPSUM BYPRODUCT. HARRISON USES HIGH MAGNESIUM LIME REAGENT.

FIGURE 10: PERFORMANCE, DESIGN AND OPERATIONAL DATA OF SOME LARGE SINGLE TRAIN SPRAY TOWER FGD SYSTEMS

Station	Matsushima #1 (500MW) EPCO, Japan	Takahara #3 (700MW) EPCO, Japan	Reidersbach #2 (160MW) OKA, Austria	Mellach #3 (220MW) STEMAG, Austria	Amercentral #8 (695MW) EPZ, Netherlands	Horne #4 (500MW) STEAG, Germany	Monticello #3 * (750MW) TUELECTRIC, Texas
SO2 Removal Efficiency %	97 - 99	96 - 98	95 - 98	98 - 99	90 - 94	95.6	90 - 95
Absorber Inlet SO2 PPM	300 - 520	294 - 600	1749-2623	600 - 700	630 - 1049	1224 - 1674	400 - 650
Absorber Shell Material	CS-FGL	CS-FGL	CS-RL	CS-RL	CS-RL	CS-RL	CS - FGL
Absorber Internals Pipes	SUS 316L	SUS 316L	CS-RL	CS-RL	CS-RL	CS-RL	CS-RL -> FRP
Absorber Recycle Pump	YST 130A	CS-RL	Alloy	Alloy	CS-RL	Alloy	CS-RL -> Alloy Impellers
Absorber Outlet Ducts	CS-FGL	CS-FGL	CS-FGL	CS-FGL	CS-RL	CS-FGL	CS; Pre-Krete --> C-276
Stack Material	Acid Brick	Acid Brick	Acid Brick	Acid Brick	Acid Brick	Acid Brick	Acid Brick
Operators Per Shift	1.5	1.6	2	2	2	2	2.6
Routine Maintenance Crew per Shift	SAM(1.5)	SAM(1.5)	SAM	SAM (2)	SAM (0.5)	SAM	SAM (2)

CS-FGL: CARBON STEEL WITH FLAKE GLASS REINFORCED PLASTIC LINING

CS-RL: CARBON STEEL WITH RUBBER LINING

SAM: SAME AS BOILER MAINTENANCE CREW

\* MONTICELLO #3 IS A THREE TRAIN SYSTEM AND INCLUDED HERE FOR REFERENCE

FIGURE 11: RELIABILITY RECORD OF SOME LARGE SINGLE TRAIN SPRAY TOWER FGD SYSTEMS

Station	Matsushima #1 (500MW) EPDC, Japan			Takehara #3 (700MW) EPDC, Japan			Reidersbach #2 (160MW) OKA, Austria		
	BOH	FOH	RF	BOH	FOH	RF	BOH	FOH	RF
1990	6853	0	100%	7338	0	100%	5559	0	100%
1989	7367	0	100%	8703	0	100%	5709	178	97%
1988	5902	0	100%	7216	0	100%	4557	0	100%
1987	7744	0	100%	7603	0	100%	4587	0	100%
1986	7205	0	100%	7255	0	100%	----	----	----

Station	Mellach #3 (220MW) STEWAG, Austria			Amercentrale #8 (645MW) EPZ, The Netherlands			Herne #4 (500MW) STEAG, Germany			Monticello #3 (750MW) TUELECTRIC, Texas		
	BOH	FOH	RF	BOH	FOH	RF	BOH	FOH	RF	BOH	FOH	RF
1990	4400	0	100%	7508	122	98%	8760	0	100%	7756	0	100%
1989	4400	0	100%	8422	606	93%				7480	4	99.9%
1988	4400	0	100%	----	----	----				6962	14	99.8%
1987	4400	0	100%	----	----	----				7026	31	99.8%
1986	4400	0	100%	----	----	----				7673	56	99.3%

BOH: BOILER OPERATIVE HOURS

FOH: FORCED OUTAGE HOURS DUE TO FGD

RF: RELIABILITY FACTOR:  $(1 - FOH/BOH) \times 100$

\* MONTICELLO #3 IS A THREE TRAIN SYSTEM AND INCLUDED HERE FOR REFERENCE



**SELECTING THE FGD PROCESS AND SIX YEARS OF  
OPERATING EXPERIENCE IN UNIT 5 OF THE  
ALTBACH-DEIZISAU NECKARWERKE POWER STATION**

**R. Maule  
P. Necker  
M. Straus  
Neckarwerke, Elektrizitätsversorgungs-AG  
Esslingen  
Küferstrasse 2  
7300 Esslingen  
Federal Republic of Germany**

**S. Negrea  
Noell, Inc.  
2411 Dulles Corner Park, Suite 410  
Herndon, VA 22071  
3780 Kilroy Airport Way, Suite 350  
Long Beach, CA 90806**



## ABSTRACT

In 1981, this power station was evaluating various FGD processes suitable to meet stringent German regulations. The paper discusses the various criteria which led to the selection of their SO<sub>2</sub> removal system.

The paper covers some of the operational experiences gained after six years of using an FGD plant with wet limestone, with gypsum by-product, using a two-stage advanced process.

Among other topics are experience with limestone as reagent, performance of alloys, contribution of reheating systems, and utilization of the gypsum by-product in the construction industry.

The paper discusses the operating results, as well as the costs of operating and maintaining this facility.

Recommendations are made for future users in areas such as material selection, spare module scrubbers, based on the performance of this FGD plant.

## INTRODUCTION

The Neckarwerke, AG, based in Esslingen is a Regional Utility Company in southern Germany near Stuttgart. In 1990, the Neckarwerke had a network peak production of 1,456 MW. In 1990, approximately 8.4 billion kWh were supplied, of which 50% were used by various industrial users. Approximately 95% of this electric power was generated in our power plants. The annual turn-over totaled 1.5 billion DM (approximately 857 million US dollars).

The distribution of various energy sources in the power generation of Neckarwerke and the comparison with the similar total for the "old" Federal Republic of Germany for the year 1990 is shown in Figure 1. This data gives a good understanding of the energy supply condition for the Neckarwerke (NW) and the position NW had in the "old" Federal Republic of Germany in 1990.

At the end of the seventies, NW realized that the planned extension of the nuclear energy plant could not be completed as fast as originally planned. Therefore, in addition to the planning of the nuclear power plant (which originally was scheduled for completion in 1984/85 [actual date was 1989], it began in 1979/80 plans for a coal power plant (Unit 5) with 420 MW net. This plant was scheduled to go into operation in 1985. Existing regulations of 1981 required that a flue gas desulphurization plant must be installed only for units with a firing capacity of more than  $> 4$  TJ/h. The new plant was designed for a firing heat capacity of 3.9 TJ/h. Nevertheless, it was decided, in order to ensure a better environmental acceptance of this power plant, to voluntarily install the flue gas desulphurization system for an initial partial gas flow of 40%. At that time, there were only 3 flue gas desulphurization plants in operation in Germany. As can be seen in Figure 2, the regulations became continuously stricter during the beginning of the 80's. This was not a good situation, neither for the plant operators, who at that particular time were constructing plants, nor for the FGD plant suppliers, who continuously were confronted with new regulatory demands.

In 1983, the large-size power plant regulations stipulated that within five years old plants with a remaining life of more than 30,000 hours have to be retrofitted with FGD-systems to comply with the same emission limits required for new plants.

Today, the tendency in approving new plants is that, although the requirements, quantitatively speaking, were not changed to this date by the Federal Environmental Protection Laws with the thought ". . . according to the status of technology . . . ", yet they are much stricter with the emission limits.

## DEVELOPMENT OF FGD-TECHNOLOGY IN GERMANY

The basic development phases of FGD-technology in Germany are shown in Figure 3.

The first plants worked with lime as an absorption agent and calcium-sulfite/sulfate-slurry was the end-product. Since only partial desulphurization was required, the reheating of the clean outlet gas could be accomplished by mixing outlet gas with untreated inlet gas. The desulphurization was still very inefficient.

Due to the difficulty with waste disposal of this type of end-product and due to Federal Government Regulations for minimizing waste disposal, and the requirement to produce usable end-products, the next development step was to oxidize the calcium-sulfite in order to obtain calcium-sulfate (i.e. gypsum); this was first done in oxidation vessels, and was later integrated by in-situ oxidation into the scrubber tower.

In Germany, similar to the United States, lime is in comparison to limestone relatively expensive. Therefore, through research and experience, it was determined that lime as reagent could be replaced by limestone, and today limestone is being used in the overwhelming majority of German FGD plants.

Because of the necessity at that time to increase the desulphurization performance to 85%, the portion of flue gas to be desulphurized had to be increased, and it became necessary to build reheating systems for the flue gas. The reheating systems were mostly developed as regenerative heat exchangers because of the familiarity of the power industry with these systems.

Due to the tendency of increasing the desulphurization efficiency towards 90% and higher and the associated requirement to maximize the desulphurized flue gas stream, we will see in the future flue gas desulphurization systems a minimization in leakage at regenerative heat exchangers, that is, leakage-free systems for reheating.

## THE DECISION FOR FLUE GAS DESULPHURIZATION OF NECKARWERKE AG IN THE YEAR 1981

The decision regarding the plant concept for Unit 5 was made in accordance with the following criteria:

- to ensure high SO<sub>2</sub> removal efficiency
- to achieve a simplified operating procedure with clearly defined process parameters
- to ensure safe operation through simple construction
- to realize low operating costs by using simple reagents
- to satisfy a safe disposal by utilization of the end-product (gypsum)
- to use known power plant-type equipment and to standardize plant elements
- If repairs are necessary, the usual power plant repair techniques should be sufficient.
- to have a high degree of automatization according to power plant standards

With this requirement profile in mind, we decided on the following plant concept:

## PROCESS

The two-loop NOELL-KRC process, with separate optimum regions for the pH-values was adopted. In the quencher area for oxidation and limestone dissolution a pH around 4 and in the absorber loop a pH of approximately 6 for SO<sub>2</sub> removal was selected. The oxidation was integrated in the scrubber.

## REAGENT PRODUCT LIMESTONE

Limestone in Germany is considerably cheaper than burnt lime (ratio 65 : 155). The advantage of transporting calcined lime, due to the smaller volume (56 : 100), cannot overcome the price difference. The cost of the limestone is independent of the primary energy price, which is an entirely different situation for the calcined lime. The result was a low and stable operational cost.

## TOTAL PLANT CONCEPT

- Since it was planned to build the system in two phases, 1985 Phase I and 1987 Phase II, Neckarwerke chose the erection of the plant with two lines.
- Stainless steel scrubbers with various alloy steel quality for various levels were selected.
- Stainless steel recycle pumps for the quencher and the absorber with the respectively required material quality were chosen.
- The reheating takes place in the regenerative heat exchanger of the second line.
- The remaining droplet evaporation (untreated gas), after the scrubber, was planned with untreated hot flue gas.
- Due to our climatic conditions and the regulations for noise protection, as well as to provide better conditions for the plant maintenance, we decided for a total enclosure of the FGD plant.
- The system is, to a great extent, fully automated.
- The FGD control room is integrated into the Main Control Center of the power plant.

The Unit 5 FGD plant schematic is shown on Figure 4 and the simplified process flow sheet can be seen on Figure 5.

## END-PRODUCT GYPSUM

Gypsum dewatering using the vacuum drum filter is followed by drying with untreated hot flue gas, and further by production of gypsum briquettes.

Commercial, high quality gypsum is the end-product which guarantees a high level of potential waste disposal safety.

## END-PRODUCT GYPSUM

The gypsum preparation simplified schematic is shown in Figure 6.

The FGD-plant was supplied by NOELL-KRC with a construction period of 2-1/2 years and was brought into operation in 1985 with the first line and in 1986 with the second line, one year earlier than originally planned. Further details are found in References 2, 3, 4, 5, and 6 listed at the end of this paper. The technical data is contained in Figure 7.

## OPERATIONAL EXPERIENCE

We have now gained an experience of six years of operation with a total of more than 30,000 operating hours with this type of FGD technology, which can be judged in total as very good. Following are some details of our experience:

### EXPERIENCE WITH THE REAGENT PRODUCT

Limestone is suitable as absorbent when applying the correct process. In order to get a large number of suppliers, the purity of the limestone was varied in tests. This, however, was not effective. A too high inert portion in the limestone leads to problems during dewatering of gypsum. For a trouble-free operation with high quality commercial gypsum as by-product, limestone with approximately 97% purity is recommended. The particle size distribution should be as follows: 80% < 63  $\mu\text{m}$  and 90% < 90  $\mu\text{m}$  respectively.

### EXPERIENCE WITH THE PROCESS

The two-loop-system with clear, controllable operating conditions for the absorber (high pH-value) and for the quencher loop (low pH-value) has proven to be effective. If the pH-values are maintained and the spray nozzles are correctly directed, deposits are prevented. The SO<sub>2</sub> removal efficiency in the scrubber is higher than 95%. Therefore, it was possible to reduce the original packing depth of the Wet Film Contact (WFC) from three layers (3 feet) to one layer (12 inches) without any significant reduction in removal efficiency. The blown-in air, integrated in the scrubber sump for sulfite to sulfate oxidation was built on the lance exhaust system located before the agitator. Thus the oxidation air can be turned off when the unit is not in operation and the power consumption can be reduced.

### EXPERIENCE WITH THE SELECTION OF MATERIALS

The materials used are shown in Figure 8 including the variation of material qualities for the alloy steel scrubber. Due to material considerations, it is of great importance to separate the high-chloride-contents (lower loop) quencher circulation (approx. 15,000 - 30,000 ppm Cl) and the (upper loop) lower-chloride-contents absorber circulation (approx. 3,000 - 5,000 ppm Cl).

## EXPERIENCE WITH THE SELECTION OF MATERIALS

Otherwise, corrosion problems in the upper circulation loop could arise. In addition, deposit problems can be expected even with high-quality materials. Deposits are therefore to be prevented by optimizing the spray levels and the flue gas exhaust, especially in the so-called bowl area separating the lower from the upper loop. For that reason an additional wash system with spray was built into both scrubber towers. The underside of the bowl was plated with a high quality alloy steel material; Figure 8 and Reference 7 deals in detail with our experience in this domain. The use of alloy steels for the scrubbers and pumps has proven to be basically effective. Corrosion can be monitored and eliminated by suitable methods for power plants during inspection shut-downs.

Reference 8 deals in detail with the partially very problematic experience of rubber-lining use by some FGD units in Germany.

Also successful was the use of all-metal pumps. We used similar-built pumps to improve the repair and spare parts inventory. The same material was used (HA 28.5 similar to 1.4464 to simplify storage needs). The quencher pumps reached a life of approximately 25,000 h, the absorber pumps are expected to have a life of 40,000 h. The slide ring seals are made without seal water.

## EXPERIENCE WITH REHEATING

By using untreated inlet gas for droplet evaporation before the regenerative reheating system (Regavo), we experienced corrosion problems at the Regavo due to temperatures under the acid dew point. To increase the SO<sub>2</sub> removal efficiency of the total system (reducing leakage) and to avoid this corrosion, the droplet evaporation system and the gas valve system at the Regavo was rebuilt. Today, this system is run with treated (outlet) gas. In Figure 9 the principle used today for reheating is presented. For bolts and other connecting elements corrosion-proof materials are used (partially Hastelloy and F.R.P. elements).

## EXPERIENCES WITH THE END-PRODUCT GYPSUM

The dewatering of gypsum with a vacuum drum filter leaves a moisture contents of approx. 10 - 12%. With band filter systems, the same values can be achieved with a simpler operation.

The drying of gypsum with flue gas has not proven to be effective. Cl was transferred from flue gas to gypsum and resulted in high Cl concentration in gypsum. We then converted the system to hot air drying (partial stream from the economizer) and today the system works without any problems. Figure 6 shows today's gypsum preparation.

The gypsum quality is excellent. The gypsum can be supplied without limitation for use in the construction industry.

## EXPERIENCES WITH THE PLANT DESIGN

The relatively expensive decision for the complete enclosure of the FGD plant was proven to be correct and met its original purposes.

The centralization and integration of the total instrumentation and control system into the main control center of the power plant and the complete automatization of the plant has proven to be excellent.

In conclusion we can say that, with the modifications mentioned above, we would build this FGD plant again. The FGD process selected has proven to be a success; we are satisfied with its operation and the high SO<sub>2</sub> removal efficiency.

Under our present regulations it would be unthinkable to put an FGD plant into operation stepwise and it is of course essential to treat from the beginning the entire gas stream. Today, progress has been made where for one boiler a single absorber tower with one ID fan can possibly be designed for plants with a capacity of up to 700 MW. The conceptual scheme for such a plant is shown in Figure 9.

Our decision for a process with limestone as reagent and gypsum as end-product, and the good experiences with the selected FGD process performance is totally confirmed by the market shares of the various FGD plants built in Germany.

Reference 8 gives details about operational experiences with FGD-plants in the Federal Republic of Germany.

From all selected alternative processes in Germany, 87% operate with limestone (or lime) and have a gypsum by-product. Figure 10 shows the technology market distribution. The double-loop process is represented in this market with a very significant share of approximately 20%. Recent developments for FGD plants burning lignite with very high SO<sub>2</sub> inlet loading to the FGD system, in the territory previously known as "East Germany", have also selected this process.

## COSTS FOR FLUE GAS DESULPHURIZATION

### Investment Costs for Neckarwerke FGD Unit 5

The costs for FGD Unit 5 including interest on construction loans totaled 135 Million DM (approximately 77 million US dollars). The breakdown of the respective contract work sections is shown in Figure 11. With a net output of 420 MW, this results in specific investment costs of 320 DM/kW (approximately 183 \$/kW). In Figure 12 the operating costs for full-load operation are summarized. This table shows the specific items which make up the total operational costs. The main costs are generated by the pressure drop produced by the FGD plant. This corresponds to a share of 1.4% of the gross power output of the unit. The use of lime instead of limestone would increase the operational hourly costs by 16% due to the higher lime price (155 : 65), without the benefit of any operational advantages.

For the operation of this FGD-plant a staff of 12 people is necessary (shift personnel, maintenance and repair).

## **COSTS FOR FLUE GAS DESULPHURIZATION**

For the calculation of capital investment costs, assumption of amortization is necessary. We believe that the period of amortization for the FGD-plant must be considerably less than the period which is usually applied for the other power plant components. Figure 13 shows the additional costs for the kWh due to the FGD-system operation in relation to the annual operation hours and an amortization period of 10 and 15 years. The additional costs by the operation of the FGD-system are between 1.5 - 2.5 pf/kWh (approximately 0.8 to 1.4¢/kWh or 8 to 14 mills/kWh) for the average load of Unit 5.

It is to be considered that the FGD Unit 5 was designed as a new plant together with the new construction of the total power plant. The labor share (German wage scale) is approximately 0.05 Pf/kWh (0.03¢/kWh or .3 mills/kWh) or approx. 3% of total costs. Maintenance costs, as an average of prior six years, are approximately 2% of investment costs; future average maintenance costs are expected to be approximately 3 - 4%.

Based on the positive experience with our FGD-system for Unit 5, we estimate savings possibilities of approximately 15 to 20% at new plants with the concept of using only one FGD line in lieu of our present two-line system.

In addition to the FGD-system, the first large-scale DeNO<sub>x</sub>-system outside Japan was also installed in Unit 5. This means that 33% of the total investment volume for Unit 5, which totaled approx. 900 million DM (approx. 515 million US dollars), was expended for environmental protection. Figure 14 shows the percentage distribution of investment costs for Unit 5.

## **SUCCESS OF ENVIRONMENTAL PROTECTION ACTIVITIES AT NECKARWERKE**

The success gained with the installation of FGD plants in SO<sub>2</sub> emission reduction for our company is most impressively shown by the emission values in Figure 15. Within five years, the construction of the new plant Unit 5, the retrofit of two old plants with FGD-systems, and the commissioning of our second nuclear power plant made it possible to lower the emission values by almost 90%. In addition to cost mitigation, a considerable contribution is also provided by the nuclear energy in the total emission reduction.

## SUMMARY

) The Neckarwerke AG decided in 1981 to build an FGD-system, Unit 5, at the power plant in Altbach-Deizisau, with the following concept:

- Limestone as reagent
- Gypsum as end-product
- Two-loop scrubber system
- Alloy steel scrubbers
- Fully-automated operation

After six years of operation of the FGD-system, we can confirm that the principle of the plant as built by NOELL-KRC has been proven successful. Due to the favorable experience, Neckarwerke AG would, today, decide on a one-line system with one scrubber tower and one I.D. fan (for the Unit and the FGD system together) instead of a two-line system. Higher-quality stainless steel would be selected for all areas of the absorbers but especially in the (lower) quencher area and in the area of the bowl.

During the six years of operation, we never experienced an interruption or non-availability of power output due to the FGD-system. The FGD-system can, without any difficulty, be integrated into the operation of the power plant. We are operating at an SO<sub>2</sub> removal efficiency higher than 90%. The SO<sub>2</sub> removal efficiency can be maintained in all operating situations.

Investment costs for the FGD system amounted to 127 million DM (approx. 72 million US dollars). Depending on the annual hours of operation, FGD costs of operation amount to 1.5 - 2.0 Pf/kWh (approx. 0.9 - 1.2¢/kWh or 9 to 12 mills/kWh); the share of FGD operational costs is approx. 0.3 Pf/kWh (approx. 0.18¢/kWh or 18 mills/kWh).

## REFERENCES

1. B. Forck. "The Emission Limitations for Power Plants in Europe." International ASME-VGB-Joint Power-Generation Conference, Boston, MA. 1990.
2. R. Maier, P. Necker, J. H. Strauss, H. Hemming and E. Landgraf. "Erection and Function of the Flue Gas System of the Power Plant Altbach/Deizisau, Unit 5." VGB-Kraftwerstechnik 67, Heft 4, April, 1987, pp 378-383.
3. R. Maüle. "Selecting an Optimal SO<sub>2</sub> Reduction Program - A German Perspective." Forum on Least Cost Options, May 1990. Research-Cottrell Companies USA, Sommerville, NJ.
4. P. Necker and J. H. Strauss. "Function and Costs of a Flue Gas Desulphurization System with a Limestone-Gypsum Wet Process with Unit 5 of the Neckarwerke at Power Plant Altbach/Deizisau as the Model." (in German) ECE-Workshop 1987, Esslingen.
5. B. Lehmann, P. Necker and J. H. Strauss. "Experience with the Flue Gas Cleaning Systems for SO<sub>2</sub> and NO<sub>x</sub> in the Power Plant of Neckarwerke Elektrizitätsversorgungs-AG." (in German) ECE-Seminar 1991, Nuernberg
6. J. H. Strauss. "A Standard Solution Does Not Exist." (in German). Zeitschrift Energie 40, Nr. 7. July, 1988.
7. R. Maier, K. U. Buschmann und J. H. Strauss. "Experiences from Operation and Maintenance after 26,000 Hours of Operation - FGD, Power Plant Altbach/Deizisau" (in German). Vortragsband VGB-Conference "Kraftwerk und Umwelt 1991", Essen
8. P. Necker. "Development and Present Status of Flue Gas Desulphurization in Germany." International ASME-VGB-Joint-Power-Generation Conference, Boston, MA. 1990

# ELECTRICAL POWER GENERATION 1990 BY ENERGY RESOURCES

Neckarwerke

WEST - GERMANY

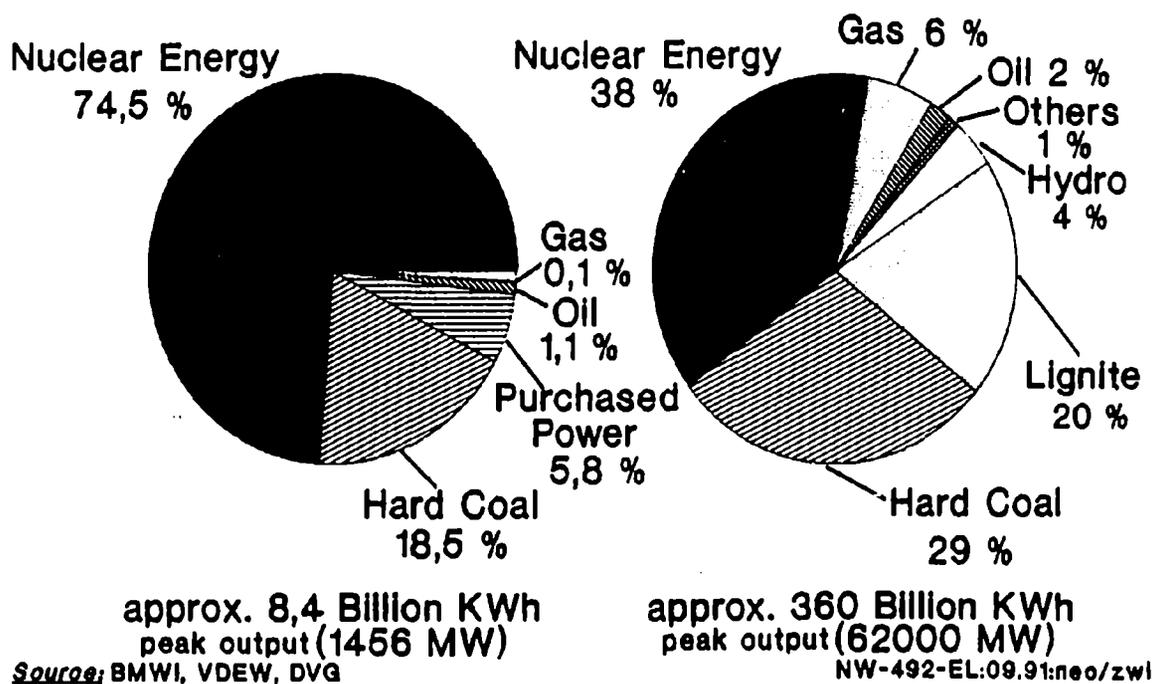


Figure 1.

## DEVELOPMENT OF THE LEGISLATION REQUIREMENTS OF FLUE GAS DESULPHURIZATION (FGD)

Year	Size of Unit	Emission Limits
1974	$< 4 \text{ TJ/h (1111 MW}_{th})$ $> 4 \text{ TJ/h}$	No FGD 1160 mg SO <sub>2</sub> /m <sup>3</sup>
1977		850 mg SO <sub>2</sub> /m <sup>3</sup>
1982		650 mg SO <sub>2</sub> /m <sup>3</sup>
1983	$> 300 \text{ MW}_{el}$ New Plants Old Plants $> 30\,000 \text{ h Residual}$ Use	} 85 %-SO <sub>2</sub> Removal Efficiency max. 400 mg SO <sub>2</sub> /m <sup>3</sup>
1988		Completion Retrofit Old Plants
from 1990:	Tendencies towards further aggravation in obtaining approvals (legal basis... dynamization clause in the BImSchG)	

NW-494\_2-EL:04.90:nec/zwI

Figure 2.

# DEVELOPMENT STEPS IN FLUE GAS DESULPHURIZATION IN GERMANY

Start up	1977	1979	1982	85/86	Further Development
<b>Requirements</b>					
State Leg. (1974)	*	*	*		*
Federal Leg. (1983)				*	
<b>Reagent</b>					
CaO	*	*	*		
CaCO <sub>3</sub>			(*)	*	*
<b>Oxidation</b>					
without	*				
with separate oxid.		*			
integrated oxid.			*	*	*
<b>Desulphurization</b>					
Flue gas volume %	20	25	60	90	98 - 100
Removal efficiency %	19	24	57	>85	> 90
<b>Reheating</b>					
without	*				
with		*	*	*	*
Leakage minimization					*
Leakage-free					*
<b>End Produkt</b>					
Sulfite/Sulfate-slurry	*				
Gypsum moist		*	*	*	*
Gypsum dried			*	*	*
Gypsum compacted			*	*	*

NW-498-EL:nec/zwl:0.91

Figure 3.

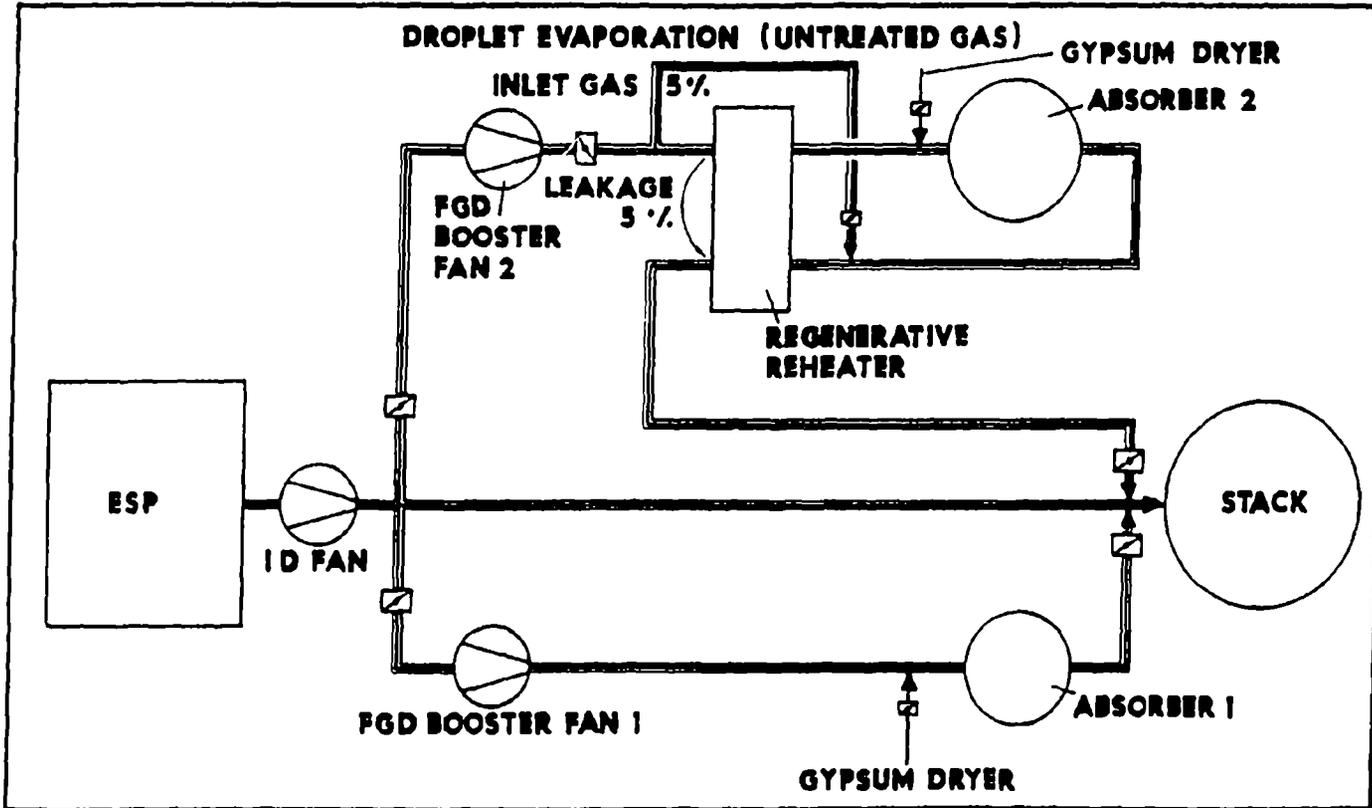


Figure 4. Plant Schematic FGD Unit 5 -Neckarwerke 1991

8A-107

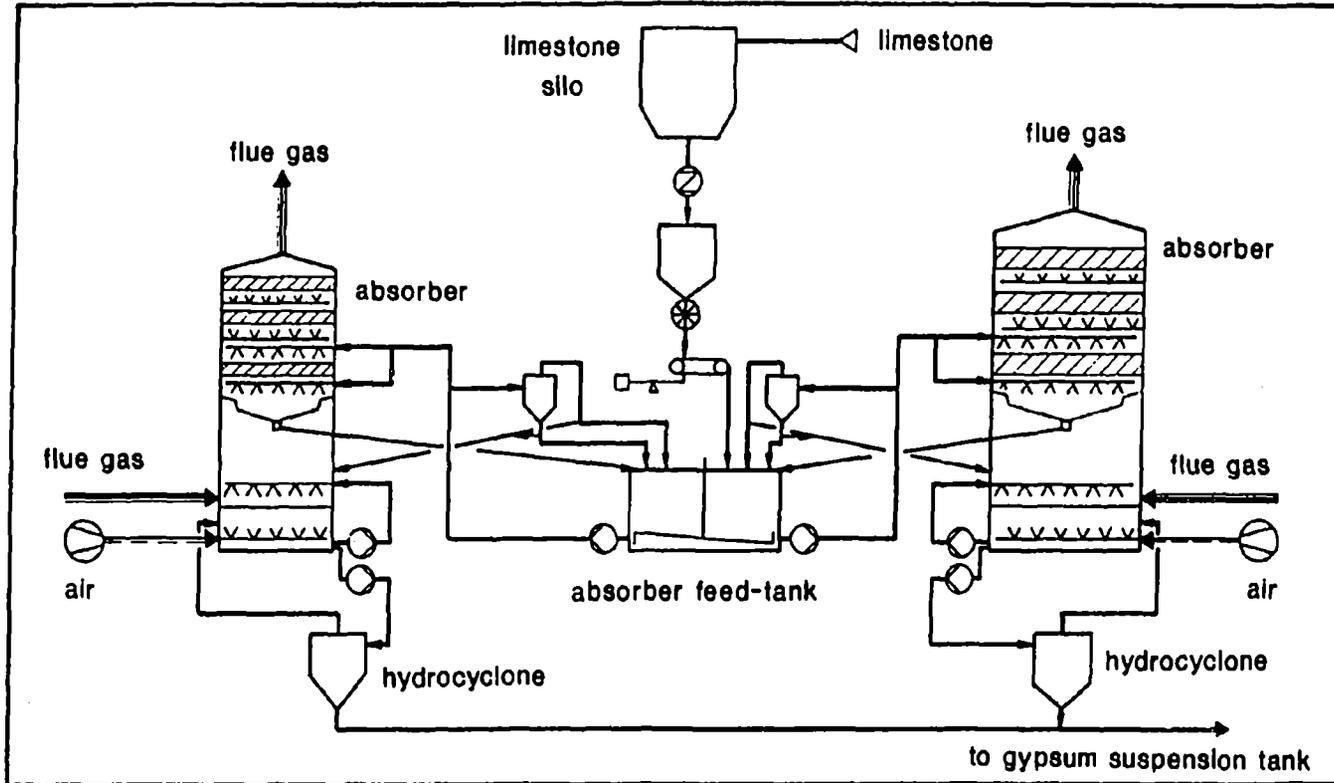


Figure 5. Altbach Power Station, Unit 5 Flow Sheet, Absorber - Neckarwerke 1991

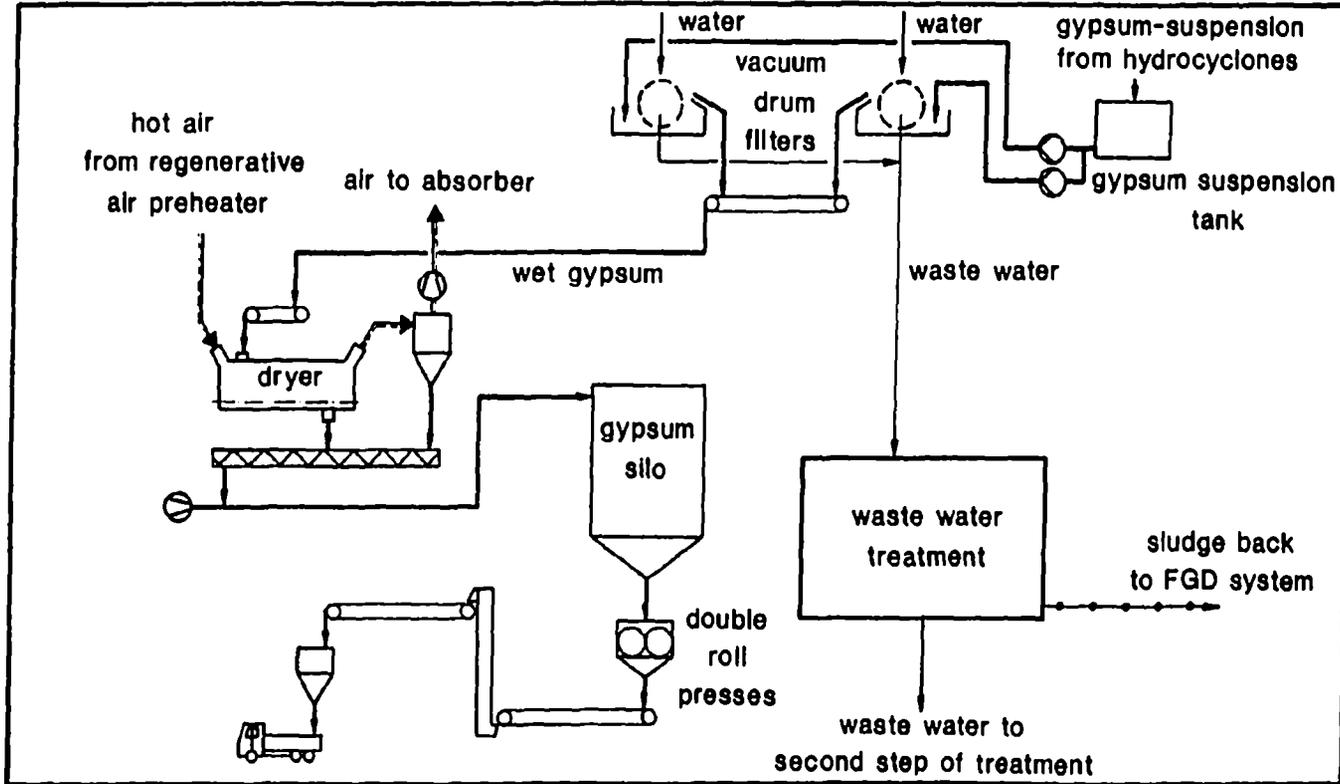


Figure 6. Altbach Power Station, Unit 5 Gypsum Preparation - Neckarwerke 1991

## Major Design Data FGD

Electric power (net)	MW <sub>el.</sub>	420
Flue gas volume	m <sup>3</sup> /h	1.4 mio
Design of untr. SO <sub>2</sub> -gas	mg/m <sup>3</sup>	2700
Limestone requirement	t/h	4
End product: gypsum	t/h	6
Energy requirement	MW	6,6
L/G - ratio	l/m <sup>3</sup> (i.N.h.)	15
Water consumption	m <sup>3</sup> /h	68
Waste water	m <sup>3</sup> /h	18
Limestone silo	m <sup>3</sup>	1500
Gypsum silo	m <sup>3</sup>	2100
Vacuum drum filter	t/h	2 * 9
Gypsum drier	t/h	18
Compactors	t/h	2 * 9

NW-489

Figure 7.

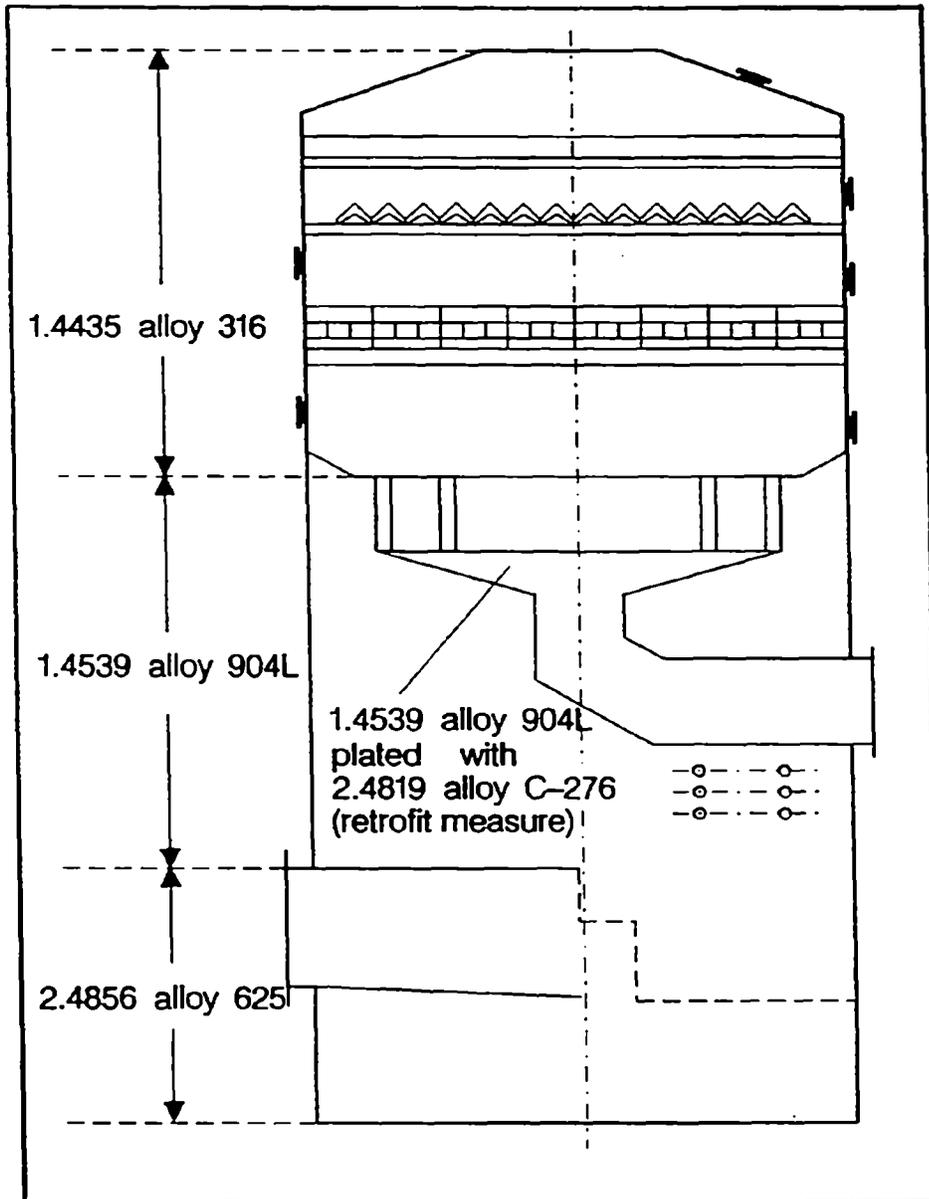


Figure 8. Absorber - Neckarwerke 1991

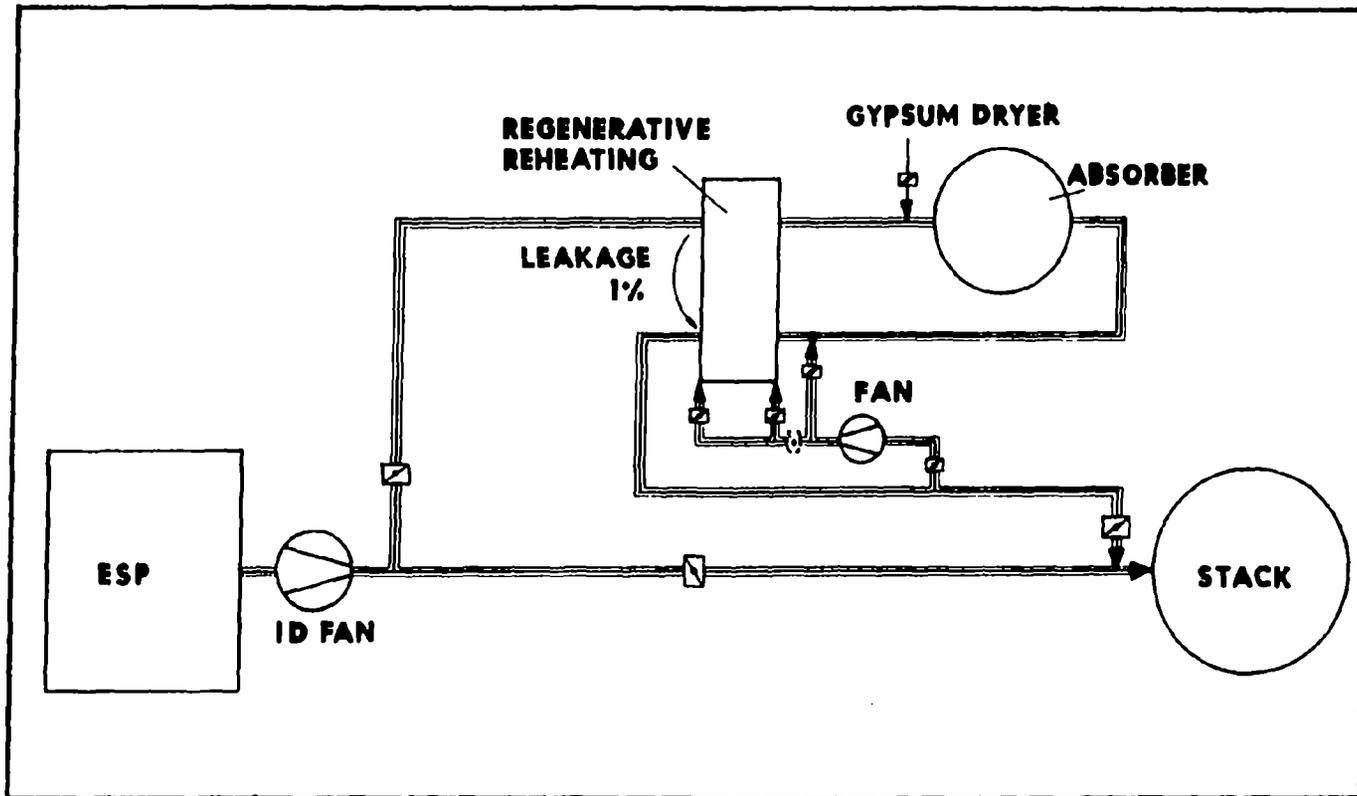
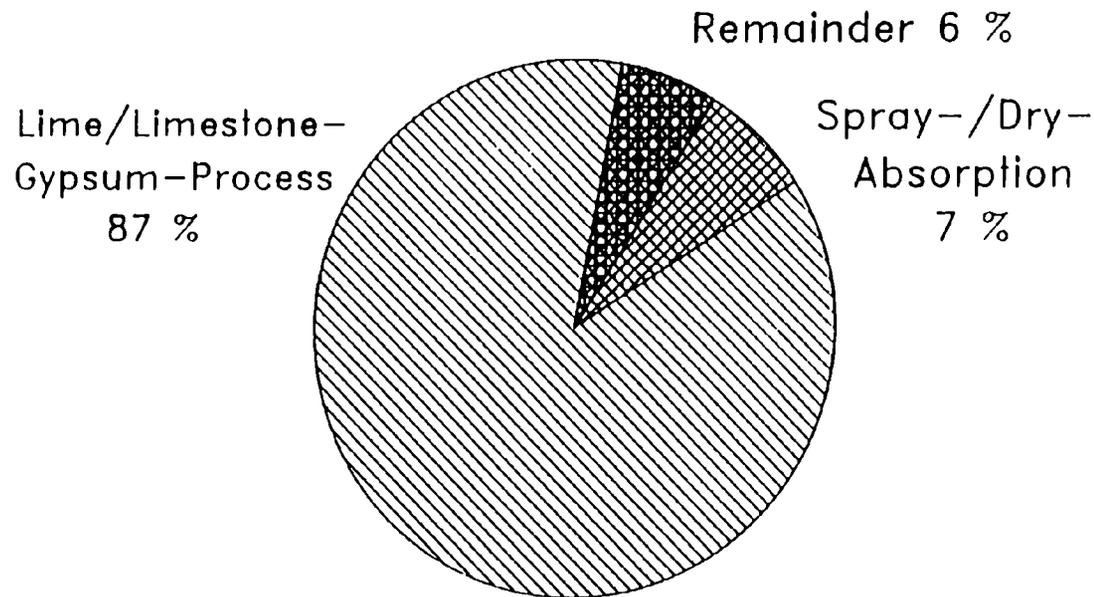


Figure 9. Standard Conceptual Schematic For FGD Plants Till Approx. 700 MW - Neckarwerke 1991

# FLUE GAS DESULPHURIZATION TECHNOLOGIES IN GERMANY (AS OF 1990)



TOTAL POWER PLANTS WITH FGD  
100 % = 38000 MW

NW-171\_2-EL:04.90:nec/zwl

Figure 10.

## INVESTMENT COSTS FGD - UNIT 5

CONSTRUCTION COSTS	11 Mio DM
PLANT DELIVERY	74 Mio DM
REGENERATIVE REHEATING	13 Mio DM
ERECTION	19 Mio DM
ELECTRICALS CONTROL AND INSTRUMENTATION	9 Mio DM
WASTE WATER TREATMENT	<u>1 Mio DM</u>
	127 Mio DM
INTEREST FOR CONSTRUCTION	<u>8 Mio DM</u>
TOTAL COSTS	<u><u>135 Mio DM</u></u>
SPECIFIC COSTS	320 DM/kW

NW-170-EL:nec/zwl

1 \$ = 1,7 DM; 1 DM = 0,6 \$

Figure 11.

# OPERATING COSTS FGD - UNIT 5 (420 MW)

	Costs per Hour Full Load Operation
LIMESTONE	170 DM/h
POWER CONSUMPTION 6,6 MW	990 DM/h
WATER TREATMENT	70 DM/h
OTHERS	30 DM/h
	<hr/>
	1260 DM/h
	<hr/> <hr/>

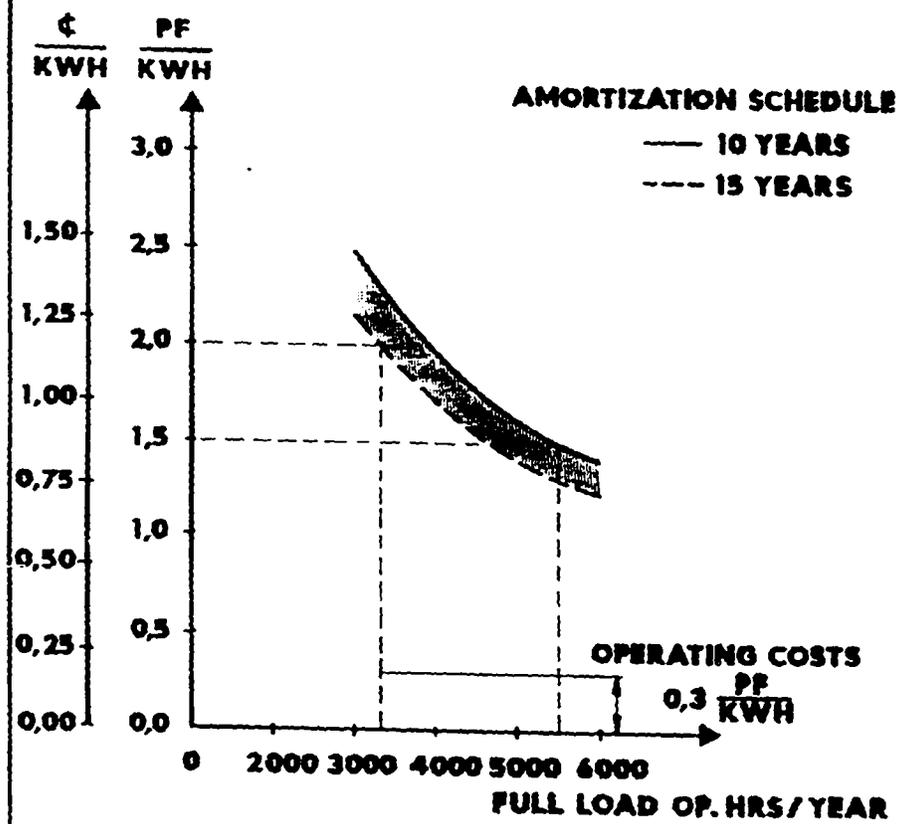
OPERATING COSTS AT 420 MW  
APPROX. 0,3 Pfg./KWh

1 \$ = 1,7 DM ; 1 DM = 0,6 \$

NW-169-EL:04.90:nec/zwl

Figure 12.

**FGD ALTBACH-DEIZISAU,  
UNIT 5: 420 MW<sub>EL</sub>**



1 \$ = 1,7 DM; 1 DM = 0,6 \$

Figure 13. Desulphurization Costs - FGD Unit 5 - Neckarwerke 1991

# DISTRIBUTION OF INVESTMENT COSTS UNIT 5

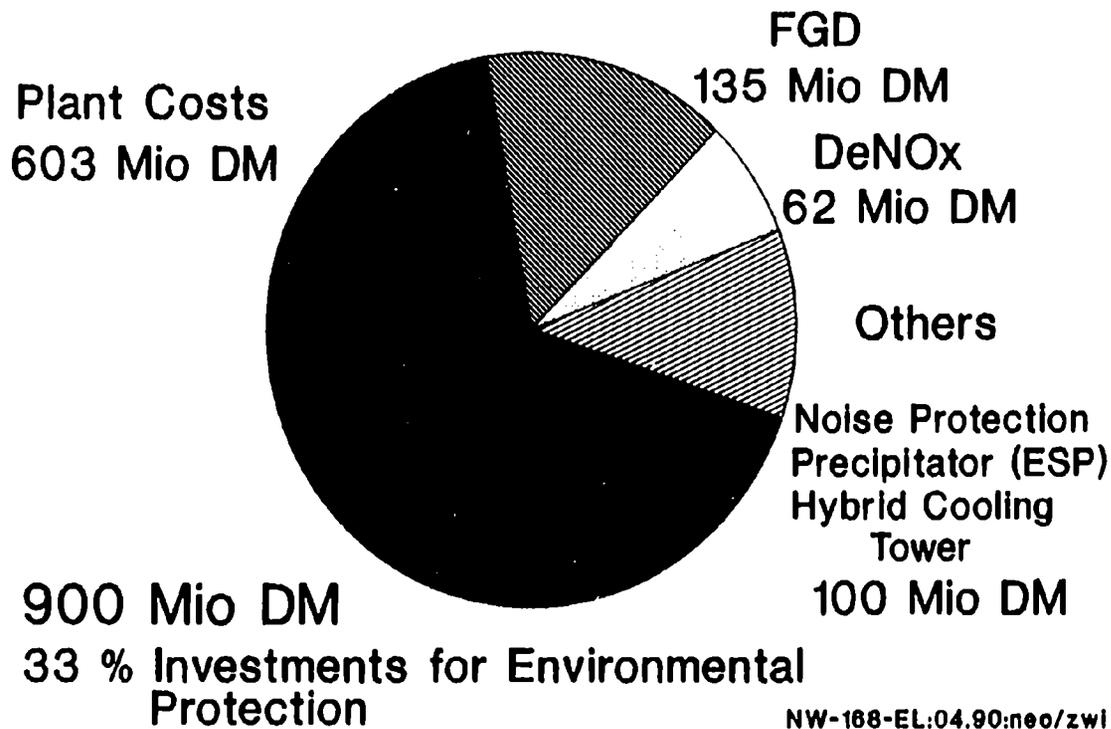
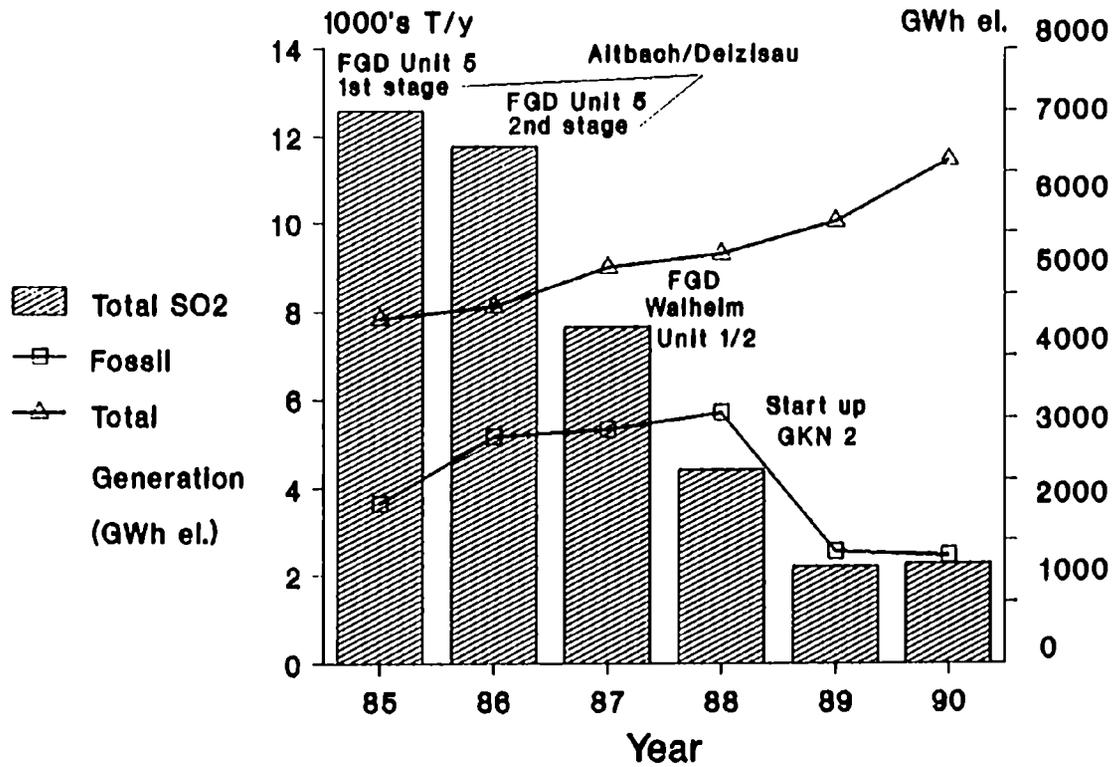


Figure 14.

# SO2 EMISSIONS OF NW 1985 - 1990



NW-493-EL:neo/zwl:09.91

Figure 15.



DEVELOPMENT AND OPERATING EXPERIENCE  
OF FGD-TECHNIQUE AT THE VÖLKLINGEN POWER STATION

- Introduction
- Saarberg-Hölter FGD Process
- S-H-U Process with Formic Acid
- Gypsum
- Cooling Tower Discharge of Flue Gas
- Measurements of Cooling Tower Discharge
- Reheat System for Forced Draft Cooling Tower
- New Power Plant Völklingen-Fenne
- Operating Experience
- Economics
- Prospects

Hans-Karl PETZEL  
Saarberg Company  
Trierer Straße 1  
6600 Saarbrücken, Germany



## Introduction

The growing awareness of ecological issues in Germany has led to the enactment of laws and regulations relating to emissions of large combustors. Since July 1st 1988 the Large Furnance Ordinance (13th Regulation on the Implementation of the Federal Act on Protection against Emissions) specifies an emission level of  $\text{SO}_2 \leq 400 \text{ mg/m}^3$  (140 ppm) and a removal efficiency of  $\geq 85 \%$ , the most stringent of these two numbers applies. The legally binding standards stipulate that none of the daily averages, calculated on the basis of half-hourly averages, may exceed the concentration allowed. The law also requires flue gases to have a minimum temperature at the stack outlet of 162 °F (72 °C) after desulfurization. All wet flue gas desulfurization systems suffer from the technical-physical drawback that the treated flue gas leaves the FGD-plant almost watersaturated at a temperature of 122 °F to 131 °F (50 °C to 55 °C). Therefore the desulfurized gas must be reheated, if it is discharged via a power plant stack. Treated flue gases do not have to be reheated if discharged via a cooling tower.

Saarbergwerke AG is the second biggest mining company in the Federal Republic of Germany and a power plant operator with an installed capacity of 2 400 MW<sub>e1</sub> at three sites.

At Völklingen - the site which I am responsible for - we operate the so-called 230 MW Prototype Power Plant. Prototype, because some very modern ideas for power generation are realized for this plant, such as fluidized bed combustion with a submersed heat exchanger, additional gas turbine for a combined cycle and treating the full flue gas quantity in an FGD unit, installed into a natural draft cooling tower.

The Prototype Power Plant Völklingen is the first power plant with cooling tower discharge of desulfurized flue gas.

It is in operation since August 1982 with meanwhile an operation time of nearly 60 000 hours. The investment costs were subsidised by the Minister of Research and Technology.

Adjacent to this unit, we operate Fenne III, a 170 MW unit, and since August 1982 a 210 MW power plant with 185 MW<sub>th</sub> for district heating also with cooling tower discharge of the desulfurized flue gas.

The largest units we are operating at Saarberg are a 707 MW unit and a 800 MW unit.

#### Saarberg-Hölder FGD Process

The coal of the Saarberg Company has a sulfur content of 1 - 1.5 %. In the seventies - without the request of a law - our company decided to develop a wet desulfurization process in cooperation with the engineering company Hölder. The development of wet scrubbers for FGD systems on calcium basis has started with lime as absorbing media as the reactive component. In a Saarberg power plant the process was tested under normal operating conditions.

And so we started in August 1982 the Prototype Power Plant Völklingen with lime as absorbent. The FGD plant was not rubber lined. We operated at that time our lime scrubber in the pH-range of about 8 - 10. The experience was that scaling took place in several places in the FGD plant. Always after an operation period of several weeks we had to shut down the plant to remove the incrustations. To avoid scaling we tested the FGD-process with a lower pH-range. Our demonstration plant was designed for a removal efficiency of 80 % and an emission level of  $\leq 540 \text{ mg SO}_2/\text{m}^3$ .

To be in compliance with the emission law July 1st 1988 we reconstructed the FGD-plant and commissioned again in 1986. Lime was replaced by limestone. As the limestone scrubbers are operating in the pH-range of 4.5 - 5.5 the FGD-plant had to be rubber lined. For some elements at the wet-dry interface at high temperatures the construction material is Hasteloy.

The main disadvantage of a limestone unit is that a limestone unit needs higher investment cost, because for a given absorption efficiency the scrubber modules have to be larger and the recycle pumps have to be larger as well.

This disadvantage of higher investment cost is partly reduced due to the fact that the oxidation to reach the final product gypsum may be done internally in the scrubber so there is no external oxidizer necessary.

The lower pH-range of limestone has several advantages listed below:

1. Oxidation may be done internally in the scrubber.
2. Due to the lower pH-value the primary product of the reaction is not calcium sulphite  $\text{CaSO}_3$ , but calcium bisulphite  $\text{Ca}(\text{HSO}_3)_2$ .

Since calcium sulphite is hardly watersoluble whilst calcium bisulphite has a much better solubility the risk for scaling in a limestone scrubber is a lot less than in a lime scrubber. It is our experience now since 1986 that scaling takes no more place.

3. To form gypsum from calciumsulphite an oxidation is necessary and this reaction goes via calciumbisulphite. The more easy and safer way obviously is not to form calciumsulphite at all, but to form calciumbisulphite directly.
4. At a lower pH-value the unit does not react sensitive against deviations in volumetric flow rate or  $\text{SO}_2$  inlet concentration, but can rather easily handle those deviations.
5. Especially due to the longer retention time the gypsum crystals formed in the limestone scrubber are larger and thus easier to dewater giving better gypsum qualities.

Additionally in the limestone scrubber the gypsum quality is constant even at fluctuating operating conditions.

6. The main advantage of a limestone scrubber is the lower operating cost since limestone is a lot cheaper than lime even taking into consideration that the amount of limestone needed is nearly twice as much as the amount of lime would be, even at the same stoichiometric ratio.

### 8-H-U Process with Formic Acid

Compared to common limestone processes the S-H-U limestone process is additionally buffered with formic acid.

This reduces the pH-range for the reaction to be in the range of appx. 4 - 5 and forms a lot more available calcium ions. All the advantages listed above are even more valid for the process using formic acid compared to processes not using formic acid.

The number of calcium ions available with formic acid is about 40 times as high as the calcium ions available without formic acid addition.

The addition of formic acid enhances the transfer of sulfur dioxide from the flue gas to the washing fluid. It buffers the washing fluid in the appropriate pH range to ensure a high rate of utilization of the limestone reagent with simultaneous high SO<sub>2</sub> absorption. The stoichiometric ratio of the absorbent in the S-H-U-process is consequently only 1.00 to 1.02 even with limestone, whereas for conventional limestone processes much higher stoichiometric ratios are common-place.

Formic acid addition also has the advantage that SO<sub>2</sub> abatement is far less impaired when chlorides are present and requires some 20 % to 25 % lower liquid-to-gas ratio with less energy needed for the washing fluid pumps.

The use of formic acid makes a compact combined scrubber feasible which is economical in space and employs integrated cocurrent and countercurrent flow stages.

Formic acid also has the advantage for the process technology that an integrated oxidation of the SO<sub>2</sub> bonded with the washing fluid can take place to form gypsum (CaSO<sub>4</sub>) in the scrubber sump simply by injecting air. There is therefore no need for a separate oxidizer.

## **Gypsum**

The gypsum produced is of high quality and is utilized by the gypsum and the cement industry. The composition and especially the reflectance of the FGD gypsum is supervised by the industry.

The German market consumes about 2.5 Mio tons/a gypsum. The coal fired stations produce about 2.5 Mio tons/a. That means the gypsum of the FGD-plants is completely utilized. By centrifuges the gypsum is being dewatered to a residual moisture of approximately 6 to 8 %. Then it is used for example for wall boards. For plaster the FGD gypsum is being additionally dried and pelletized.

## **Cooling Tower Discharge of Flue Gas**

As an alternative to reheating solutions Saarbergwerke AG and Saarberg-Hölter Umwelttechnik GmbH (S-H-U) have developed a different approach which is internationally protected by patent. The desulfurized flue gas is mixed with the cooling air of the cooling tower and transported into the atmosphere. In principle, no stack is required for the normal operation of this type of power plant.

The application to avoid costly reheating of desulfurized flue gas made its world debut 1982 in the 230 MW coal-fired Saarbergwerke power plant Völklingen. The S-H-U flue gas desulfurization unit is integrated into a cross-flow natural-draft cooling tower. It is located in the center of the cooling tower and measures approximately 31 m x 18 m. The four outlet tubes with a diameter of some 3 m end at a height of appr. 40 m. The height of the cooling tower is 100 m.

The walls of the cooling tower are likely to be affected by harmful residues since conglomerated water drops are falling back into the tower as well as condensation of vapor occurring at the shell. Carbon dioxide is particularly harmful. The causative factor is carbonization of the concrete which occurs when carbonic acid is present simultaneously with water vapor.

Without adequate protection inside the shell, the concrete as well as the steel reinforcement would be attacked.

As a result of tests we decided that concrete with Portland Cement P/45 F HS and a water-cement factor of  $\leq 0.5$  has to be used for the shell and the tower pillars. Furthermore the inside of the shell must be coated. As with certain wind speeds the plume is touching the outside of the shell, also the outer shell was protected.

In the Prototype Power Plant Völklingen directly after the concrete work continuously a primer was applied. Then the shell was coated twice with epoxy-resin. After an operation time of 17 000 hours on the upper third inside the shell we experienced peeling.

It is very likely, this was caused due to the fact that the temperature during application was below + 5 °C, so that the primer could not be applied correctly. In the time to the next summer the surface of the concrete was no longer clean, so that the primer on the surface did not accomplish the actual bond.

In a height between 80 and 100 m the inside of the shell was sand blasted, the primer was applied again and twice coated with two layers of epoxy resin. We inspected the shell. Up to now (60 000 h operation time) the coating of the shell shows no fissuring and no cracks.

The cooling tower of the new plant was totally completed and then the shell was cleaned by high pressure water. Then we followed the same procedure: a primer was applied and then the shell twice coated with two layers of epoxy resin.

#### Measurements of Cooling Tower Discharge

To substantiate the theory of cooling tower discharge comprehensive measurements were taken in the winter 1984 and the summer 1985 by several university institutes. The results are published at several meetings.

It is essential that cooling tower plumes are able to pierce non-turbulent layers of atmospheric inversion and to reach higher levels. This is a particular advantage when there are non-turbulent weather situations (smog).

In our case the desulfurized flue gas is mixed with the cooling air and piercing the inversion layer. Also during smog situation we are allowed to continue the operation of the power plant.

- The cooling tower and a stack have different effects on ground level concentrations in the immediate area. Because of its higher temperature and greater thrust the cooling tower plume remains more compact for a longer period.
- This is due to the internal circulation mechanism. Since the cooling tower plume disperses at a greater altitude, the "emission" is lower with this type of discharge than in the case of flue gases released from stacks.
- Due to an additional separator installed in the flue gas the concentration of dissolved pollutants and particles sticking to droplets is further reduced by a factor of approx. 2.

**SAARBERG**

**Comparison of Flue Gas Discharge  
via Stack or Cooling Tower**

	<b>Stack Cleaned Gas</b>	<b>Cooling Tower cleaned gas a. C. T. air</b>
Velocity	5	1
Mass	1	14
Impulse	1	3
Amount of Heat	1	6
Draft	1	10
SO <sub>2</sub> Concentration	12	1

A further advantage of cooling tower discharge is that the concentration of pollutants is reduced by a factor of 24 compared with stack discharge at the emission outlet.

The theoretical predictions about the performance of the cooling tower, the dispersal pattern of the plume in the atmosphere and the chemical and physical transformations in the plume were confirmed by these measurements.

This discharge of flue gas into the cooling tower and mixing into the plume is now fully approved as alternative to the stack. The provisions of the clean air standard are complemented by special appraisal.

#### **Reheat System for Forced Draft Cooling Tower**

The 170 MW unit Fenne III has two forced draft cooling towers. Therefore we could not apply the cooling tower discharge. The desulfurized flue gas has to be reheated. We decided for a heat exchanger system. The untreated flue gas transfers the heat to the water in a heat exchanger. Then in a second heat exchanger the warm water heats up the cooled desulfurized flue gas to a temperature of above 162 F (72 C). The flue gas is then released via a stack. The material of the heat exchanger tubes is a PTFE basis. This system also operates without difficulties. Compared to the design of a regenerative heat exchanger the advantages are

- due to lower temperatures of the raw gas condensation does occur giving lower concentrations of pollutants
- due to the principle of the heat exchanger no leakage occurs; thus the concentration of pollutants is lower

#### **New Power Plant Völklingen-Fenne**

The new power plant at the Völklingen site has a counter flow natural draft cooling tower. The FGD-plant is located besides the cooling tower.

The location of the FGD plant outside the cooling tower has the advantage that the dimensions of the cooling tower only have to fit the thermodynamic requirements.

The following comparison demonstrates this:

Both units the Prototype Power Plant and the new power plant have the same output

The basic diameter of the cooling tower for the

Prototype power plant is	90 m
new power plant	is 60 m.

### Operating Experience

Since 1986 we are operating all our FGD-units in the Saarberg company with formic acid, limestone and a low pH-value. All units are rubber lined. The material in the quenching zone is Hasteloy.

The straightforward technical construction of the basic flow diagram is matched by an equally uncomplicated, fully automatic process. This ensures that there is no need for any labor-intensive chemical operations in the power plant. The FGD-unit is controlled on a side panel in the control room of the plant. No additional operators are required in the control room to run the FGD-unit. The fully automatic start-up and shut-down procedures via the control units require no lengthy preparation or special measures, such as separate start-up of the various pump circuits. The unit attains its full desulfurization capacity within 5 to 7 minutes.

During operation since 1986 the power plant complex has suffered no restrictions on availability whatever due to FGD. According to emission law the power plants could be operated 240 hours/a without FGD. Due to the high availability we installed no bypass and also no stack - also not for the new power plant.

The cooling tower discharge of flue gas to avoid costly and energy intensive reheating is gaining ground in Europe. The RWE (Rheinisch-Westfälische Elektrizitätswerke AG) was the first major German energy producer to decide to discharge treated gases via cooling towers in all its power plants with natural-draft-cooling-towers with a total capacity of 6.000 MW (6 x 600 MW, 8 x 300 MW). Meanwhile more than 20 units are in operation with cooling tower discharge of desulfurized flue gas.

Our Prototype Power Plant Völklingen has the most experience with an operation of 60 000 hours. The advantages of cooling tower discharge are proved

- no use of external energy for reheat
- no operating costs for reheat
- availability of system 100 %
- stackless power plant

### **Economics**

When we compare the cooling tower discharge with a reheat system there are additional investment costs not only for a gas heat-exchanger, but also for steel construction foundation and additional flue gas ducts. Power is needed for a rotating gas heat-exchanger and more significant for covering the pressure drop of about 14 mbar.

Similar considerations apply to the costs of operating, maintaining and cleaning a gas heat-exchanger. In addition you have to consider the costs for a stack.

None of these considerable investment and operating costs were incurred with the Völklingen cooling discharge (stackless power plant).

The solution adopted in Völklingen involves reduced investment costs of approx. DM 10,2 MW (\$ 6 MM) compared with a conventional FGD unit with reheating and stack.

The Völklingen Economics are

- lower energy consumption
- no maintenance and cleaning
- higher availability
- 5 - 7 % lower operating costs per year

## Prospects

Wet-scrubbing desulfurization processes on lime or limestone will remain dominant with over 90 % of the market.

There will be a growing emphasis on those desulfurization systems which use less energy (electricity) and, above all, those which obtain high levels of availability, for example by using organic additives.

In Europe, the main FGD end-product permitted in the future will be gypsum alone. This can be used by the gypsum and cement industry. By contrast, there will be little interest in Europe in end-products from so-called dry scrubbing processes with unreacted lime components because of the need for expensive, environmentally unacceptable special storage facilities.

The Völklingen plant with an S-H-U flue gas desulfurization unit with cooling tower discharge is in its tenth year of operation and has successfully demonstrated that there is a more effective and far cheaper alternative to the costly and energy intensive conventional reheating of desulfurized flue gases and with a high availability.



**ADVANTAGES OF THE CT-121 PROCESS  
AS A THROWAWAY FGD SYSTEM**

M. J. Krasnopoler  
G. Shields  
Bechtel Power Corporation  
9801 Washingtonian Blvd.  
Gaithersburg, MD 20878-5456

Y. Shoji  
Chiyoda Corporation  
2-12-1, Tsurumi-Chuo  
Tsurumi-Ku  
Yokohama 230, Japan

8A-134

## **ABSTRACT**

Over 3,900 MW of flue gas desulfurization plants utilizing the CT-121 process are installed and in design. The majority of these produce high-quality marketable gypsum. For the North American market, however, process design of CT-121 has been optimized to produce throwaway gypsum

Bechtel is currently marketing the Chiyoda CT-121 process for a number of United States flue gas desulfurization (FGD) retrofit applications. These CT-121 designs typically address high sulfur (4%) and high chloride (0.4%) coal and require high SO<sub>2</sub> removal efficiencies (95% and above). The designs produce a throwaway gypsum byproduct and often include zero liquid discharge from the FGD process.

Current designs use large non-redundant absorbers, called jet bubbling reactors (JBR), that achieve consistent high SO<sub>2</sub> removals at relatively high liquor chloride concentrations. The unique gas/liquid contacting action of the JBR also removes most of the particulate from the inlet flue gas. The large gypsum crystals produced in the CT-121 process allow single-step dewatering of the gypsum slurry in a gypsum stack or vacuum filters.

This paper reviews the various design options available and emphasizes the advantages of the CT-121 process in the United States retrofit FGD market. These same advantages will be important to the next generation of coal-fired power plants.

## **ADVANTAGES OF THE CT-121 PROCESS AS A THROWAWAY FGD SYSTEM**

### **INTRODUCTION**

The Chiyoda Thoroughbred 121 (CT-121) process has been well proven in nine commercial plants worldwide with an installed capacity totalling 1,600 MW. Current designs underway total a further 2,450 MW. These installations have primarily been in Japan where the high-quality gypsum is utilized either for wallboard or cement manufacture. In the United States, the 40 MW Abbott plant at the University of Illinois operates on high sulfur coal and produces byproduct gypsum which is landfilled due to the lack of a commercial market. The 100 MW Plant Yates, scheduled to startup in 1992, will also produce throwaway gypsum.

This paper will demonstrate that the inherent advantages which the CT-121 flue gas desulfurization (FGD) process has over other limestone forced oxidation processes can be similarly applied to a throwaway byproduct FGD process. It will highlight the following:

- Process and mechanical simplicity
- High SO<sub>2</sub> removal efficiency
- High particulate removal
- Scaleup
- Layout features
- Single-step gypsum dewatering
- Zero-liquid discharge capability

### **CT-121 PROCESS SIMPLICITY**

The CT-121 process is an advanced, wet limestone FGD process that uses a unique gas/liquid contacting device, the jet bubbling reactor (JBR) as its absorber. The three following general issues capture the simplicity of CT-121:

1. All process reaction steps occur simultaneously in the JBR.
2. Complex slurry recycle systems are eliminated.
3. Byproduct gypsum dewatering is achieved in a single stage.

The simplicity of the CT-121 process is clearly depicted in Figure 1. This simplicity results in significant benefits in terms of capital and operating costs.

The four major FGD process steps which occur simultaneously in the continuous liquid phase of the JBR are:

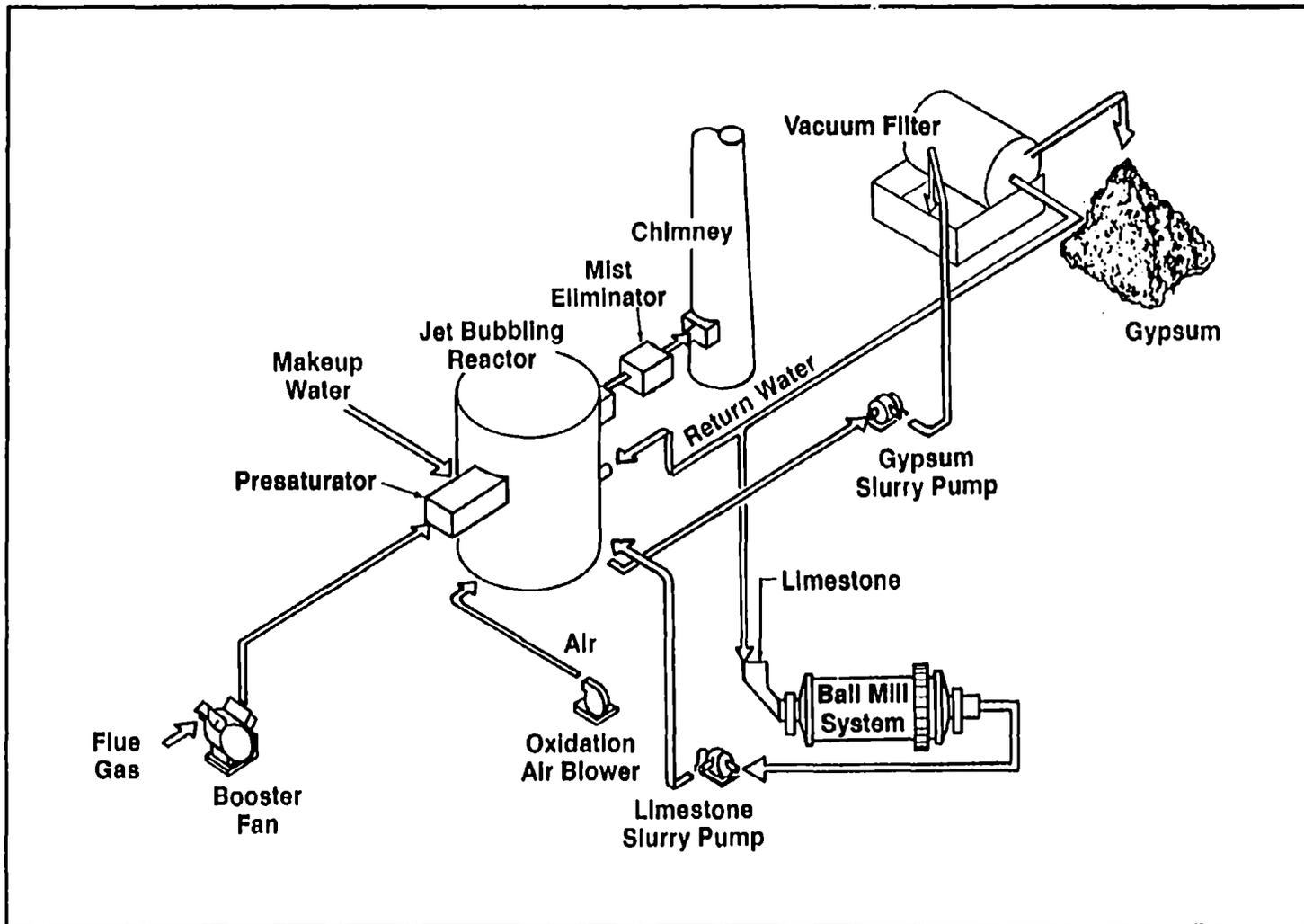
- SO<sub>2</sub> absorption
- Oxidation of acid sulfites
- Neutralization with limestone
- Gypsum crystal growth

The significant innovation of the CT-121 process reverses the conventional concept by making the JBR slurry the continuous phase. Conventional FGD using spray towers have flue gas as the continuous phase. This change from other limestone FGD processes enhances the mass transfer and chemical reaction mechanism and accounts for the unique characteristics of the CT-121 process. The most important enhancement of CT-121 is its low-pH operation and the resultant benefits yielded by different reaction chemistry. CT-121's improved gas/liquid contact also increases the particulate removal capability.

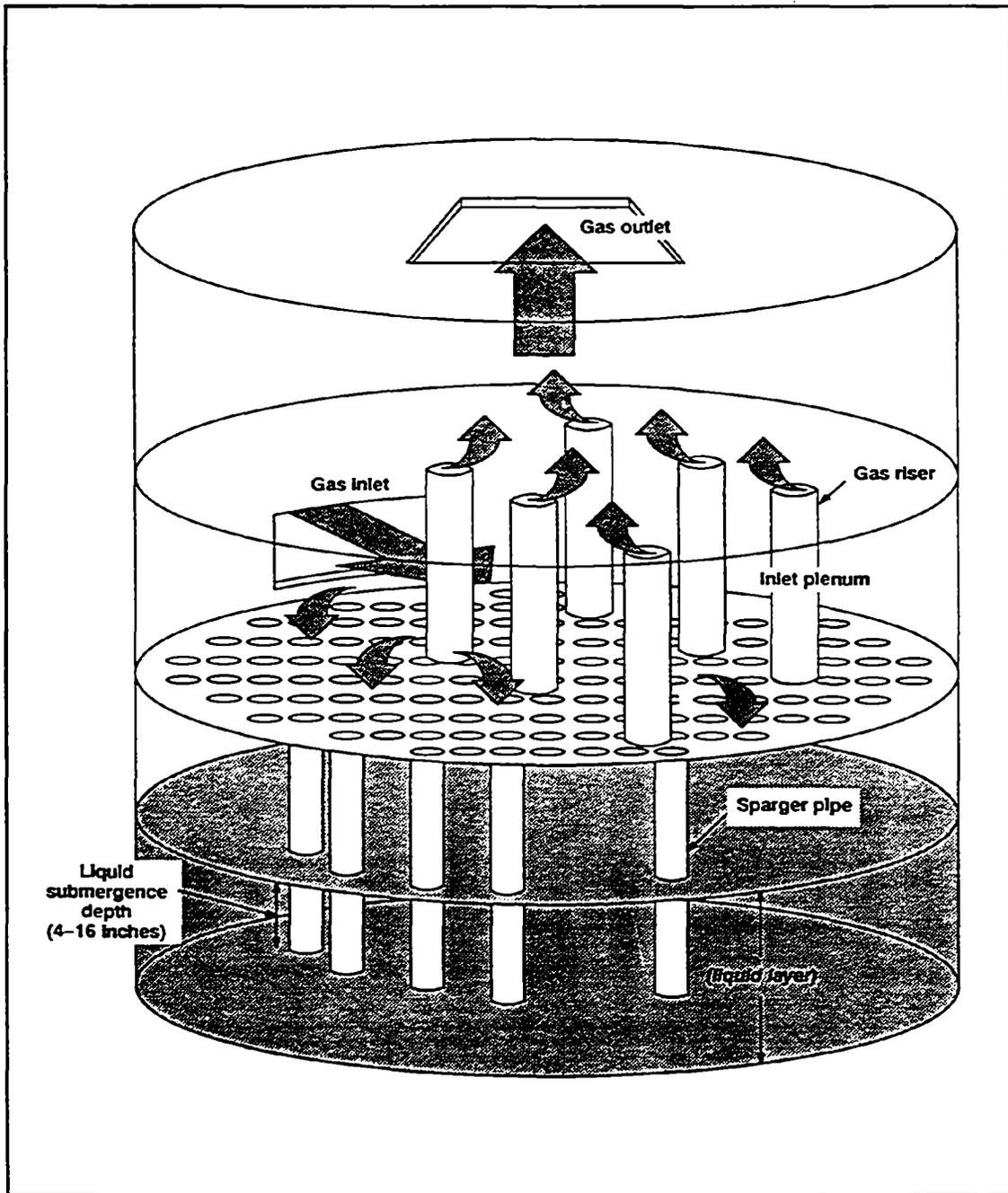
#### Process Description

Figure 1 shows the entire CT-121 process and Figure 2 depicts the heart of the process, the JBR. Flue gas enters the system through a presaturator duct and then is finely dispersed into the JBR slurry through gas spargers. SO<sub>2</sub> is absorbed as the flue gas bubbles up through the slurry. The treated flue gas then flows up through the gas risers, into the plenum above the upper deck, and out of the JBR to the mist eliminator and chimney.

Oxidation air is introduced into the JBR to oxidize the acid sulfites (HSO<sub>3</sub><sup>-</sup>) to sulfates (SO<sub>4</sub><sup>-</sup> + H<sup>+</sup>). Limestone slurry is added to neutralize the acid sulfates to form gypsum and to maintain the pH. The JBR is designed for a slurry residence time of 15 to 25 hours to achieve large crystal growth and efficient limestone conversion.



**Figure 1.** CT-121 Flow Diagram. *The CT-121 process is simple because it eliminates mechanical equipment such as the large recycle pumps and primary dewatering equipment of other FGD processes.*



**Figure 2.** Gas Flow in the JBR. *The even spacing of the JBR's gas spargers and gas risers assure uniform flue gas distribution.*

A bleed stream of JBR slurry is pumped to the dewatering system, either a vacuum filter or a gypsum stack. Return water from dewatering is pumped to the ball mill for limestone slurry preparation and back to the JBR.

### Process Features

The major FGD process steps occur in CT-121's JBR because the slurry is the continuous phase. Conversely, in other FGD processes, SO<sub>2</sub> absorption and partial oxidation occur in the spray section while other reaction steps occur in the recycle tank. Large recycle pumps circulate substantial flowrates of slurry from the recycle tank to the spray nozzles. By contrast, the slurry circulation required in the JBR is supplied by large-diameter low-speed turbine agitators and supplemental mixing from the flue gas and oxidation air spargers. Thus, the CT-121 process eliminates the large recycle pumps and spray headers, making it mechanically less complex than conventional spray tower FGD systems.

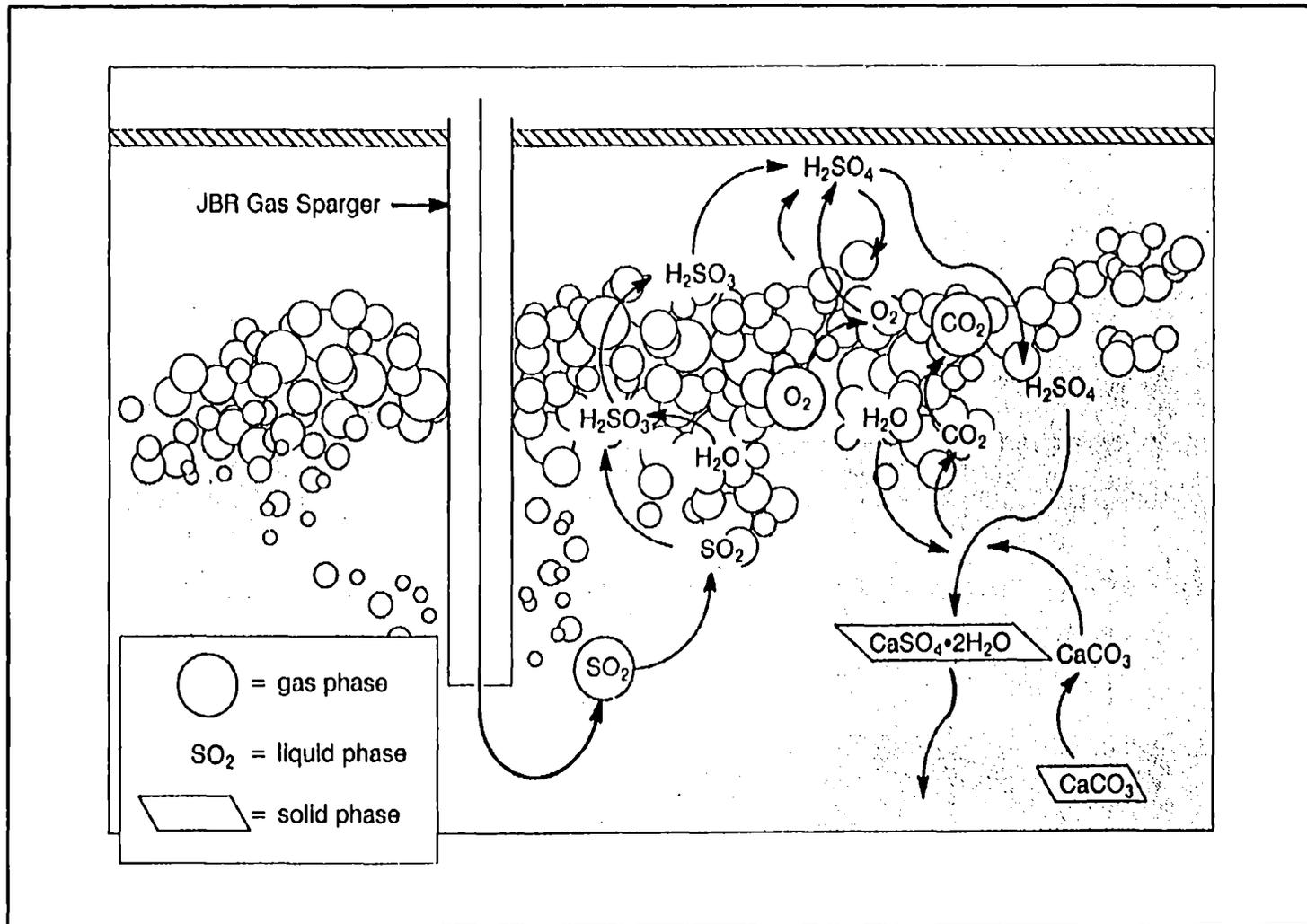
Figure 3 summarizes CT-121's process chemistry and shows that H<sub>2</sub>SO<sub>3</sub> is rapidly oxidized to H<sub>2</sub>SO<sub>4</sub> before it is neutralized by limestone. Thus, SO<sub>2</sub> absorption in the JBR is essentially independent of dissolved alkaline species. Conversely, conventional spray tower designs operate at relatively high pH levels (5.5 to 6.0) and do depend on dissolved alkaline species to provide the driving force for SO<sub>2</sub> removal.

Oxidation of dissolved sulfite to sulfate in the CT-121 process occurs virtually instantaneously after SO<sub>2</sub> absorption. Thus, SO<sub>2</sub> backpressure from sulfite in solution is eliminated and high removal efficiencies can be maintained. Complete oxidation and low pH also eliminate the potential for scaling.

Operation at low pH is the key to scrubbing effectively with limestone, because of enhanced limestone dissolution and sulfite oxidation. Limestone dissolution is 100 times faster at CT-121's typical pH of 4.5 than at other FGD system's typical pH of 5.5. The limestone dissolution rate is a function of hydrogen ion concentration or acidity:

$$r = K [\text{CaCO}_3] [\text{H}^+]$$

where  $r$  is the limestone dissolution rate,  $K$  is the rate constant,  $[\text{CaCO}_3]$  and  $[\text{H}^+]$  are the concentrations of calcium carbonate and hydrogen ion. Since  $\text{pH} = -\log_{10}[\text{H}^+]$ , for example, a decrease in pH of 2 corresponds to a 100-fold increase in hydrogen ion



**Figure 3.** Sequence of CT-121 process chemistry in the JBR. *The enhanced mass transfer and improved chemistry of the CT-121 process allow low-pH operation.*

concentration and thus limestone dissolution rate. CT-121's fast limestone dissolution and long JBR liquid residence time creates high limestone utilization, typically over 99 percent.

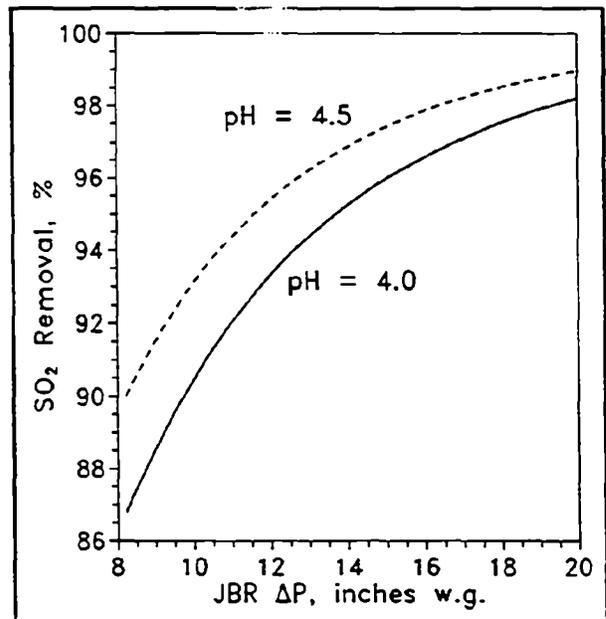
To summarize, CT-121's process features are:

- Mechanical simplicity
- Low pH operation
- No potential for scaling
- Complete oxidation
- Extremely high limestone utilization
- Large, easily dewatered gypsum crystals

#### HIGH SO<sub>2</sub> REMOVAL EFFICIENCY

The CT-121 process can consistently achieve greater than 95 percent SO<sub>2</sub> removal over a full range of coal sulfur and chloride levels and at significant turndown ratios. As shown in Figure 4, SO<sub>2</sub> removal may be increased by increasing either the JBR pressure drop or system pH. Pressure drop is increased by increasing the submergence of the sparger tubes and pH is controlled by the limestone addition rate.

Careful design and layout of the JBR gas spargers and gas risers as well as system backpressure assure excellent gas distribution and high-level SO<sub>2</sub> removal even at turndown to 25 percent of design gas flow. Figure 2 depicts the gas flow through the JBR and shows the even spacing of the gas spargers and gas risers. To achieve high SO<sub>2</sub> removal in a conventional spray tower, the liquid to gas (L/G) ratio and consequently the recycle slurry flowrate must increase. One possible limitation of high



**Figure 4.** Typical CT-121 SO<sub>2</sub> Removal Efficiency. *The CT-121 process can achieve high SO<sub>2</sub> removal efficiencies by increasing the JBR pressure drop or pH.*

L/G's is inadequate gas-liquid distribution, in particular where turndown is required. Thus, the JBR uniform gas distribution is a significant advantage over spray towers.

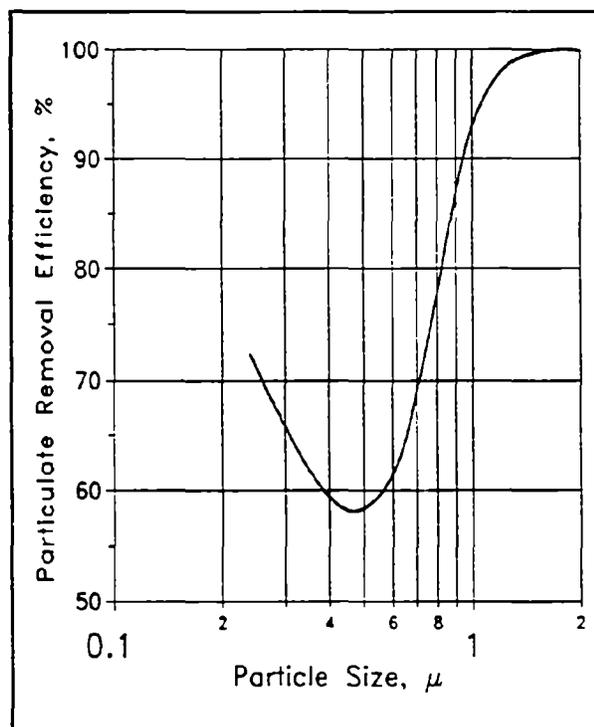
The CT-121 systems on the Mitsubishi Petrochemical (85 MW) and Nippon Mining (75 MW) CT-121 plants which burn high sulfur oil achieve 98 percent SO<sub>2</sub> removal. The 225 MW CT-121 process at Kashima treats gas from a high-sulfur oil-fired boiler and removes 97 percent of the inlet SO<sub>2</sub>. The CT-121 system at the 40 MW stoker-fired boiler at the Abbott Plant achieved 93 to 96 percent SO<sub>2</sub> removal while operating on coals ranging from 1.5 to 4.5 percent sulfur. The aggregate past performance of the CT-121 system establishes its capability to achieve consistent high SO<sub>2</sub> removal efficiencies while burning high sulfur coal.

#### HIGH PARTICULATE REMOVAL

Due to the unique gas-liquid contactor, the JBR, the CT-121 removes most of the particulates from incoming flue gas. This has been demonstrated in pilot and commercial plants<sup>1</sup>. This high particulate removal efficiency is due to the improved gas-particulate/liquid contacting created by:

- Turbulent two-phase flow of flue gas and JBR slurry
- High gas-side pressure drop
- Large interfacial contacting area of small collapsing gas bubbles

As shown in Figure 5, the JBR achieves high levels of particulate removal in the sub-micron range<sup>2</sup>. This can compensate for the performance of a marginal electrostatic precipitator and reduce particulate levels to meet New Source Performance Standards (NSPS).



**Figure 5.** CT-121 Particulate Removal Capability. *The CT-121 process can achieve high particulate removal efficiencies.* (Source: Reference 2.)

This benefit of lower particulate emissions is achieved without any increase in the capital or operating costs of the CT-121 process.

The resultant particulates removed by the CT-121 scrubbing action collect in the gypsum byproduct which can be safely landfilled. CT-121's particulate removal capability will be increasingly more important as environmental regulations on air toxics are tightened and the need to remove a larger percentage of heavy metals from stack gases increases.

### **SCALEUP**

CT-121's unique gas/liquid contacting device, the JBR, is ideally suited for scaleup to large sizes. Scaleup of the CT-121 process simply means increasing the number of JBR spargers and increasing the JBR diameter to accommodate them. Each sparger in the JBR is designed for the same set gas flowrate, so scaling up a JBR simply means increasing the number of spargers. For example, to double the gas flow capacity, the number of spargers are doubled. Uniform gas flowrate per sparger and SO<sub>2</sub> removal efficiency are thereby maintained. Conversely, the scaleup of conventional spray tower systems is limited as spray header designs become very complex and the risk of maldistribution of flue gas or spray droplets increases.

The largest CT-121 unit in operation is a 350 MW oil-fired unit operating at over 90 percent SO<sub>2</sub> removal on 2.9 percent sulfur oil. Currently in the design or construction phase is a single absorber CT-121 system for a 500 MW coal-fired utility boiler, as well as a 1000 MW single-absorber CT-121 system.

Chiyoda and its clients are confident in the scaleup of CT-121 to these large sizes because of design simplicity and past operating history. Table 1 indicates an aggregate reliability of major CT-121 units in excess of 99 percent. In all instances these units operate with a single JBR. In fact, no CT-121 plant has ever used a spare absorber. The ability to scaleup the CT-121 process to large capacities provides economies of scale and capital savings. This should prove to be of major benefit to the future North American FGD market.

**Table 1**  
**CT-121 PROCESS RELIABILITY PARAMETERS**

<i>Period:</i>	<b>Mitsubishi Petrochemical Yokkaichi</b>	<b>Nippon Mining Co. Chita</b>	<b>Toyama Kyodo Electric Power Unit 1</b>	<b>Toyama Kyodo Electric Power Unit 2</b>	<b>Kashima Northern Joint Power Co.</b>	<b>Hokuriku Electric Power Kusajima</b>	<b>University of Illinois Abbot</b>
<i>From</i>	<i>May 11, 1982</i>	<i>Nov. 10, 1983</i>	<i>July 9, 1984</i>	<i>Aug. 23, 1984</i>	<i>Nov. 15, 1985</i>	<i>July 24, 1987</i>	<i>Aug. 18, 1988</i>
<i>To</i>	<i>Dec. 31, 1990</i>	<i>Dec. 31, 1990</i>	<i>Dec. 31, 1990</i>	<i>Dec. 31, 1990</i>	<i>Dec. 31, 1990</i>	<i>Dec. 31, 1990</i>	<i>Sept. 2, 1989</i>
<b>Hours of operation</b>	<b>71,043</b>	<b>57,071</b>	<b>48,408</b>	<b>47,572</b>	<b>39,859</b>	<b>17,906</b>	<b>6,605</b>
<b>Hours called upon to operate</b>	<b>71,929</b>	<b>57,488</b>	<b>48,414</b>	<b>47,572</b>	<b>40,202</b>	<b>17,906</b>	<b>6,663</b>
<b>Reliability, %</b>	<b>98.8</b>	<b>99.3</b>	<b>100.0</b>	<b>100.0</b>	<b>99.1</b>	<b>100.0</b>	<b>99.1</b>
<b>Hours available</b>	<b>72,208</b>	<b>59,475</b>	<b>53,367</b>	<b>51,248</b>	<b>42,905</b>	<b>29,142</b>	<b>8,536</b>
<b>Hours in period</b>	<b>75,756</b>	<b>62,580</b>	<b>56,794</b>	<b>55,714</b>	<b>44,928</b>	<b>30,150</b>	<b>9,120</b>
<b>Availability, %</b>	<b>95.3</b>	<b>95.0</b>	<b>94.0</b>	<b>92.0</b>	<b>95.5</b>	<b>96.7</b>	<b>93.6</b>

**Reliability** = Hours the CT-121 process was operated divided by hours the CT-121 process was called upon to operate

**Availability** = Hours the CT-121 process was available for operation (whether operated or not), divided by the hours in the period

## **SINGLE-STEP GYPSUM DEWATERING**

The CT-121 process produces a completely oxidized, easily dewatered gypsum byproduct that is easily dewatered and is suitable for landfill disposal without the need for fixating with flyash. In Japan, most CT-121 installations produce wallboard or cement quality gypsum; however, CT-121's process simplicity advantages apply equally to throwaway system designs that predominate in the U.S.

Contrary to conventional forced oxidation FGD systems, CT-121 does not experience crystal attrition due to the high speed recycle slurry pumps. Rather, CT-121 attains large gypsum crystals due to the long residence time and high concentration of gypsum slurry in the JBR.

The benefit of the large gypsum crystals from a CT-121 process is that they dewater easily. At Abbott, absorber slurry with 15 to 25 weight percent solids is fed directly to the vacuum filter which produces a 93 weight percent solids cake. Primary dewatering by thickeners or hydrocyclones is eliminated. Table 2 shows a comparison of gypsum dewatering from a CT-121 process and conventional in-situ forced oxidation process. Elimination of the primary dewatering step creates significant advantages in terms of capital and operating costs.

**Table 2**  
**GYPSUM DEWATERING**

<u>Parameter</u>	<u>CT-121 Process</u>	<u>Other Forced Oxidation FGD Processes</u>
Mean Crystal Size, $\mu$	80 – 100	50
Feed Slurry, % solids	15 – 25	40 (thickener/hydrocyclone)
Vacuum Filter Cake, % solids	90 – 93	85 – 90

The gypsum byproduct produced by the CT-121 process is suitable for landfilling. Recent tests show that CT-121 gypsum easily passed standard leaching tests used to define hazardous wastes<sup>3</sup>.

An alternative to gypsum filtration is gypsum stacking. Gypsum stacking has been used extensively in phosphoric acid production operations and simply involves filling a diked area with gypsum slurry piped directly from the JBR. Return water from the gypsum stack is pumped back to the FGD process. Gypsum is excavated from the center of the stack and used to build up the walls of the dike. The solids content in the stack walls reaches up to 80 percent because of the ease of dewatering. The walls can readily support the vehicular equipment needed to build the stack. Gypsum stacking requires about the same space as landfill disposal. It is environmentally safe and can eventually be grassed over.

The simplicity of dewatering the gypsum byproduct is a significant advantage for CT-121 over other throwaway FGD processes, whether filtration or gypsum stacking is utilized.

#### **LAYOUT FEATURES**

The smaller space requirements of the CT-121 process are an advantage to both retrofit FGD plants and new generation plants. The CT-121 system is a highly compact because:

- No spare absorber is needed.
- Large non-redundant JBRs (up to 1000 MW) can be provided.
- Large recycle pumps are not needed.
- Thickeners and sludge fixation equipment are not needed.

A major cost impact in plant retrofits is the ductwork arrangement. Depending on site-specific factors such as the location of the existing stack, routing the ductwork may be difficult. The CT-121 process offers the following advantages that can lead to economic ductwork system design:

- CT-121's JBR height is lower than other absorbers.
- The outlet duct can be horizontal at almost any orientation.
- The outlet duct can be vertical through the roof of the JBR.

CT-121's flexibility and the significantly lower height of the JBR compared to a spray tower, reduce both the length and complexity of the ductwork.

## **ZERO-LIQUID DISCHARGE**

Regulations governing surface discharge of wastewater in the U.S. are becoming increasingly more stringent. Thus, FGD processes which can function with minimum or zero wastewater discharge will be of premium importance. In such processes, impurities are concentrated in the scrubbing solution and are ultimately purged in the throwaway gypsum.

The primary impurity affecting a closed water balance is dissolved chlorides which originate from coal. These dissolved chlorides result in high dissolved calcium concentrations, as  $\text{CaCl}_2$ . The resulting "common ion effect" causes dissolved  $\text{CaCl}_2$  to interfere with the dissolution of the  $\text{CaCO}_3$  from limestone. Inhibition of  $\text{CaCO}_3$  solubilization means less dissolved alkalinity and pH suppression. In extreme cases, in conventional FGD processes, high chloride pH suppression has led to failure of the system to maintain the design  $\text{SO}_2$  removal efficiency.

The  $\text{SO}_2$  removal efficiency of CT-121 is not impacted by such high chloride concentrations. This is because of the unique process chemistry, explained earlier, which allows CT-121 to operate at low pH and quickly solubilize fresh limestone feed. Operation at 95 percent  $\text{SO}_2$  removal with chloride levels up to 70,000 ppm has been demonstrated in the laboratory. Further testing of this attribute in commercial facilities is planned.

A further complication of closed loop operation is the accumulation of dissolved fluoride ions. (Fluoride and aluminum originate in the coal.) If the fluoride concentration is too high, aluminum fluoride can precipitate from solution and coat undissolved limestone particles, thereby causing limestone blinding which inhibits limestone dissolution and utilization<sup>4</sup>. Aluminum fluoride blinding is not a problem in the CT-121 process because at its lower pH, limestone is rapidly solubilized.

The ability of the CT-121 process to operate at high concentrations of ionic impurities and achieve zero discharge is therefore much greater than conventional forced oxidation FGD processes. This means CT-121 can be operated more efficiently over a wide range of coal impurity levels. It also allows greater flexibility in the use of a variety of sources of plant water for makeup to the CT-121 process.

### Wastewater Treatment

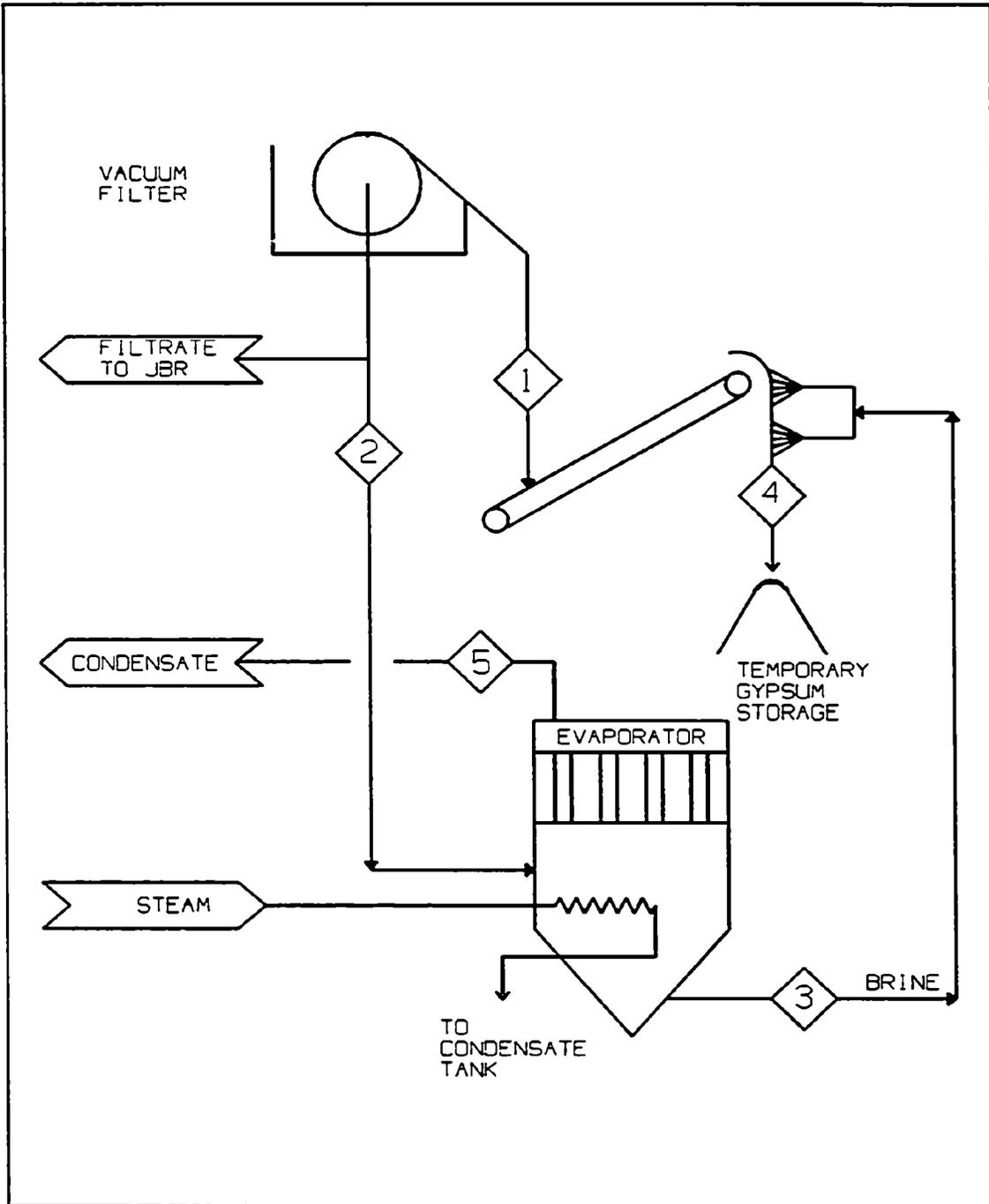
An alternative to closed-loop operation is to purge a blowdown stream from the FGD system. To keep the overall system zero-discharge, this blowdown must be treated, typically in an evaporator/spray dryer wastewater treatment system. The blowdown is concentrated to a brine in the evaporator with clean condensate returning to the FGD system. The spray dryer evaporates the remaining water in the brine to produce a solid powder for waste disposal. The blowdown flowrate, and so, the wastewater treatment equipment will be smaller for a CT-121 system than other FGD systems because CT-121 can handle higher chloride concentrations.

The CT-121 FGD system can eliminate the spray dryer if a zero-discharge wastewater treatment system is needed. Since CT-121 gypsum easily dewateres to over 90 percent using a Bird-Young drum vacuum filter, the evaporator brine can be sprayed on the dry gypsum byproduct. The final gypsum and evaporator brine waste byproduct is still relatively dry and is suitable for landfill disposal. By spraying the brine onto the gypsum, a second separate solid waste from the spray dryer is eliminated. Figure 6 is a schematic of the process steps.

The CT-121 process will tolerate higher chloride concentrations than other FGD systems. Thus, in many cases the CT-121 FGD process can be operated with a closed water balance. If wastewater treatment equipment is needed it will be smaller for a CT-121 system.

### **CONCLUSION**

The advantages of the CT-121 process discussed here provide significant capital and operating cost savings when applied to production of a throwaway byproduct gypsum. The CT-121 process requires less space, process equipment, piping, and ducting than conventional systems. The simple mechanical design results in high reliability, straightforward operation, and low maintenance. Elimination of major mechanical components such as a spare absorber, large recycle pumps, spray nozzles, and thickeners reduces the capital costs and simplifies the operation and maintenance of the CT-121 process.



**Figure 6. Process Schematic of Wastewater Treatment and Gypsum Disposal. The CT-121 process can eliminate the spray dryer in a zero-discharge wastewater treatment system by spraying the brine on the 90+ % solids filter cake.**

The CT-121 process can achieve over 95 percent SO<sub>2</sub> removal efficiency with limestone and without chemical additives. Its high particulate removal efficiency translates into cost savings when the existing electrostatic precipitator is inadequate and will provide added benefits as air toxics regulations are implemented.

The improved chemistry and unique absorber of the CT-121 process simplify the overall system design. It can eliminate or minimize zero-discharge wastewater treatment equipment because of its ability to operate with high chloride concentrations. Primary dewatering equipment is not needed because of CT-121 large gypsum crystal size. If gypsum stacking is used, no dewatering equipment is needed. The unique advantages of CT-121 make it a very attractive choice for future North American FGD applications.

#### REFERENCES

1. K. Wataya, A. Hori, N. Hashimoto, H. Koshizuka, and D. D. Clasen, "Operating Results of Toyama Kyodo Electric Power's Chiyoda Thoroughbred 121 Flue Gas Desulfurization System." Presented at the EPA/EPRI Ninth Symposium on Flue Gas Desulfurization, Cincinnati, Ohio, June 1985.
2. Y. Hozumi and Y. Yoshizawa, "Numerical Analysis of Dust Particles Motion inside Gas Bubble for Flue Gas Desulfurization in Jet Bubbling Reactor." Presented at the Forum on Micro Fluid Mechanics, ASME, 1991.
3. D. D. Clasen, "Commercial Status of the Chiyoda Thoroughbred 121 Flue Gas Desulfurization Process." Presented at the Canadian Electric Association Seminar on Flue Gas Desulfurization, September 1983, Ottawa, Canada.
4. J. B. Jarvis, R. W. Farmer, and D. A. Stewart, "Description and Mechanism of Limestone FGD Operating Problems due to Aluminum/Fluoride Chemistry." Presented at EPA/EPRI Tenth Symposium on Flue Gas Desulfurization, Atlanta, Georgia, November, 1986.

**Session 8B**  
**BY-PRODUCT UTILIZATION**

**GERMAN EXPERIENCE OF FGD BY-PRODUCT DISPOSAL AND UTILIZATION**

J. Demmich  
E. Weißflog  
G. Roeser  
GFR  
Aufbereitung und Verwertung  
von Reststoffen mbH  
8700 Wurzburg  
Federal Republic of Germany

F. Ghoreishi  
Noell, Inc.  
3780 Kilroy Airport Way, Suite 350  
Long Beach, CA 90806

**ABSTRACT**

Worldwide, increasingly restrictive requirements have been regulated for flue gas treatment at coal fired power stations. Increased flue gas cleaning has led to an increase of hazardous materials, originally contained in the fuel and combustion residues, finding their way in the fly ash and flue gas cleaning systems process by-products.

The paper will review the types, quantities, and compositions of various residues from different flue gas cleaning systems. Depending upon the physical and chemical properties of these materials, they could be directly utilized or, they require treatment with suitable techniques in order to be safely disposed.

Examples of FGD gypsum, ashes from fluidized bed combustors (FBC), and spray dry absorbers (SDA) by-products will be discussed insofar as their potential for utilization in the gypsum and sulfuric acid industries and/or the construction industry.

Process for treatment and disposal of non-utilizable residues carried out in Germany by the authors will be covered. Among topics for discussion are disposal of mixtures of fly ash and gypsum, FBC ashes, SDA products, and design of mono disposal site without additional binder, and comparative costs.

## INTRODUCTION

During combustion of fossil fuels in power plants and industrial incinerators, various residues remain due to incombustible particles of the coal, such as slag and fly ashes. Further flue gas cleaning, such as removal of acid gaseous components, especially sulphur oxides, result in various by-products, depending on the Flue Gas Desulphurization (FGD) process.

German legislation primarily requires to avoid and/or utilize those residues. Specific characteristics or the composition of some residues can, however, interfere with their utilization.

Therefore, the question of utilization and disposal of residues can only be answered if detailed information is available regarding quantities and compositions (Reference 1 to 5).

## TYPE, QUANTITY AND COMPOSITION OF POWER PLANT RESIDUES

At this time, coal-fired power plants use various procedures for cleaning flue gas. Mainly, they are dust collection and wet scrubbing processes. The various types of power plant residues, dependent on the type of FGD cleaning process, are shown in Figure 1. Basically, residues can be divided into four categories:

- Fly ashes, particulate, or dust collection without reaction products, which are not discussed in this paper.
- Ashes from fluidized bed combustion with dry additive process as a mixture from fly ashes and reaction products; i.e. desulphurization at high temperatures directly in the furnace.
- Residues from dry and semi-dry absorption FGD processes as a mixture from fly ashes and reaction products with a fly ash content, which is dependent on the quality of the dust collection system used; i.e. desulphurization at low temperatures after the boiler.
- Residues from the wet absorption process, basically FGD-gypsum and FGD waste water.

Most of these residue materials are dry and free flowing. Normally, only FGD-gypsum is produced in moist, fine particles or, after drying/briquetting, in form of briquettes.

## QUANTITIES

Depending on the type of the various FGD-processes, different quantities of residues are formed in coal-fired power plants. Figure 2 shows the varying residue quantities obtained by combusting one ton (1,000 kg) of hard coal by using the limestone scrubbing process, the semi-dry absorption process or the fluidized bed combustion with dry additive process. The figures shown are relative, since they depend on the type of coal and its contents.

The contribution of different types of power stations and power supply companies to flue gas desulphurization and distribution of flue gas cleaning systems in respect to total electricity output in Germany is shown in Table 1.

Residue output quantities from the combustion of coal and the related FGD are shown in Table 2.

## COMPOSITION OF POWER PLANT RESIDUES

The FGD residues of coal-fired power plants differ at times considerably in their chemical and mineral composition. Table 3 shows a comparison of the main and trace components of natural gypsum and FGD-gypsum. The main components of residues from the dry flue gas cleaning process are shown in Table 4.

## UTILIZATION OF FGD-GYPSUM

Location, time of the year, and availability as well as quality are important for utilizing FGD-gypsum, especially in the gypsum industry.

The requirements of the gypsum industry for the FGD-gypsum quality are stated in Table 5. Normally, these requirements are achieved by using additional processes like hydroclone classification and filtration/washing.

Following are important industries for gypsum utilization (Reference 9):

### GYPSUM INDUSTRY

The gypsum industry is, of course, the main user of FGD-gypsum; FGD-gypsum is used in construction (stucco and gypsum-plaster) and for gypsum wallboards.

### CEMENT INDUSTRY

Following the gypsum industry, the cement industry is another large consumer of FGD-gypsum and anhydrite.

In the cement production, approximately 5% milled  $\text{CaSO}_4$  (a mixture of FGD-gypsum/anhydrite) is added to the cement clinker as a retarding agent.

## MINING INDUSTRY

In recent years, the mining industry also uses FGD-gypsum and the building material produced from the gypsum. Part of the natural anhydrites can sometimes be substituted by FGD-gypsum after processing it to anhydrate or  $\alpha$ -hemihydrate.

## OTHER UTILIZATION

FGD-gypsum from hard coal-fired power plants is sometimes used for earth and landscape projects (Reference 4), particularly if there is no market demand or the product does not meet the required specifications (Table 5). For this use it is mixed with fly ash and, if necessary, with bonding agents. FGD-gypsum of lignite-fired power plants, mixed with free calcium containing fly ashes, is almost entirely processed to a fixated product ("stabilisate") and disposed in abandoned lignite mines above ground.

This utilization will continue to be an important possibility of using either a seasonal or a regional surplus.

The various utilizations of FGD-gypsum are listed in Figure 3.

## PROCESSING AND CONDITIONING OF FGD-GYPSUM

Normally, FGD-gypsum is produced in fine particles with a moisture of approx. 10% by weight. Only where the existing utilization installations are retrofitted from natural gypsum (rocks) to FGD-gypsum, can it be used in this form. However, this requires a tremendous amount of handling. Therefore, many power plants compact their FGD-gypsum with excess heat to form briquettes, which then can be used like natural gypsum. See Figures 4 - 7.

In addition, energy and transportation costs can be saved, and the handling is significantly reduced. These briquettes can be stored outside, occasionally covered, without costly storage installations or silos, so that there is a buffer for the seasonal fluctuations in production.

"Converting" into  $\alpha$ - or  $\beta$ -hemihydrate (HH) or anhydrite as further refining steps creates other possibilities to introduce FGD-gypsum to the construction industry. Several new installations are already being built or in operation for the burning of  $\beta$ -HH through the "gypsum boiling process" and for producing  $\alpha$ -HH through autoclaving.

## UTILIZATIONS FOR OTHER FGD-PRODUCTS

As already stated above, some more FGD-residues are produced, depending on the type of combustion and the FGD-process (see Figure 1).

In the past, there were only limited utilization possibilities for these residues, since their physical properties and their chemical/mineral composition have a vast variation in comparison to the washed FGD-gypsum.

## ASHES OF FLUIDIZED BED COMBUSTORS AND DRY ABSORPTION PROCESSES

The actual utilization potential of these FGD-products lies in their self-solidification properties due to their contents of calcium sulfate (anhydrite) as well as parts of silicate and aluminate, and the free calcium oxide (CaO).

Listed are examples for utilizations which have been realized:

- Drying and solidification agent for various sludges (e.g. sewage sludges).
- Additives for producing mining cements.
- Utilization in road and dam constructions.
- Application as a soil improvement material and for ground stabilization.

By mixing different power plant residues with ashes of fluidized bed combustors, water and, if necessary, small amounts of hydraulic bonding agents, "late"-supporting mining cements can be produced which conform with the environmental and hygienic requirements of mining. The compressive strength requirements for "late"-supporting construction cements of > 2 MPa after 28 days can be achieved.

"Early"-supporting mining cements (> 20 MPa after 2 days) can also be produced by using conditioned FGD-gypsum and cement with up to 20% (by mass) ashes of fluidized bed combustors.

## FGD-PRODUCTS OF DRY AND SEMI-DRY ABSORPTION PROCESSES

As discussed previously, there are different flue gas treatment systems on a dry or semi-dry basis. There is either a separate dust collection system for the fly ashes or the fly ashes are collected together with the FGD-product at the end of the flue gas stream.

Due to the low temperatures, the low residence time, and the low moisture in a semi-dry absorption system, calcium sulfite hemihydrate ( $\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$ ) is the main component in the residues of a dry or semi-dry FGD-process. The low temperatures are also the reason that calcium sulfate forms as  $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ .

In addition, the semi-dry absorption process, in comparison to the dry absorption process, eliminates the flue gas component HCl and HF almost completely. They are found in the FGD-residue as  $\text{CaCl}_2$  and  $\text{CaF}_2$ .

The utilization of these residues is difficult in comparison with the fly ash of fluidized bed combustors; that is because of the vast variations in the composition and the above-mentioned components.

If the contents of reactive fly ash and unreacted absorbents (calcium hydroxide) is sufficient, those residues have a limited self-solidification property which can be used to produce filling materials by mixing it with fly ashes of fluidized bed combustors as discussed above. A more elegant utilization for the products of a dry or semi-dry absorption system is possible if the following main components can be used:

- Sulphur carriers such as calcium sulphite and calcium sulphate
- Calcium oxide
- Mineral components of the fly ash

## FGD-PRODUCTS OF DRY AND SEMI-DRY ABSORPTION PROCESSES

An actual possibility, is the gypsum-sulfuric acid process (also known as Müller-Kühne-process) which is run by the "Schwefelsäure and Zement GmbH" (DSZ) in Wolfen (recently founded by GFR and located in what was previously referred to as East Germany).

For over four decades, according to the classical process, natural gypsum or anhydrite was reduced with coke and was cracked thermally. Together with additives which contain silicon oxides, aluminum oxides and iron oxides (sand, clay, residual metals), cement clinker was burnt in a rotary furnace. By adding milled gypsum as a retarding agent, they produced approximately 100,000 tons per year of Portland cement.

The cement clinker produced is low on alkali and chromate and therefore has a very interesting marketing potential.

The highly concentrated sulphur dioxide gas, which is set free during the reducing, thermal cracking of the anhydrite (calcium sulphate), was purified, cooled, and converted into sulfuric acid (94 - 96%), or oleum (approx. 100,000 tons per year) by an additional contact process. Lignite was used as primary energy source.

Meanwhile, this process was modified so that the above-mentioned raw materials can be replaced by suitable residues (Figure 8).

Particularly the main component, the natural anhydrite, was replaced by the products of the dry and semi-dry absorption process. The specific composition of those FGD-products has all the components which are necessary for the cement clinker and sulfuric acid production and furthermore, they need less cracking energy and reduction material. A comparison of the main reactions (old and new) is shown in Figure 9.

By using other residues such as used casting sands, fly ashes, and residues with a high caloric value (e.g. acid resins, acid tars, used oils, plastics) it is possible to convert this old and inefficient process plant into an economic one.

At this time the plant is brought up to Western environmental standards while in operation.

## PROCESSING AND DISPOSAL

There are seasonal fluctuations in production of the FGD-residues in Germany with less summertime demand for electricity at the same time that construction industry business activity is strong. This means that in the summer there may not be sufficient FGD-residues to meet demand. Conversely, during winter, there is a slow down in the construction industry and larger amounts of FGD-products are available.

Depending on the location of the power plant and the processing plant, or poor quality of the residue, it is important to have waste disposal possibilities in addition to the above-noted utilizations. Because the various FGD-products appear in dust or slurry form, it becomes necessary to condition them prior to their disposal.

## PROCESSING AND DISPOSAL

The specifications for disposing the FGD-products are:

- sufficient stability and material suitable for transportation with trucks (minimum pressure strength)
- minimum water permeability
- environmentally acceptable leaching levels of heavy metals.

These specifications can be met by producing specific mixtures of different residues and occasionally adding water to fixate the material. This stable material is normally handled and compressed in a slightly moist condition with bulldozers and vibrating rollers. For several days up to weeks, after the disposal, pozzolanic reactions take place which finally lead to a disposal product which is environmentally safe. This mono-disposal needs an additional mineral seal at the base (several layers of clay) with a water permeability of less than  $1 \times 10^{-9}$  m/s. After the disposal site is filled, it also needs to be sealed on the top. In case water permeability is too high, an evacuation system for the infiltration water and a cleaning system is necessary.

GFR developed and executed two different disposal methods, dependent on the FGD-products. They are discussed below.

## FLY ASHES AND FGD-GYPSUM SLURRY

While FGD-gypsum and fly ashes of hard coal power plants are utilized widely in the Federal Republic of Germany, as presented above, the residues of lignite-fired power plants are mostly disposed after processing.

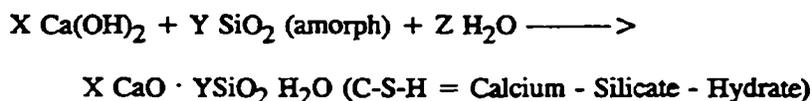
For processing and disposing dry fly ashes and the residues of wet absorption systems they are mixed together and occasionally FGD waste water and calcium hydroxide is added.

When the fuel is German lignite, fly ashes with a free calcium oxide content up to 30% (by mass) are obtained. By adding FGD-gypsum slurry or FGD waste water to those fly ashes, an exothermic slaking reaction takes place. In these cases, slaking is to occur prior to the actual mixing.

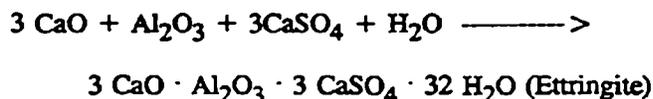
## FLY ASHES AND FGD-GYPSUM SLURRY

The silica and alumina components of the fly ash react after mixing with calcium hydroxide, calcium sulfate and respective parts of water to produce cementitious mineral phases. These very complex reactions are also known as pozzolanic reactions.

Pozzolanic Reactions (Simplified):



Etringite Formation:



These solidification reactions have the capability to, at least partially, immobilize heavy metals by causing them to adhere to the crystal structure.

Products of Dry and Semi Dry Absorption Systems, Fly Ashes of Dry Additive Systems and Fluidized Bed Combustors, and Other not Utilizable Fly Ashes.

These dry residues, which normally consist of varying fractions of fly ashes and FGD-products, as well as excess absorbents (see above), are not disposable "as is", because they produce dust and have uncontrolled leaching properties of hazardous components. Therefore, a special conditioning (mixing the different FGD by-products together with water) is necessary to produce a disposable fixated product.

## CONDITIONING PROCESSES

Special mixtures of residues are made according to results of laboratory tests. An exactly defined amount of water is added to achieve a good solidification. The product is disposed in a slightly moist condition. A flow sheet of a processing plant is shown in Figure 10. Figure 11 shows an aerial photograph of a processing plant which is operated by GFR.

The fixated product, processed as described above, is disposed by bulldozer in layers (Figure 12) and is compacted several times by a vibration roller (Figure 13). This disposal technique and the occurring solidification reactions meet the specifications (Table 6) of the permitting authorities. The necessary quality assurance of the disposal end-product is continuously monitored by regulatory agencies and our own test personnel. This supervision is done using drilling cores. Examination of those cores is done for their density, single-axial compression strength, permeability of water, and the leachability. These conditioning processes have been developed by GFR for various FGD-products and fly ashes, which cannot be usefully utilized, or directly disposed otherwise in a guaranteed environmentally safe manner.

## **SUMMARY**

It was shown that the FGD-processes used in Germany result in various FGD-product compositions, depending on the system used, which have various utilization potentials based on their specific composition. While FGD-gypsum can be used almost entirely in the gypsum and construction industries, other FGD-products have a limited utilization, mostly in the mining industry.

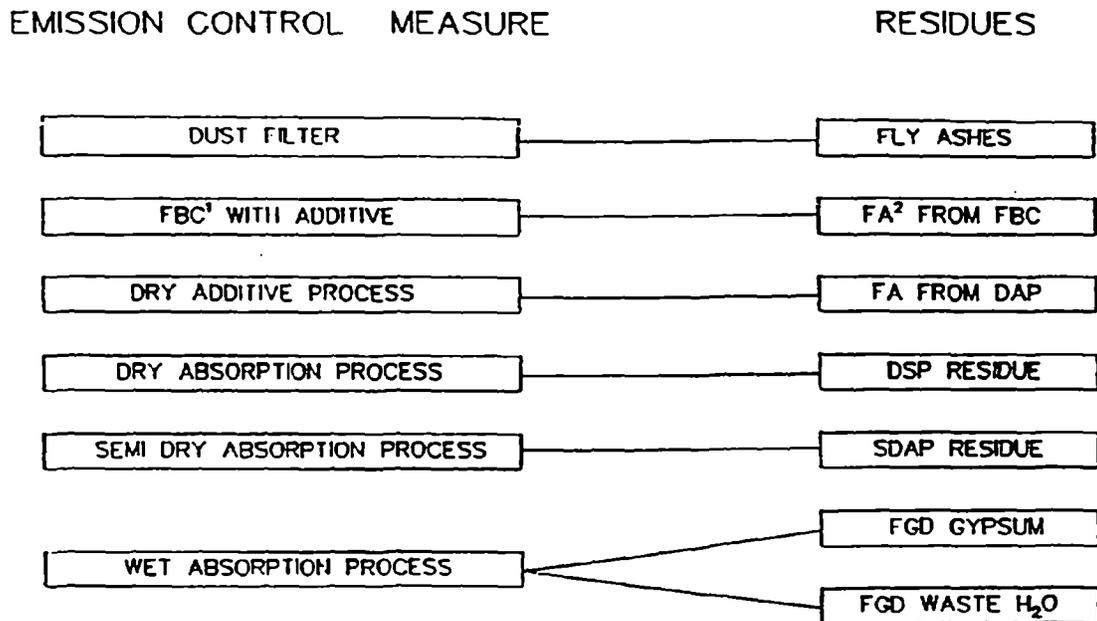
For certain dry and semi-dry absorption by-products, a recently developed high-quality utilization potential exists, using the components contained in the residues for the production of cement and sulfuric acid.

In conclusion, it should be emphasized that even with all the utilization possibilities, it is advisable to plan for safe disposal of some residues. To achieve this, process technologies are necessary which take into account the properties of the various FGD-products and fly ashes.

## REFERENCES

1. Residues from Flue Gas Cleaning (in German) Insert 29, "Müll und Abfall" (publ. by D. O. Reimann/J. Demmich), Erich Schmidt Verlag Berlin, 1990
2. Ministry of Environment Baden Württemberg: Disposal of Residues from Flue Gas Cleaning (in German) - Part II: Großfeuerungsanlagen - Issue 1 "Luft, Boden, Abfall", 1988
3. Winkler, Gruber, Hammerschmid, Rentz: Disposal of Residues from Flue Gas Cleaning at Large Combustion Plants Cement - Lime - Gypsum (in German), 41st Year, No. 11, pp. 576-582, 1988
4. VDEW/VGB-Gemeinschaftsausschuß "Residues and Waste Materials" (in German); Utilization Concepts for Residues from Coal-burning Power Plants - REA-Gips, March 1986
5. VDEW/VGB-Gemeinschaftsausschuß "Residues and Waste Materials" (in German); Utilization Concepts for Residues from Coal-burning Power Plants - Aschen, September 1988
6. M. Hildebrand: Status of Flue Gas Cleaning in the Western States of the Federal Republic of Germany VGB-Seminar "Flue Gas Cleaning and Disposal of Residues in Power Plants, Industry and Heating and Power Plants" (in German) Cottbus, November 29 - 30, 1990
7. W. vom Berg: Utilizing Combustion Residues (in German) Publication, see 6.
8. J. Beckert: Comparison of Natural Gypsum and FGD-Gypsum (in German) VGB-Conference "Kraftwerk und Umwelt 1989", Essen
9. F. Wirsching: Utilization of FGD-Gypsum Publication, see 6.
10. J. Demmich, E. Weißflog: Utilization and/or Disposal of the Semi-Dry Absorption Process Product (in German) Publication, see 6.
11. F. Risse, et al. By-products from Coal-Burning Power Plants and Residues from Garbage Incinerating Plants in the Federal Republic of Germany (in German) VGB Kraftwerkstechnik 71 (1991) Issue 5, pp. 504 - 508
12. E. Weißflog, J. Demmich: The Disposal of Ashes from Fluidized Bed Combustion and/or Flue Gas Desulphurization (in German) VGB-Conference "Kraftwerk und Umwelt 1989", Essen
13. F. Wirsching and E. Weißflog: Environmentally Safe Disposal of Residues from Hard Coal Burning Power Plants (in German) VGB-Kraftwerkstechnik 68, Issue 12 (Dec. 1988)
14. F. Wirsching in Winnacker-Küchler, Vol. 3 Anorganical Technology II (in German) (Carl-Hauser-Verlag München - Wien 1983), pp 262 - 275

## TYPES OF FLUE GAS CLEANING RESIDUES IN REFERENCE TO THE CLEANING PROCESS

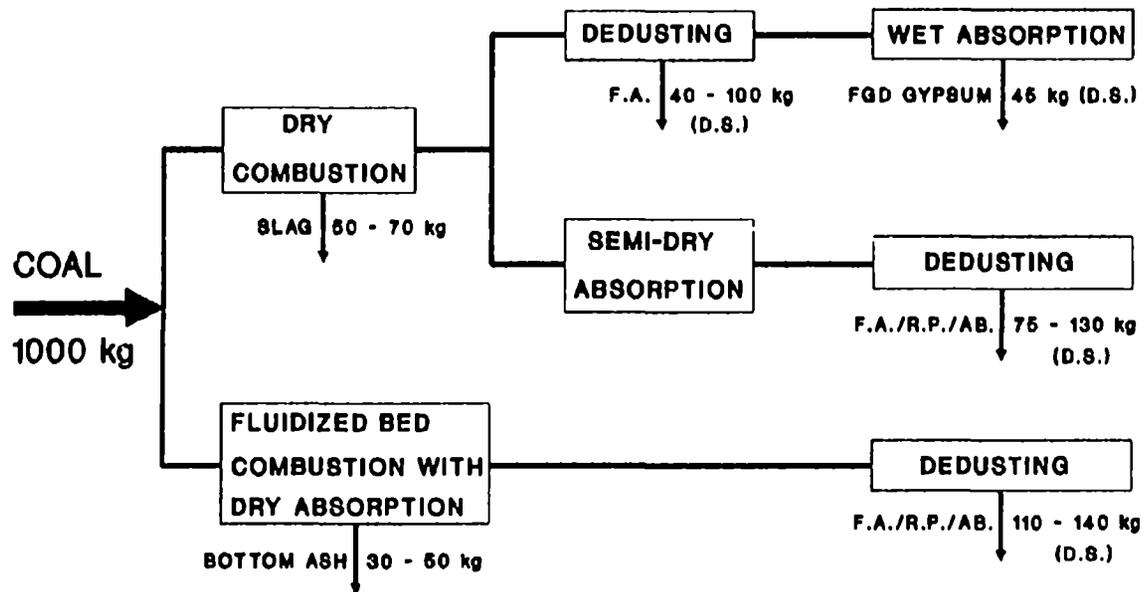


<sup>1</sup> FLUIDISED BED COMBUSTION

<sup>2</sup> FLY ASHES

Figure 1.

## METHODS OF FLUE GAS PURIFICATION (EXAMPLES) AND RESPECTIVE RESIDUES OF COAL FIRED POWER STATIONS



D.S. • DRY SOLIDS  
 R.P. • REACTION PRODUCTS  
 F.A. • FLY ASH  
 AB. • ABSORBENT

Figure 2.

**WAYS FOR THE USE OF FGD-GYPSUM**

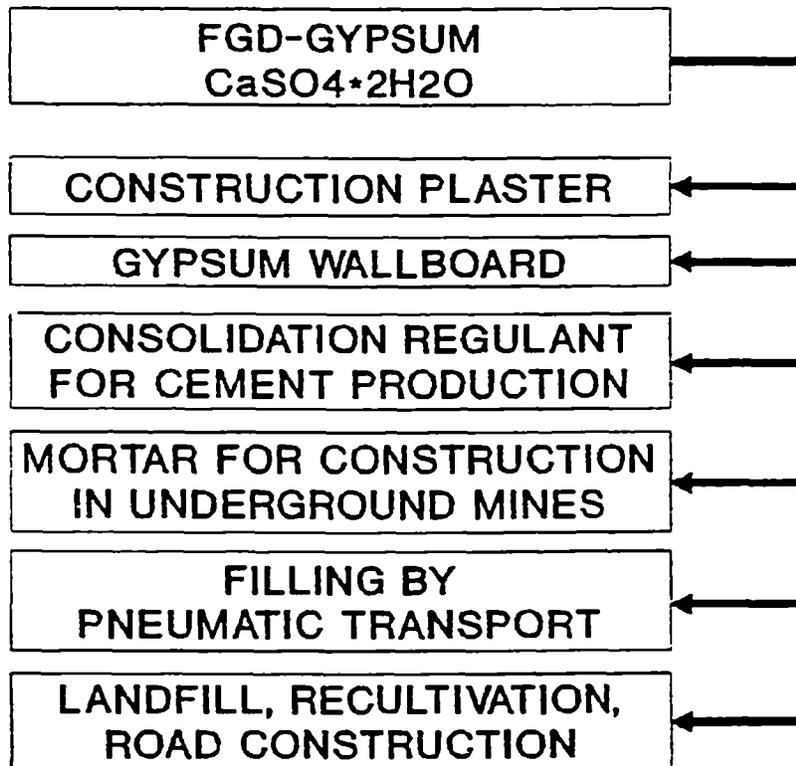


Figure 3.

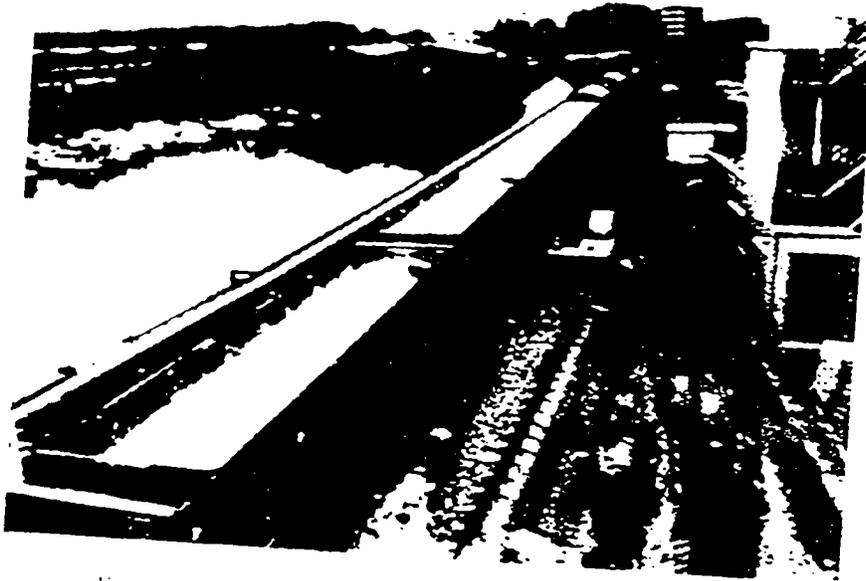


Figure 4. Railway Transport of Moist FGD-Gypsum

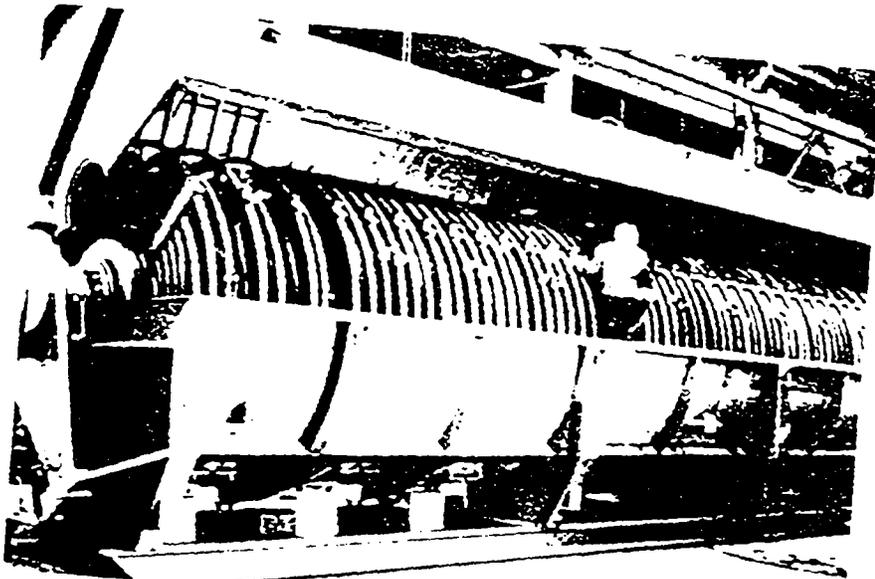


Figure 5. Drying Apparatus for FGD-Gypsum

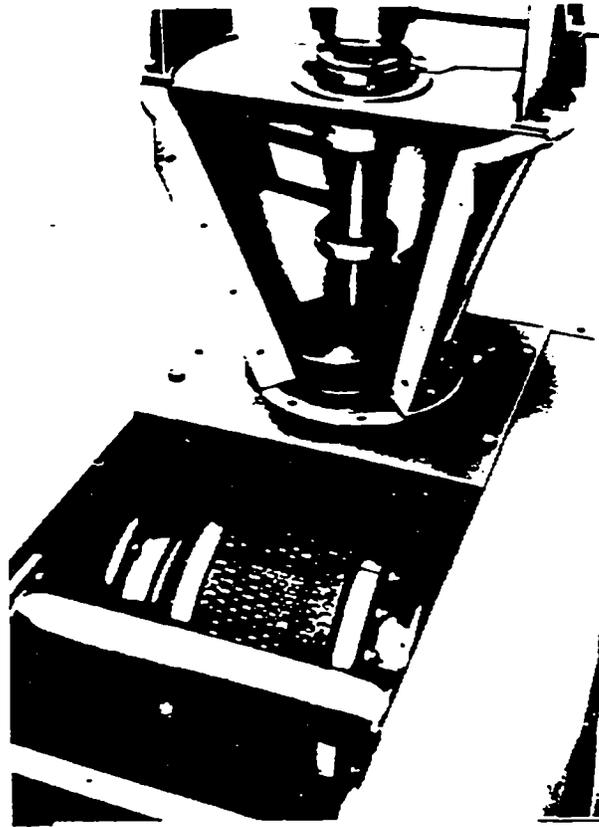


Figure 6. Rotating Briquetting Press



Figure 7. Use of Processed FGD-Gypsum E.G. for Mining-Construction

FLOW CHART : GYPSUM-SULFURIC ACID-PROCESS  
WITH CHEMICAL/ENERGETICAL USE OF RESIDUES

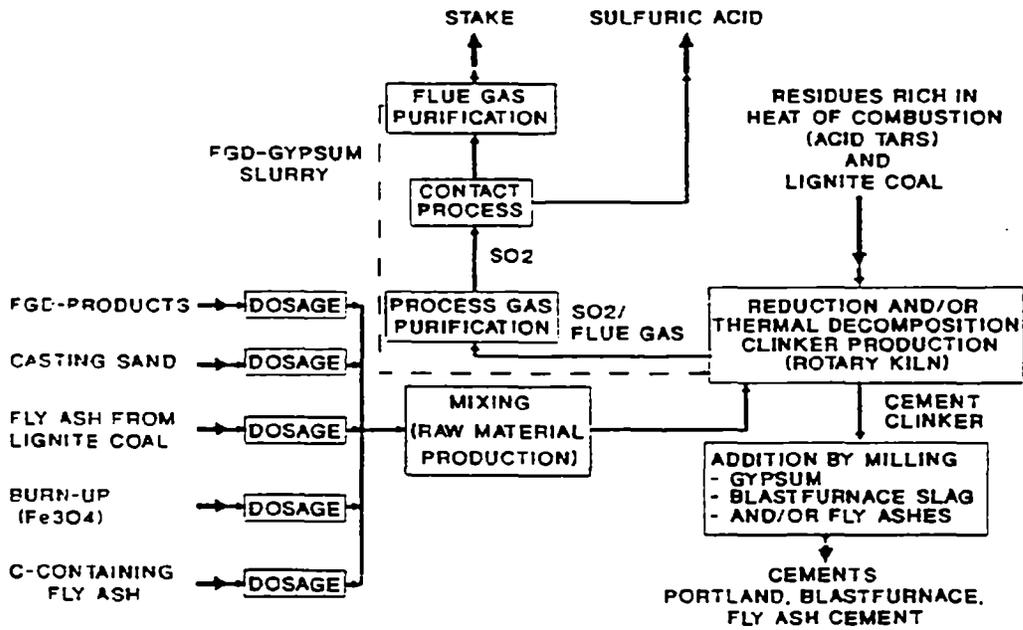


Figure 8

REDUCTION/DECOMPOSITION OF CaSO4



DECOMPOSITION REACTIONS OF CaSO<sub>3</sub>·1/2SO<sub>2</sub>

- 1) > 300 C      INERT GAS  
 $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O} \longrightarrow \text{CaSO}_3 + 1/2\text{H}_2\text{O}$  (DEHYDRATATION)
- 2) > 600 C  
 $\text{CaSO}_3 \longrightarrow \text{CaO} + \text{SO}_2$  (DECOMPOSITION)
- 3) > 680 C  
 $4\text{CaSO}_3 \longrightarrow 3\text{CaSO}_4 + \text{CaS}$  (DISPROPORTIONING)
- 4) > 780 C  
 $3\text{CaSO}_4 + \text{CaS} \longrightarrow 4\text{CaO} + 4\text{SO}_2$  (COMPROPORTIONING)

Figure 9

PROCESSING PLANT FOR DISPOSAL

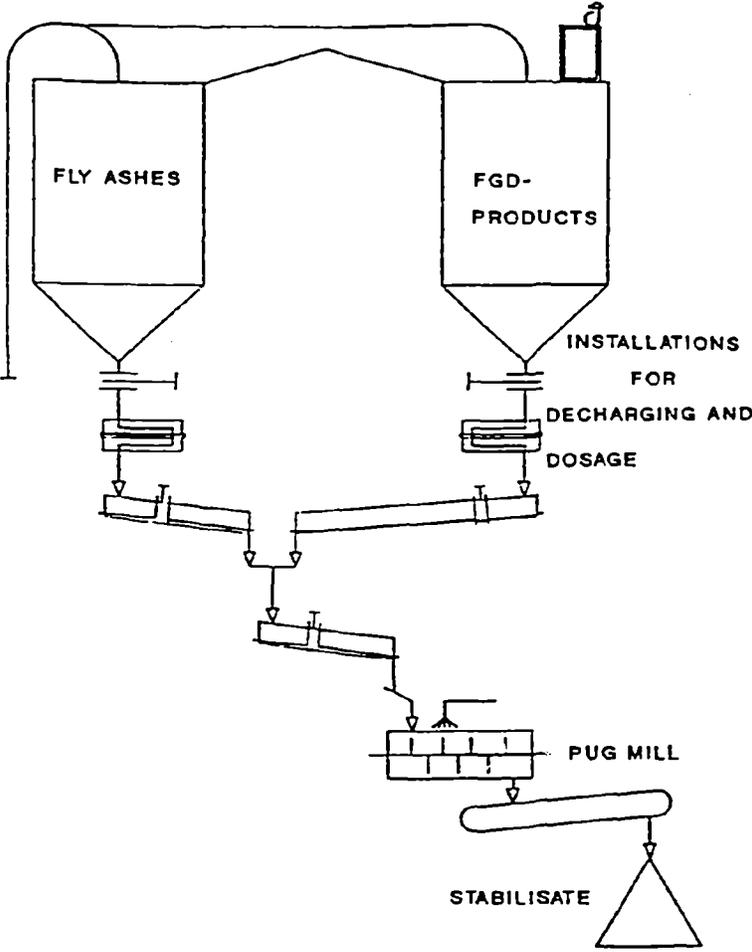


Figure 10

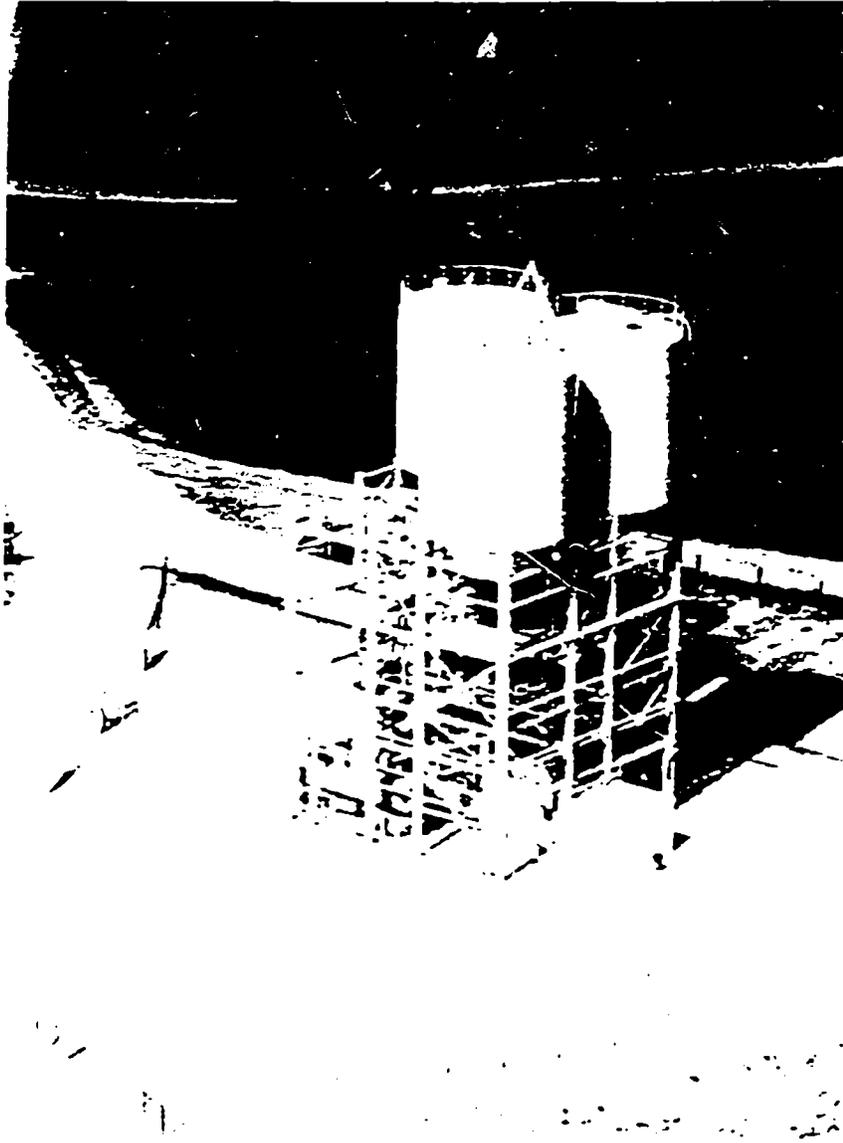


Figure 11: Processing Plant for FGD-Stabilisate



Figure 12: Spreading of Stabilisate by Bulldozer

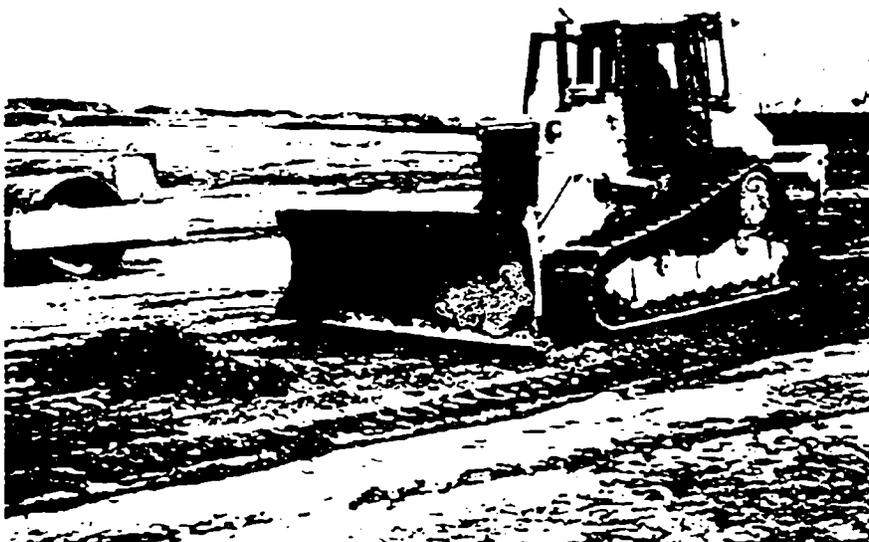


Figure 13: Compression of Stabilisate by Vibration Roller

	HARD COAL FIRED P.S.	LIGNITE COAL FIRED P.S.	OIL FIRED P.S.	TOTAL
POWER/MEGA- WATTS (ELEC.)	26.890	10.950	354	38.194

P.S. = POWER STATIONS

	WET PROCESSES	SEMI-DRY ABSORPTION	DRY ADDITIVE FLUIDIZED BED COMBUSTION
QUANTITY OF TOTAL POWER SUPPLY (%)	86	7,7	3,7

Table 1: Contribution of Different Types of Power Stations of Power Supply Companies to Flue Gas Desulfurization and Distribution of Flue Gas Purification Systems in Respect of Total Electricity Output

	GRANULATE COARSE ASHES (MIO T/A) *	FLY-ASHES (MIO T/A) *	RECYCLING RATE (%)
HARD COAL FIRED POWER STATIONS	3,17	3,11	90,6
LIGNITE COAL FIRED P.S.	1,21	4,87	2,1

	FGD- GYPSUM (MIO T/A) *	RECYCLING RATE %	FBC	SDA <sup>+</sup> (MIO T/A)	DAP
HARD COAL FIRED P.S.	1,8	> 90	APPR. 0,39	APPR. 0,35	APPR. 0,08
LIGNITE COAL FIRED P.S.	1,2	-	-	-	-

Table 2: Residue Output From Combustion of Coal and Flue Gas Purification

		NATURAL GYPSUM		FGD-GYPSUM	
MOISTURE	WEIGHT-%	2		7	- 10
PH-VALUE	WEIGHT-%	6	- 7	5	- 8
CaSO <sub>4</sub> ·2H <sub>2</sub> O	WEIGHT-%	78	- 95	98	- 99
Cl	WEIGHT-%		< 0,01		- 0,01
Na <sub>2</sub> O	WEIGHT-%		0,02		0,01
INERT COMPONENTS	WEIGHT-%	5	- 20		-
As	PPM	0,22	- 3,79	0,21	- 2,70
Pb	PPM	0,46	- 21,4	0,27	- 22,0
Cd	PPM	0,03	- 0,30	0,003	- 0,29
Cr	PPM	0,65	- 24,9	1,02	- 9,72
Ni	PPM	0,3	- 13,4	0,3	- 12,9
Hg	PPM	0,006	- 0,05	0,03	- 1,32

Table 3: Main and Trace Components of Natural Gypsum in Comparison to FGD-Gypsum

PARAMETER	DAP ASH	FBC ASH	DSP PRODUCT	SDA PRODUCT
FLY ASH	25 - 80	50 - 80	1 - 10	3 - 85
RESIDUAL C CaSO <sub>4</sub>	3 - 25 3 - 25	3 - 25 15 - 30	0.1 - 2 -----	0.5 - 10 -----
CaSO <sub>4</sub> ·1/2H <sub>2</sub> O	-----	-----	5 - 25	5 - 35
CaSO <sub>3</sub> ·1/2H <sub>2</sub> O	-----	-----	5 - 30	5 - 70
CaCO <sub>3</sub>	3 - 10	3 - 10	10 - 30	5 - 30
CaO	3 - 30	7 - 25	-----	-----
Ca(OH) <sub>2</sub>	-----	-----	10 - 30	1 - 15
CaCl <sub>2</sub>	0.1 - 0.5	0.1 - 1.0	2 - 4	2 - 8

Table 4: Main Components of Residues from Dry Flue Gas Cleaning Process (Typical Extent of Fluctuation)

## REQUIREMENTS OF GYPSUM INDUSTRY FOR FGD-GYPSUM QUALITY

FREE MOISTURE	≤ 10% (WEIGHT PERCENT)
CaSO <sub>4</sub> ·2H <sub>2</sub> O	≥ 95%
MgO WATER-SOLUBLE	≤ 0.1%
CHLORIDE	≤ 0.01%
Na <sub>2</sub> O	≤ 0.06%
SULFUR DIOXIDE (SO <sub>2</sub> )	≤ 0.25%
pH-VALUE	6-9
COLOR	WHITE (DEGREE OF WHITENESS:80%)
ODOR	NEUTRAL
TOXIC COMPONENTS	NONE

Table 5

### Disposal-Site-Requirements for Processed FGD-Residues

1. ≥ 30 Weight-% Fly Ash of Sufficient Pozzolanic Reactivity
2. ≥ 3 Weight-% Ca(OH)<sub>2</sub>/CaO
3. Optimal Field Density ≥ 1,0 Grams/CM<sup>3</sup> (Dry Solids)
4. Solidity, Useability for Vehicles Right After Compression, Setting Time
5. Unconfined Compressive Strength ≥ 0,5 MPA (28 D)
6. Permeability:  $K < 5 \cdot 10^{-8}$  m/s
7. Leachability: Testing Procedure Dev-S4; Class II Disposal Site Category (For Mineral Residues) Due to the Proposal of a Guide-Line For North-Rhine Westphalia, Part 2, 1987

Table 6

**The Elimination of Pollutants from FGD Wastewaters**



M. K. Mierzejewski  
Infilco Degremont Inc.  
2924 Emerywood Parkway  
Richmond, Virginia 23294

**ABSTRACT**

Limestone forced oxidation systems producing saleable gypsum and throwaway wet FGD systems operated in an open loop configuration both yield wastewater streams. In order that pollutants, such as heavy metals, are not merely shifted from the gas phase to the liquid phase, special treatment techniques must be applied to these wastewaters.

Over the last 6 years a specific treatment process has been developed to eliminate pollutants from these wastewaters, and 22 such treatment plants are currently operating in Europe, with 2 more under construction. The first such plant in the U.S. is due to be started up in 1992.

This paper reviews the factors influencing the composition of these wastewaters and describes the technology of their treatment.

## INTRODUCTION

The latest amendments to the 1970 Clean Air Act will undoubtedly lead to an increase in the number of flue gas desulfurization (FGD) installations at fossil-fuel fired power plants. In most cases it appears likely that the sludge produced in either dry or wet FGD systems, will be disposed of to landfill, i.e., the FGD system will be of the "throwaway" sludge type. At some power plants, certain factors may allow selection of an FGD system which produces gypsum as a marketable product, precluding the need to landfill any sludge. Under such circumstances, a wastewater stream will be produced, requiring appropriate treatment to eliminate pollutants so that it may be discharged into the environment or, if this is restricted, to be treated to a higher standard and reused on the power plant.

The wet limestone FGD system which produces a marketable product incorporates forced oxidation of calcium sulfite, the intermediate by-product, to calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , known as gypsum. Such a system is termed LSFO (limestone forced oxidation), sometimes with the designation WB for "wallboard", the predominant use of such gypsum.

The gearing-up of the utility industry to address tighter  $\text{SO}_2$  and  $\text{NO}_x$  discharge limits in the U.S. is similar to that seen earlier in West Germany, with the Federal TA Luft and GFAVO programs started in 1983. By July 1, 1988, West German stations larger than 110 MW were required to meet new  $\text{SO}_2$ ,  $\text{NO}_x$  and flyash limits. This represented a relatively short period, similar to that now faced by U.S. utilities, with the Phase I deadline of the Clean Air Act Amendments being January 1, 1995. In total, Phase I will affect 110 power plants in the U.S., with a combined capacity of almost 90,000 MW. Phase II will impose stricter emission limits still for the start of the next century.

In West Germany, 86% of FGD installations are wet and the majority of these are of the LSFO-WB type<sup>(3)</sup>. The shortage of available land area for disposal essentially pushed all the utilities toward this technology and, since there were (and still are) strict controls on aqueous discharges, there was a parallel growth and development of appropriate FGD wastewater treatment technology.

The demand for gypsum on the one hand and the cost of landfilling on the other will be strong determinants of how many LSF0-WB installations will be seen in the U.S. Of the utilities that have started seriously evaluating different FGD technologies, about six to date have elected to use this technology on selected power plants. In each case, the problem of wastewater treatment will need to be addressed.

#### ORIGINS OF WASTEWATER

Except on small units, cost analyses have shown that dry scrubbing is not an economic means of achieving compliance<sup>(2)</sup>. Although capital costs are generally lower than wet limestone systems, overall operating costs, in terms of \$/ton SO<sub>2</sub> removed, are high, due to high reagent consumption. In addition, dry scrubbing may not a feasible economic option where the existing electrostatic precipitators (ESP) are unable to remove the additional solids load, necessitating costly modification or replacement.

It is likely that most of the stations on the Phase I list which will be installing FGD equipment will adopt wet scrubbing alternatives. There are many different wet scrubbing technologies available but, from the point of view of wastewater (discounting processes like the Wellman-Lord), the choice comes down to whether the sludge produced is disposed of to landfill, i.e., a throwaway process, or is washed and sold as a useful by-product.

A system producing a throwaway sludge can be designed either to operate at a relatively low chloride concentration in a so-called "open loop", in which case a wastewater stream is produced, or at a higher chloride concentration, in a "closed loop", without the inconvenience of the wastewater (see Figure 1). In both cases water is entrained in the sludge formed in the scrubber. The sludge may be dewatered to, say, 80% dry solids (d.s.), with the 20% residual moisture having the same composition as the liquid phase in the scrubber. Hydrogen chloride is present in the flue gas, and is taken out under the wet alkaline conditions in the scrubber. Without a chloride blowdown, this species would build up, adversely affecting the efficiency of SO<sub>2</sub> removal<sup>(3)</sup>. In a closed loop, the chloride concentration in the scrubber is elevated so that the moisture entrained in the sludge represents the chloride sink, rendering a separate wastewater stream unnecessary. Open loop operation, conversely, does not allow sufficient chlorides to be "lost" from the system without an additional blowdown from the scrubber, and it is that blowdown which represents the wastewater stream.

The apparent advantage of not requiring wastewater treatment in closed loop operation may be out-weighted by the cost of more expensive materials of construction of the scrubber and all associated wetted parts, in order to withstand the more corrosive environment due to the higher chloride concentration. Which option is selected at a particular installation depends on case-specific factors.

Limestone reacts with  $\text{SO}_2$  in the scrubber to form calcium sulfite which, on further oxidation (if selected) forms gypsum. The reaction product is continuously removed from the scrubber and fresh limestone is returned to the reservoir. In both open and closed loops the dewatering of the sludge gives rise to a liquid stream: in an open loop only a portion of this stream, depending on chloride content, cake dryness, etc. can be returned to the scrubber, in the form of slurry make-up, without jeopardizing the chloride balance. In closed loop operation the complete stream can be returned.

This "open loop versus closed loop" choice does not exist in LSF0-WB systems, since current requirements in the U.S. call for the saleable product to have no more than 120 mg chloride per kg of dry solid. This requirement, together with the fact that a much higher dryness (90% d.s. minimum) is demanded by the gypsum user, means that the sludge cannot be used as a chloride sink. Saleable gypsum must be washed thoroughly to achieve the purity standards required: the washings, being of low salinity, can be re-used in the scrubber. Figure 2 shows sources of wastewater on an LSF0-WB scrubber.

In summary, a throwaway system may or may not produce wastewater, whereas a system producing a saleable cake always will.

FGD wastewater flows are typically low, and for a given unit size are related to the chloride concentration in the scrubber and to the calorific value and chloride content of the coal being burned. Typical values lie in the range 0.05-0.2 gpm/MW scrubbed. Other than sulfur, the majority of which is taken out in the scrubber, the wastewater contains most of the pollutants present in the coal, limestone and makeup water. In order that it can be discharged into the environment, certain chemical species, particularly heavy metals, must be removed.

#### FACTORS DETERMINING FGD WASTEWATER CHARACTERISTICS

FGD wastewaters are typically acid, highly saline solutions with varying quantities of suspended solids, heavy metals, chlorides, fluorides and COD. Table 1 shows

typical compositions before and after treatment, taken from numerous operating Degremont installations. Since FGD operates on a continuous basis, the wastewater is produced and treated likewise, such that only limited cooling occurs as it passes through the gypsum dewatering stages and collects in an equalization tank. Treatment is normally carried out at about 40-50°C.

The pH of the wastewater usually lies in the range 5.0-6.5 S.U. Buffered systems using carboxylic acids are designed to maintain a pH of 4.8-5.5 S.U., the optimum for the reaction of sulfur dioxide with limestone.

Coming as it does from a warm gypsum-rich environment, the wastewater is normally supersaturated with gypsum when it reaches the wastewater treatment plant (WWTP), although the degree of this supersaturation depends to a large extent on the nature of and retention time in the concentrating and dewatering stages upstream of the WWTP proper. Magnesium, aluminum and iron are all elements of major importance in the design of a FGD wastewater treatment facility. Since pH elevation is a key process in treatment, these metals will come out as hydroxides, and represent a solids load to the clarifier/thickener.

The high concentration of chloride (10-40 g/l) at which the scrubber operates is the same as that in the wastewater, balanced principally by calcium and magnesium cations. The resulting corrosive property of the wastewater has considerable impact on the WWTP materials of construction. Another halogen, fluorine, is present in coal and also volatilizes as the hydrogen compound; however, its lower concentration in coal and the low solubility of its calcium salt render it only a minor constituent of FGD wastewaters.

The Chemical Oxygen Demand (COD) of FGD wastewaters, typically about 100-150 mg/l, is due largely to unreacted calcium sulfite (though this contribution is low) and organics present in the makeup water.

The quantity and quality of the wastewater is determined by the following factors:

- rated capacity of the unit boiler
- scrubber chloride concentration
- efficiency of flyash removal
- type and efficiency of dewatering installation
- type of FGD process
- chemical composition of coal, limestone and makeup water

### Rated Capacity of The Unit Boiler

All other factors being equal, the wastewater flow will be directly proportional to the unit capacity.

### Scrubber Chloride Concentration

Similarly, the flow is directly proportional to the chloride concentration at which the scrubber operates. The higher design chloride concentrations seen in recent years has led to the need for smaller wastewater plants.

### Efficiency of Flyash Removal

A poorly optimized ESP will allow large quantities of flyash to pass into the scrubber, with the attendant risk of contaminating the gypsum to the extent that it is not marketable. However, even a well-operated ESP will have difficulty in intercepting small flyash particles, in the 5-10 um range, which will then be taken out in the wet scrubber, from where they may pass into the wastewater purge.

There is an additional effect caused by the passage of fine flyash particles into the scrubber. Many heavy metals appear in the aqueous phase of the wastewater by volatilizing during the combustion of the coal and then, in the boiler outlet duct, condensing on flyash particles. The metals are then leached from the flyash at the low pH conditions encountered in the scrubber. This effect is enhanced by the fact that the small particles, unintercepted by the ESP, have high specific surface areas for the condensation of these elements<sup>(4)</sup>.

### Type and Efficiency of Dewatering Installation

Dewatering of the gypsum slurry is achieved by belt presses, vacuum filtration or centrifugation, usually preceded by a pre-concentration stage such as hydrocyclones. Since the overflow from these units represents the flow to the WWTP, their operating efficiency determines the total suspended solids (TSS) in the influent. In particular, flyash particles, with a density similar to water, frequently escape capture in these units and appear in the wastewater.

### Type of FGD Process

The use of chemical additives to modify the conditions inside the scrubber, for example to inhibit sulfite oxidation or to enhance SO<sub>2</sub> absorption, has been used on several FGD systems. An example of the latter is the use of dibasic acid (DBA), a mixture of adipic, glutaric and succinic acids which, although more frequently used in natural oxidation or inhibited systems, has been proposed for LSF0. In Germany, one FGD supplier uses formic acid, at concentrations of about 1 g/l, in a similar way to DBA, i.e., as a pH buffer to obtain optimum SO<sub>2</sub> absorption. Being in solution, these carboxylic acids appear in the wastewater, considerably elevating its COD.

If, in addition to desulfurization, the flue gas is treated to remove NO<sub>x</sub> through the use of, for example, Selective Catalytic Reduction, ammonia is added to the flue gas stream. Although the process is optimized so as to minimize ammonia wastage, some ammonia will pass through the DeNO<sub>x</sub> system and be removed in the air preheater and the ESP. The small amount remaining after the ESP will be taken out in the scrubber, giving rise to 50 mg/l ammonium ion or less in the wastewater.

In installations where there is a prescrubber ahead of the limestone scrubber, the pH of the blowdown will be very low (0-2 S.U.) with a high chloride, fluoride and heavy metal content, in addition to high TSS levels due to flyash (up to 6 wt.%).

### Chemical Composition of Coal, Limestone and Makeup Water

As would be expected, the compositions of the coal, limestone and makeup water determine the chemical analysis of the FGD wastewater influent. The coal is, of course, the primary source of sulfur, chloride and many metals which appear in the wastewater. The limestone similarly affects wastewater composition, particularly as regards its aluminum, iron and magnesium content. The limestone purity will also affect the TSS in the wastewater since impurities such as fine clay particles can form suspensions which are difficult to remove during the gypsum dewatering phase.

In addition to being used in slurry preparation and mist elimination, makeup water is added to the scrubber to compensate for evaporation losses. The contaminants in this water are concentrated by evaporation in the power plant cooling system -- if this is the source of the water -- and in the scrubber itself.

### Availability of Analyses

The numerous factors above would suggest that FGD wastewaters can be quite variable in composition and this is, in fact, the case. It is also in the nature of the FGD projects that the WWTP has to be designed at about the same time as the FGD system. Consequently, the design of the WWTP has to be based on the known analyses of coal, limestone and make-up water. Only a water treatment company with a wide experience of treating FGD wastewaters can determine the appropriate treatment process and provide meaningful discharge guarantees. Extensive tests will be performed at the new FGD installation at Northern Indiana Public Service Company's Bailly Station in 1992-1995 under the Department of Energy's Clean Coal Technology Program<sup>(5)</sup>. These tests will evaluate different coals and should generate a wealth of information on how this parameter affects the wastewater.

### TREATMENT OPTIONS

The degree of treatment of the wastewater is determined by the National Pollutant Discharge Elimination System (NPDES) permit discharge limits imposed by the regional EPA. Since these limits are getting progressively tighter, increasingly higher levels of treatment are being required.

The minimum level of treatment encountered has been the adjustment of pH to  $7 \pm 2$  S.U. and the removal of suspended solids to less than 30 mg/l. Most NPDES permits do however limit heavy metal concentrations and, in addition, there may be limits on fluoride, sulfide, ammonia, COD, etc. Where the power plant is located close to the sea, the chloride content of the discharge, being of the same order of magnitude as that of seawater, about 20 g/l, has not been a problem. To date, this same reasoning has been applied to inland stations located on large lakes or rivers. However, some installations, because of state requirements or their specific locations, are having to address the removal of chlorides, and hence total dissolved salts (TDS), from the blowdown.

The options of wastewater treatment are as follows:

- i) treat the FGD WW in a dedicated physico-chemical treatment plant, using coagulation, sedimentation, etc.
- ii) treat the FGD WW by evaporation/crystallization.

The choice between these options is straightforward, with evaporation/crystallization only being selected where there is an absolute zero water discharge requirement. The advantages of evaporation/crystallization, namely its small footprint and the fact that it produces high quality water reusable elsewhere on the power plant, should be balanced against the disadvantages of very high power consumption and high sludge production. More importantly, there is little experience in the evaporation of FGD wastewaters at present; indications are that a high level of pretreatment may be required.

The possibility of co-treating the FGD wastewater with other power plant wastewaters should only be considered if the required treatments are complimentary and guarantee effluent values can be met. In particular, there is a risk of heavy metal complexation in co-treatment, making them difficult to remove.

Most of the emphasis to date has been on the elimination of pollutants physico-chemically in dedicated treatment plant and numerous such installations exist in Germany and Japan -- although these differ greatly in concept (compare (6) and (7)) -- with the first due to start up in the United States in 1992.

#### ELIMINATION OF POLLUTANTS BY PHYSICO-CHEMICAL MEANS

The "complete" WWTP described below will render the water non-scale forming, substantially remove cadmium, mercury, nickel, copper, zinc, lead and other metals, and clarify it prior to discharge. The treatment scheme was developed by the Philipp Mueller Company of Degremont Group in Europe through a combined use of related technologies. Experience in the treatment of brines, the removal of heavy metals, fluorides, etc., together with numerous designs of clarifiers, thickeners and filters, was used in developing a design for the treatment of these unique wastewaters. Over the last 6 years some 22 installations have been started-up and the process scheme has been refined to that shown in Figure 3.

The first stages of treatment, namely oxidation, pH elevation/desaturation, heavy metal precipitation and coagulation are carried out in individual reaction tanks, vigorously mixed by axial flow agitators. This is important in view of the different retention times and mixing energies required.

The reaction tanks provide a series of complimentary chemical environments, where reagents are dosed either proportional to flow or to adjust the pH, precipitating various species from solution. The wastewater leaving these tanks contains all

influent solids, precipitated products and recycled gypsum solids (see later). Typical chemical dosing is shown in Table 2. The next stage of treatment provides for the settling of these suspended solids and hence the clarification of the water.

Other stages of treatment include the conditioning and dewatering of the sludge settled in the clarifier, and final pH adjustment. In some European installations, COD is removed by adsorption on granular activated carbon (GAC).

It has been found that the optimum design for the system is to elevate the reaction tanks such that the water flows by gravity through the complete plant; in this way floc particles are not destroyed by re-pumping and are able to settle well in the clarifier downstream. With only one fixed recycle and this type of WWTP is easy to operate.

The treatment stages are described more fully below.

#### Treatment Stages

Oxidation. This stage will only be required if the influent sulfite concentration exceeds 100 mg/l  $\text{SO}_3^{2-}$  and there is a discharge limit for COD. In cases where oxidation of calcium sulfite to sulfate in the absorber is incomplete, this reaction can be brought near completion by blowing air through the liquid in the first reaction tank. The approximate sizing of this, and other, reaction tanks is given in Table 3.

Elevation of pH/Desaturation. Typically, FGD wastewaters have pH values in the 5.0-6.5 S.U. range. In this stage, an alkali, either calcium hydroxide or sodium hydroxide, is added to obtain pH 8.5-9.2. If the wastewater originates from a prescrubber, and is highly acid, pH adjustment is achieved in two stages (two tanks): the pH in the first tank is adjusted to about pH 4.3, and in the second tank to pH 8.5-9.0, the optimum pH for treatment.

Since pH elevation is an important part of the wastewater treatment process, the concentrations of the abundant metals which form insoluble hydroxides and oxyhydroxides (i.e., aluminum, magnesium and iron) are important in the sizing of the treatment facility, as they represent a major solids load to the clarifier/thickener. Most of the heavy metals also present in the waste stream are removed at these higher pH values, but their much lower concentrations represent a negligible load.

The other function of this tank is the "desaturation" of gypsum from the wastewater, since this compound has a tendency to supersaturation. If not brought to equilibrium, this supersaturation can exist for several hours; when equilibrium is achieved, calcium sulfate comes out of solution, causing severe scaling in the clarifier, pipes, etc. In order to accelerate the rate of desaturation, and to have it take place in a controlled manner, "young", thin sludge is returned from the main clarifier/thickener to the reaction tank. This sludge flow rate is equal to about 50% the influent flow, so as to maintain a minimum concentration of 2.5-3.0 wt.% solids in the tank. This sludge contains already-formed gypsum crystals which act as crystallization nuclei for the calcium sulfate in solution. In this way, gypsum "scales" sludge particles rather than the equipment.

Heavy Metal Removal. The removal of heavy metals as their hydroxides alone would not allow the strict regulatory requirements to be met. Since the solubility products of all heavy metal sulfides are lower than their corresponding hydroxides, it follows that the addition of sodium sulfide, for example, should allow stricter standards to be met. In fact, rather than this reagent, an organosulfide such as sodium trimercapto-s-triazine is used. These organosulfide-heavy metal complexes have very low solubility products, of the same orders of magnitude as the inorganic sulfides. One advantage of using the organosulfide is that it is non-toxic. Unlike sodium sulfide, whose use must be carefully controlled to ensure that the toxic sulfide ion does not escape in the discharge, there is no risk with this reagent if dosed in excess.

As well as allowing better removal, this two-stage precipitation of heavy metals, both as hydroxides and sulfides, has an added advantage. Except in the case of metals such as zinc and lead, a higher pH will tend to remove more of the heavy metal from solution -- an argument for using as high a pH as practicable. However, at about pH 10, all the magnesium in solution would precipitate, and even so, at the selected pH of 8.5-9.0, some magnesium hydroxide,  $Mg(OH)_2$ , does precipitate, representing additional solids to be dewatered. Since Mg is not usually subject to discharge controls and, further,  $Mg(OH)_2$  is difficult to dewater, keeping the pH lower rather than higher is beneficial. Selection of a limestone with a low  $MgCO_3$  content is also important since each gramme of magnesium introduced by the limestone yields 2.42 g of  $Mg(OH)_2$  sludge.

Coagulation. Iron (III) chloride is used as the mineral coagulant of choice in FGD wastewater treatment in preference to aluminum sulfate because of its wider pH range of application and the denser floc it produces. As this reagent hydrolyses to form

iron (III) hydroxide, other metals are co-precipitated and some soluble organic matter is destabilized.

Flocculation, Clarification and Thickening. The latest WWTP designs use a combined reactor-clarifier-thickener for the separation of influent solids and precipitation products from the wastewater<sup>(9)</sup>. In the reaction zone, there is a high energy input where sludge is recycled and densification occurs. The fast-settling nature of this dense sludge enables high rise rates (and hence smaller equipment) to be used in clarification. The solids settle in the raked thickener portion, while the clarified water passes through honeycomb-type lamellar modules, which trap any rogue particles that may not have settled. Effective gypsum desaturation is essential if these lightweight modules are to function well, and not act as a matrix for scale deposition.

The sludge composition determines the surface loading and rise rate used for the thickener design. Typically, sludges with a high metal hydroxide content (greater than ca. 30%) will require low solids loadings and rise rates of approximately 0.1 gpm/sq.ft., while those with a high gypsum content can be applied at rise rates of up to 0.4 gpm/sq.ft. and higher loadings. Sludge is withdrawn from the thickener unit in two zones using progressing cavity pumps: older, thicker sludge is removed from the cone bottom of the unit for dewatering, while younger sludge is removed higher up the cylinder to be returned to the desaturation stage.

COD Removal. If required, COD removal is effected after clarification. While the sulfite can be removed by oxidation, the organics need to be removed by adsorption through GAC. Where carboxylic acids are dosed, and are responsible for high COD values, they can be removed biologically<sup>(9)</sup>.

pH Adjustment. The pH value of the wastewater is re-adjusted prior to discharge using hydrochloric or sulfuric acid.

Sludge Dewatering. The 10-20 wt. % sludge extracted from the thickener is transferred to an agitated sludge holding tank where lime, if available, is dosed to 10-15% by weight to aid dewaterability and, as has been found with other power plant wastewaters<sup>(10)</sup>, to fix the heavy metals in the sludge once it has been landfilled. Dewatering is achieved by filter presses operating at 225 psig (15 bar g) so as to produce a cake of 50-55 wt.% dry solids content for easy truck disposal.

### Materials of Construction

The precautions taken against corrosion in the scrubber, due to the high chloride environment of FGD, have similarly to be adopted in the design of the WWTP.

All wetted parts (tanks, pipework, mixers, pumps) should be rubber-lined carbon steel, or FRP. In the case of the former, precautions have to be made against oils and greases in the wastewater (which in any case are unlikely to exceed 5 mg/l) as these can perish the rubber lining. In the case of FRP, this should be resistant to abrasion by gypsum and flyash particles. Where rubber lining of wetted parts is not possible, as for example with progressing cavity pump rotors or knife gate valves, then special alloys (e.g., Hastelloy C) must be used.

The high suspended solids concentration of the wastewaters, as well as its corrosive nature, necessitates the use of appropriate instrumentation such as magnetic flow meters, diaphragm type pressure indicators and suitable self-cleaning pH probes.

### OTHER ISSUES

#### Zero Discharge

Pilot tests are scheduled in Europe later this year on the evaporation of FGD wastewaters using a vertical tube falling film unit. To date, very little information is available on the treatment of FGD scrubber blowdown by this means, although it is known that the requirements for a very low influent TSS and a non-scaling characteristic will necessitate some pretreatment. Further, if the salt reject is evaporated to give a dry cake, which may perhaps be used as road salt, prior heavy metal removal will be required. In effect, then, the zero discharge option may mean a complete physico-chemical plant, as described above, preceding the evaporator/crystallizer.

#### Biological Treatment

If organic acids start being widely used for LSFO systems, then WWTP will have to be adapted to allow for treatment to remove the resultant COD. So far, two installations in Germany, Bexbach and Fenne, have biological trickling filters after physico-chemical treatment, to remove formic acid dosed in the FGD process. Pilot tests conducted prior to installation of these treatment stages indicate removals in

excess of 90% from influent levels up to 1,000 mg/l COD, with chloride concentrations up to 9,000 mg/l.

With the expected higher chloride concentrations in modern FGD systems, further work will have to be performed on COD removal in FGD wastewaters. Experience in the treatment of other wastewaters indicates that inhibition of biological processes starts at about 10,000 mg/l chloride.

### Sludge Disposal

Unlike the gypsum produced in the scrubber which, if 95% pure  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and complying with other purity standards, can be sold, the sludge from the WWTP needs to be disposed of to waste. Transportation and lining costs, as well as licensing issues need to be addressed. The costs associated with such disposal partially offset the savings made through not having to landfill the gypsum from the scrubber. Some tests have been performed in Europe where the WWTP sludge was dumped on the coal pile, combusted and then taken out with the bottom ash.

### SUMMARY

Although some of the stations required to achieve Phase I compliance by January 1, 1995, will use an FGD process producing saleable gypsum, it is not clear how widespread this technology will become. This will be determined to a large extent by the market for gypsum in the construction, agricultural and other industries.

It is only where this process is selected that a wastewater stream will definitely be produced. Economics have determined this route to be favored in Germany; conversely, in the U.S. throwaway systems have been favored. Throwaway systems can be operated on an open or closed loop basis, and only in the former case will wastewater treatment be required.

The wastewaters are saline, corrosive waters containing heavy metals at levels unacceptable for environmental disposal. A full knowledge of these waters and experience of current treatment practices ensures the removal of these and other pollutants.

### ACKNOWLEDGEMENTS

My thanks to Johannes Weinig of Philipp Mueller Company, Stuttgart, Germany for his review of this paper.

#### REFERENCES

1. Weiler, H. & Ellison, W., "Progress in European FGD and SCR Applications", EPA/EPRI SO<sub>2</sub> Control Symposium, New Orleans (1990)
2. Metzler, A.R., Gallardy, P.B., McLaughlin, B.R., Ireland, P.A. and Spengel, W.J., "Evaluation of Acid Rain Alternatives", Conference Papers, III & IV, 3rd International Power Generation Industries Conference, Orlando, Florida, 1990, pp. 225-245.
3. Downs, W., Johnson, D. W., Aldred, R. W., Tonty, L. V., Robards, R. F. and Runyan, R. A., "Influence of Chlorides on the Performance of Flue Gas Desulfurization", EPA/EPRI Symposium on Flue Gas Desulfurization, New Orleans, (1983).
4. Taylor, M.R.G., Heaton, R. and Baty, R., "The Impact of Flue-Gas Desulphurization on the Water Environment", J.IWEM 3, pp. 227-234 (1989)
5. Wrobel, B., and Seelaus, T.J., "Acid Rain Compliance - Advanced Co-current Wet FGD Design for the Bailly Station", Conference Papers, III & IV, 3rd International Power Generation Industries Conference, Orlando, Florida, 1990, pp. 343-357.
6. Bursik, A. & Dieterle, E., "FGD Wastewater Treatment - State of the Art in the Federal Republic of Germany" Proceedings, 49th International Water Conference, Pittsburgh IWC-88-38, pp. 373-379 (1988)
7. Etoh, Y., Takadoi, T. & Itoh, I., "Sludge Reduction in Coal-Fired Power Plant Flue Gas Desulfurization Wastewater Treatment", Proceedings 41st Purdue Industrial Waste Conference, pp. 545-553 (1986).
8. Mierzejewski, M.K., Rovel, J.M., and VandeVenter, L.W., "The Use of a High-Rate Combined Reactor/Clarifier/Thickener for the Treatment of Industrial Wastewaters", Proceedings, 44th Purdue Industrial Waste Conference, pp. 519-526 (1989).
9. Frick, B.R., "Flue Gas Purification - Shifting Pollution from Air to Water?", Vom Wasser 65.Band, pp. 145-156 (1985) (Germany).
10. Manzione, M.A., Merrill, D.T., McLearn, M.E., Chow, W., Stine, J.F., Kobayashi, S., and Martin, W.J., "Removal of Trace Elements from Power Plant Waste Streams by Iron Adsorption/Coprecipitation", Proceedings 49th International Water Conference, Pittsburgh IWC-88-36, pp. 361-372 (1988).

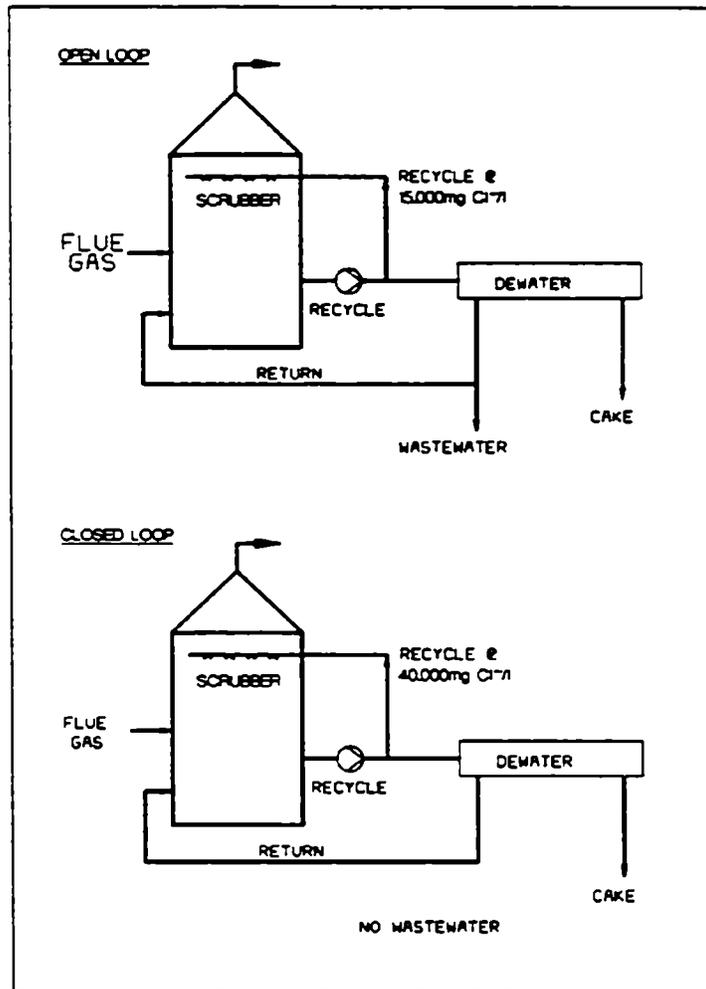


Figure 1. Open and closed loop operation of an FGD scrubber. By operating at a higher chloride concentration (e.g. 40,000 mg Cl<sup>-</sup>/l) the closed loop system avoids a separate wastewater stream as chloride blowdown.

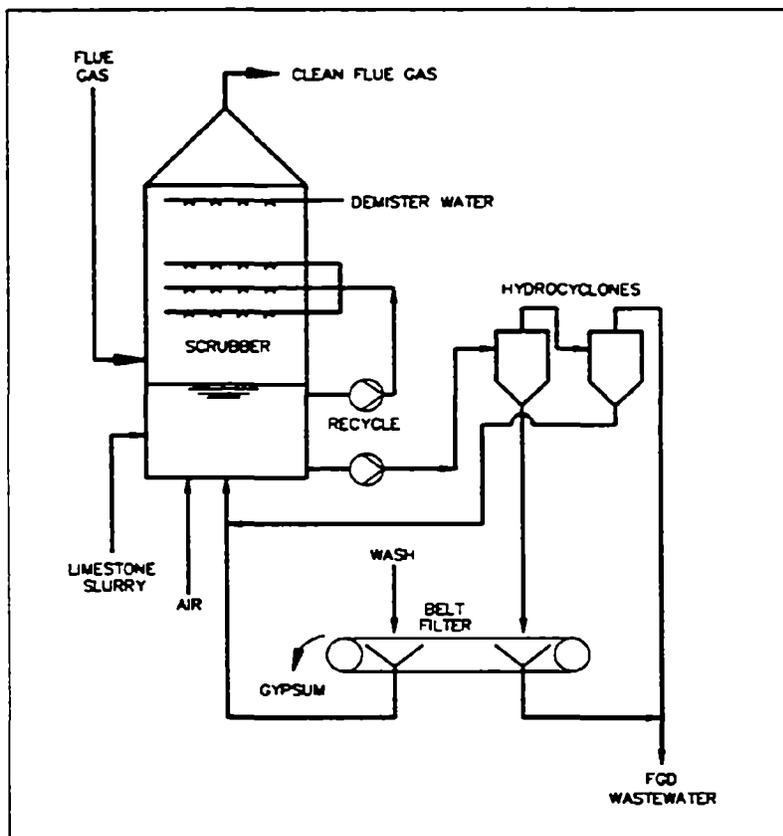


Figure 2. Schematic of water use on a LSF0-WB scrubber (after Weiler and Ellison [1]).

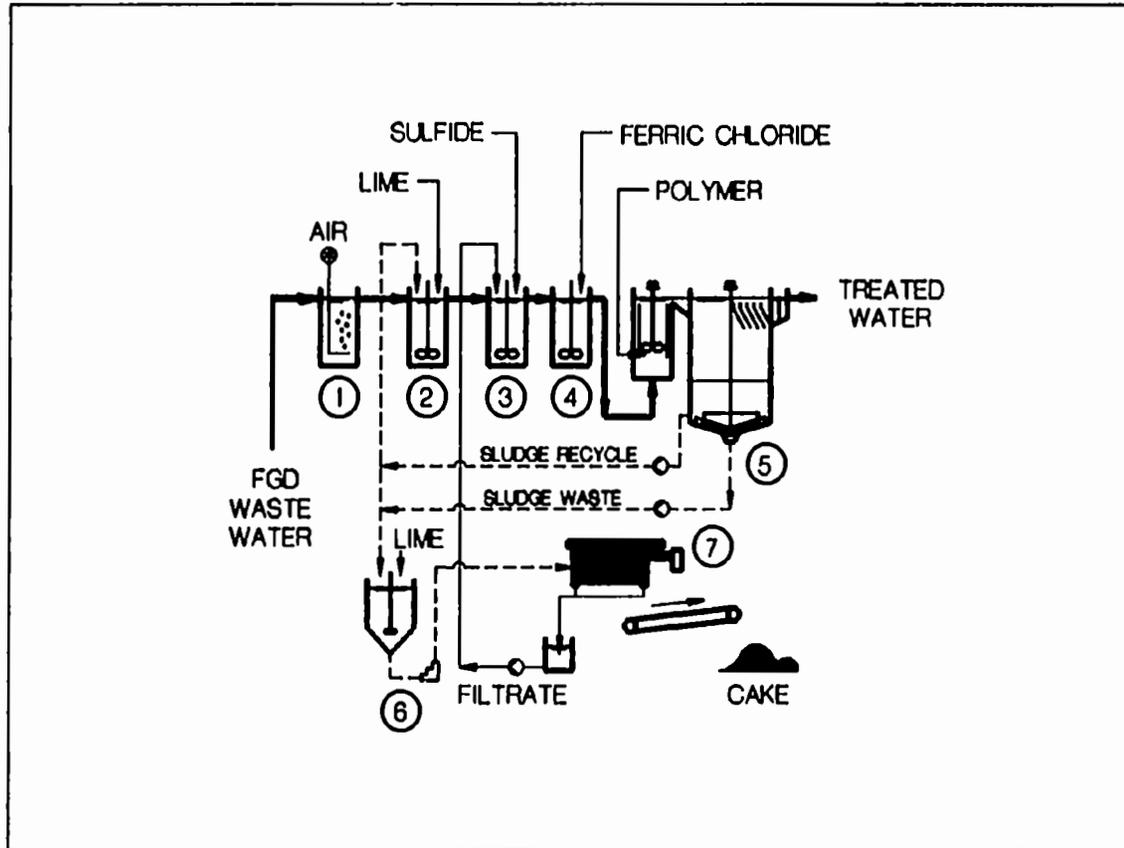


Figure 3. Flow scheme for physico-chemical treatment of water

- |                |                             |                        |
|----------------|-----------------------------|------------------------|
| 1. Oxidation   | 2. pH Elevation/Description | 3. Heavy Metal Removal |
| 4. Coagulation | 5. Clarification/Thickening | 6. Sludge Conditioning |
|                | 7. Sludge Dewatering        |                        |

TABLE 1  
TYPICAL RANGES OF CONSTITUENTS  
IN FGD WASTEWATERS BEFORE AND AFTER TREATMENT

<u>PARAMETER</u>	<u>BEFORE *</u>	<u>AFTER *</u>
CHLORIDE (Cl)	10,000 - 40,000	10,000 - 40,000
SULFATE (SO <sub>4</sub> )	1,500 - 8,000	800 - 2,500
NITRATE (NO <sub>3</sub> )	300 - 1,400	300 - 1,400
FLUORIDE (F)	30 - 200	<15
CALCIUM (Ca)	4,000 - 20,000	5,000 - 25,000
MAGNESIUM (Mg)	200 - 5,600	200 - 2,000
SODIUM (Na)	75 - 1,200	75 - 1,200
IRON (Fe)	30 - 400	<0.5
ALUMINUM (Al)	50 - 800	<2.0
ARSENIC (As)	0.05 - 3.0	<0.05
BORON (B)	20 - 40	20 - 40
CADMIUM (Cd)	0.04 - 0.5	<0.1
COBALT (Co)	0.05 - 0.4	<0.1
CHROMIUM (Cr) -TOTAL	0.3 - 5.0	<0.1
COPPER (Cu)	0.1 - 0.85	<0.1
MERCURY (Hg)	0.05 - 0.8	<0.05
NICKEL (Ni)	0.2 - 6.0	<0.1
LEAD (Pb)	0.1 - 3.0	<0.1
SELENIUM (Se)	0.2 - 1.0	<0.2
ZINC (Zn)	0.4 - 8.0	<0.1
AMMONIUM (NH <sub>4</sub> )	50	50
COD	100 - 150	100 - 150
pH	4 - 7	7 - 9
TSS	300 - 10,000	<15

\*-All units are mg/l; pH in Standard Units.

TABLE 2  
CHEMICAL DOSING IN FGD WASTEWATER TREATMENT

CHEMICAL	DOSE	UNITS
CALCIUM HYDROXIDE (95% PURE)	1,500-4,000*	g/m <sup>3</sup>
ORGANOSULFIDE (eg. TMT 15)	50	ml product/m <sup>3</sup>
FERRIC CHLORIDE (as FeCl <sub>3</sub> )	30-50	g/m <sup>3</sup>
POLYMER	1-1.5	g/m <sup>3</sup>
SULFURIC ACID	**	--

\* assuming influent pH 5-6, and dependent on water composition.

\*\* dependent on effluent pH required.

TABLE 3  
REACTION TANK SIZING

TANK FUNCTION	HYDRAULIC RETENTION TIME (MINS)
OXIDATION	60
pH ELEVATION/ DESATURATION	60
HEAVY METAL REMOVAL	15
COAGULATION	5
POLYMER FLOCCULATION	12

**The Influence of FGD Variables on FGD Performance  
and By-Product Gypsum Properties**



F. W. Theodore, M. R. Stouffer, D. C. McCoy, and N. Yoon  
Consolidation Coal Company  
Research and Development  
Library, Pennsylvania 15129

J. E. Smigelski, P. J. Szalach, and J. A. Weist  
New York State Electric and Gas Corporation  
Binghamton, New York 13902

D. R. Owens  
Electric Power Research Institute  
Palo Alto, California 94303

#### ABSTRACT

The paper describes a project designed to better understand the influence of wet FGD process variables on FGD performance and the production of salable gypsum. Results obtained from FGD pilot plant testing at the EPRI High Sulfur Test Center are discussed. The variables studied were dissolved chloride content (15,000-75,000 ppm), limestone grind size, and process configuration (single-tank and double-tank). Short-term (24-hour) runs were made to determine SO<sub>2</sub> removal and limestone utilization as functions of the process pH. These results were used to set the conditions for the long-term (5-day) gypsum production runs. The FGD process performance and the preliminary characteristics of the product gypsum are reported. The gypsum produced during the long-term runs will be tested as a feed material for wallboard production. New York State Electric and Gas Corporation, Consolidation Coal Company, EPRI, Empire State Electric Energy Research Corporation, and U.S. Gypsum are project participants.

## INTRODUCTION

In anticipation of increasing disposal costs for wet flue gas desulfurization (FGD) waste, New York State Electric and Gas (NYSEG) initiated a project directed at converting the Kintigh (formerly Somerset) Station to a forced oxidation FGD to produce a salable gypsum by-product. The focus of the work described in this paper is the relationship between FGD performance and the resulting gypsum quality. The overall project objectives are:

1. To expand the existing data base for forced oxidation FGD, with emphasis on the effects of FGD operating variables on gypsum properties.
2. To provide data to support the conversion of the inhibited oxidation wet limestone FGD system at NYSEG's Kintigh Station to a forced oxidation FGD system to produce a salable gypsum by-product.
3. To evaluate the influence of FGD gypsum properties on wallboard manufacture.

In order to achieve these objectives, NYSEG assembled a project team with expertise in all areas of gypsum utilization from FGD operation to wallboard manufacture. In addition to NYSEG, the co-funding project participants are the Electric Power Research Institute (EPRI), the Empire State Electric Energy Research Corporation (ESEERCO), the United States Gypsum Company (USG), and Consolidation Coal Company (Consol).

The initial phase of this project was a literature study of forced oxidation FGD and the impact of FGD operating variables on gypsum properties. The literature study indicated that there are research areas with potential to advance forced oxidation FGD technology and the production of by-product wallboard-quality gypsum. In

addition, the study identified those design variables which could be set based on literature information. A staged experimental program in conjunction with process economic studies was recommended.

Based on this preliminary work, a pilot-scale test program was developed to provide data on forced oxidation FGD performance for the conversion of the Kintigh Station FGD system to forced oxidation. Such data would allow confirmation of the feasibility of the conversion and would be used in economic studies to optimize the process design. This pilot test program focused on the effects of key process chemistry variables and was conceived as a first-test phase, to be followed by additional test phase(s) for process optimization, if necessary.

This paper discusses the results obtained from this initial phase of the test program. The paper will focus on the influence of the key FGD variables on FGD performance and the resultant gypsum properties, namely, purity and crystal size. A detailed evaluation of the by-product gypsum quality and its influence on wallboard products is in progress and will be reported at a later date.

#### TEST PROGRAM

The pilot-scale program was conducted at the EPRI High Sulfur Test Center (HSTC)<sup>1</sup> wet FGD pilot plant (4 MW<sub>e</sub>). The specific test objectives were:

1. To determine the effect of process configuration on FGD performance and gypsum properties.
2. To determine the effects of process variables, including pH, dissolved solids (Cl<sup>-</sup> concentration), limestone grind, and L/G ratio on FGD performance and gypsum properties.
3. To generate data for process optimization for the Kintigh forced oxidation conversion.
4. To generate gypsum samples for by-product quality evaluation.

#### Test Variables

The pilot test program was conducted in two test blocks: (1) process configuration tests, and (2) process variable tests. The process configurations evaluated were

a combined oxidizer-reaction tank system (single-tank mode) and a separated oxidizer and reaction tank system (double-tank mode). The process configuration tests were conducted with the other process conditions held constant: 35000 ppm  $\text{Cl}^-$  (average), 89% -325 mesh limestone, and 130 L/G. The process conditions used for the configuration tests were within a range which represents the projected conditions for the Kintigh Station conversion. The L/G ratio used in the pilot tests was higher than projected for Kintigh to reflect differences in absorber mass transfer capacities between the pilot and Kintigh equipment. The process variable test block was designed to investigate the effects of key process operating variables (i.e., dissolved solids concentration, limestone grind, and L/G ratio) with a fixed process configuration (double-tank).

The FGD design and operating parameters which were not varied for the tests were fixed to match those expected in the converted Kintigh FGD system. The inlet  $\text{SO}_2$  concentration was held constant for the entire program at 2000 ppm  $\text{SO}_2$ . The limestone now used at Kintigh was used in the pilot tests. Concentrations of dissolved chemical species ( $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) were maintained in the same ratio as currently found at Kintigh. The liquid retention time for both the oxidizer and reactor tanks were set to approximate their counterparts at Kintigh, namely, 4.4 min and 3.8 min, respectively. The solids content of the circulating slurry was controlled at 12%. Finally, a hydroclone and vacuum belt filter were used for dewatering of the product gypsum.

The oxidation air system was not optimized in this program; rather, the air sparge rate was set to achieve 99%\* oxidation efficiency. Because the pilot plant oxidizer height was limited, substantially more air was required than expected for commercial size systems.

#### Test Procedure

There are several factors that determine gypsum purity. Two components that are related to both gypsum purity and FGD performance are the calcium sulfite concentration (percent oxidation) and calcium carbonate concentration (limestone utilization). As noted above, the degree of oxidation was maintained constant at a high level, typically greater than 99%, during the program. Limestone utilization was used as a performance parameter because it is a governing variable in the by-product gypsum purity and because it controls solid-phase alkalinity which controls  $\text{SO}_2$  removal. Therefore, limestone utilization and  $\text{SO}_2$  removal together define the performance of a forced oxidation FGD system. Testing proceeded on this basis to

evaluate the effects of key process variables on utilization and SO<sub>2</sub> removal. A series of short-term, pilot plant parametric tests were conducted. Short-term tests were 24 hr long, which was based on the time required for the system limestone loading to reach equilibrium. These tests consisted of measuring the limestone utilization and SO<sub>2</sub> removal at different absorber feed slurry pH levels with limestone grind, chloride level, and L/G held constant. Figure 1 presents typical short-term test data, the utilization and SO<sub>2</sub> removal as functions of feed slurry pH. The data from the test series were analyzed to determine optimum operating conditions for long-term tests. The purpose of the long-term pilot plant tests was to generate gypsum samples, representative of solid-phase equilibrium and stable steady-state operation, for use in by-product quality evaluation studies. Long-term runs were greater than five days in length. This allowed for about three solid-phase residence time changeouts.

Measured SO<sub>2</sub> removals in the HSTC pilot plant absorber were expected to be less than for the Kintigh absorbers at the same L/G ratio and process conditions, primarily because of increased wall effects in the smaller unit. In addition to wall effects, other factors affecting mass transfer could not be duplicated in the pilot plant (for instance, absorber gas distribution, absorber slurry distribution, slurry droplet size, etc.). Hence, the pilot tests were conducted at higher L/G ratios (most at 130 gal/1000 acf) than used at Kintigh (currently, 79 gal/1000 acf). In order to better define the correlation between the HSTC pilot plant performance and Kintigh Station absorber performance, some pilot runs were conducted under inhibited oxidation conditions to simulate Kintigh operation.

## RESULTS AND DISCUSSION

As stated earlier, the objectives of the test program were multipurpose and a complete analysis of the test results is beyond the scope of this paper. In addition to summarizing results, the following discussion will focus on how the results influence the conversion of Kintigh to a forced oxidation unit producing salable gypsum. Preliminary data are presented which characterize the gypsum produced during the five long-term runs. The gypsum from these five runs will be analyzed further for acceptability as a wallboard feed and the results will be reported at a later date.

In dealing with the results of this study, we will focus on the limestone utilization, since this variable is a key in establishing the by-product gypsum

purity. Low utilization results in gypsum containing high levels of unreacted  $\text{CaCO}_3$ .  $\text{CaCO}_3$  is an inert material that adversely affects the properties and economics of wallboard production. The chlorides and other soluble impurities can be washed out, but carbonates will remain in the gypsum. If the goal is to sell gypsum, then a high (90-95+%) limestone utilization must be achieved, and the desired  $\text{SO}_2$  removal must be achieved by adjusting other control variables, (L/G, etc.). The FGD run data are summarized in Table I.

### FGD Performance

Process Configuration. The two process configuration modes discussed in this paper are the single-tank and double-tank. The two major differences for the double-tank configuration tests, as compared with single-tank tests were: (1) longer solids residence time (about double) due to additional tank volume, and (2) separation of the oxidation tank upstream from the limestone addition point. The process configuration test block was not designed to distinguish between the effects of these two factors on the performance.

Figure 2 shows the FGD performance ( $\text{SO}_2$  removal versus limestone utilization) for the two process configurations. As can be seen, there is little if any difference in performance between the two configurations at limestone utilizations below 90%. As the limestone utilization increases above 90%, the double-tank configuration achieves greater  $\text{SO}_2$  removal. At a very high utilization (98%), the  $\text{SO}_2$  removal is 5-8 % absolute greater for the double-tank case. The graph suggests that if one is attempting to obtain high limestone utilization (high purity gypsum) greater than 90%, then the double-tank configuration case becomes attractive.

The probable reason for better performance of the double-tank system is that at a constant utilization, the double-tank system was operable at a higher pH. The increase in operating pH gave a higher liquid-phase alkalinity, which accounted for the higher  $\text{SO}_2$  removals. The increased residence time and separation of the oxidation and limestone addition steps from each other are likely responsible for the increase in operating pH level for the double-tank configuration. As noted above, system equipment limitations during the test program prevented isolation of the relative importance of these two factors.

In the case of the Kintigh Station, the existing FGD plant was designed for a future retrofit and has the tankage in place for a double-tank system. Because the Kintigh Station already had equipment for a double-tank configuration and because the pilot

double-tank results were equal to if not better than the results for the single-tank system, the remainder of the program was conducted in a double-tank mode.

Chloride Concentration. The base case chloride concentration used in this study was 35,000 ppm. This level of chloride was chosen since it is in the middle of the chloride range being considered for the Kintigh Station. As stated earlier and as shown in Table I, the other dissolved solids species ( $Mg^{2+}$  and  $Na^+$ ) were increased and decreased in proportion to the  $Cl^-$  concentration in order to maintain the same ratio as currently found at Kintigh. The chloride concentration is determined by the plant water balance. The design chloride level for Kintigh will depend on the cost of chloride control versus the costs for improving FGD performance at higher chloride levels.

Figure 3 shows the FGD performance achieved during the pilot tests at four different chloride levels (15,000, 35,000, 55,000 and 75,000 ppm). The data for the lower three chloride levels include data from long-term runs. The 75,000 ppm chloride data were taken during a series of short-term runs. The individual data points are plotted over regression curves generated from the entire data set. As shown in Table I, the chloride concentration in the three high chloride level runs deviated from the 75,000 ppm  $Cl^-$  set point. This fact explains the deviation of the individual points from the regression curve (Figure 3).

The detrimental effect of higher chloride levels on FGD performance is obvious from the results shown in Figure 3. For any given limestone utilization, the absorber  $SO_2$  removal decreases with dissolved chloride.

Furthermore, at higher limestone utilization, the  $SO_2$  removal is sensitive to small changes in utilization. This is not an unexpected result because as the limestone utilization levels are increased, the solid-phase alkalinity decreases, which reduces the availability of reagents in the absorber if slurry circulation (L/G) remains constant. The result emphasizes that at the high utilization required to produce a high purity by-product gypsum, the resulting  $SO_2$  removal is more sensitive to system chemistry than at lower utilization.

Limestone Grind Size. The limestone grinds used in this study are related to that used at the Kintigh Station in the following ways. The coarsest grind, 67% -325 mesh, is equivalent to the current Kintigh grind. The middle grind, 89% -325 mesh, corresponds to the limit achievable at Kintigh without an additional ball mill. The

finest grind (94% -325 mesh), would require the addition of another ball mill at Kintigh. For the three limestone grind sizes tested in the pilot plant, use of finer grinds moderately improved desulfurization performance. The exact improvement was influenced by the levels of other variables. As an example, the influence of grind size appeared to be stronger at a low chloride level (15,000 ppm) than at a higher chloride level (55,000 ppm).

Figure 4 shows SO<sub>2</sub> removal versus utilization curves for the three different grind sizes at a 55,000 ppm Cl<sup>-</sup> concentration. At constant limestone utilization, SO<sub>2</sub> removals increased by 2 to 4% absolute from the coarsest to the finest grind. For example, at 95% utilization, SO<sub>2</sub> removals were evenly spaced (77%, 79%, and 81%, respectively). At lower utilizations, however, the middle grind size (89% -325 mesh) performance approached that of the coarse grind; whereas the finer grind gave 3% absolute higher SO<sub>2</sub> removal than the other two. It was concluded that for the projected Kintigh Station operating conditions (85% SO<sub>2</sub> removal and 95% limestone utilization), the base case grind (89% -325 mesh) gave satisfactory performance and would eliminate the need for a new mill to meet Kintigh's proposed conditions.

Liquid-to-Gas Ratio (L/G). At the completion of the last long-term run (51), a series of short-term runs was made to investigate the effect of L/G on SO<sub>2</sub> removal. The conditions for these runs, coarse limestone grind, 15,000 ppm Cl<sup>-</sup>, and a pH of approximately 5.9, were comparable to those of run 51. The limestone utilization was not strongly affected by L/G over the narrow range tested. The utilization varied randomly by less than 4% absolute for an L/G range of 130-162 gal/1000 acf. Below is a summary of the data.

L/G, gal/1000 acf	130	142	162	205	65	100
pH	5.91	5.91	5.91	5.90	6.11	5.92
SO <sub>2</sub> Removal, %	80.7	83.3	85.3	92.2	57.1	67.6
NTU = ln (SO <sub>2</sub> in/SO <sub>2</sub> out)	1.64	1.79	1.92	2.56	0.85	1.13
Limestone Utilization, %	95.8	94.4	98.3	--	--	--

The SO<sub>2</sub> removal data are plotted as number of transfer units (NTU) versus L/G in Figure 5. As shown, the SO<sub>2</sub> removal expressed in NTUs is directly proportional to L/G, which corresponds to previous natural oxidation FGD data.<sup>2</sup> Based on this series of runs, it is assumed that for other conditions used in the pilot plant, the SO<sub>2</sub> removal in NTUs is a linear function of L/G and that utilization is independent

of L/G. This is a very useful relationship since it allows calculation of required L/G for any SO<sub>2</sub> removal, assuming performance is known at one L/G level.

### Gypsum Crystals

Samples of gypsum from both long- and short-term tests were analyzed for crystal size using the Malvern Laser Diffraction Analysis method. The results shown in Table II are the averages of duplicate analyses of each sample. The absolute measured crystal size is dependent upon the specific method and procedure used for the size determination. However, by using only one method for size determination, the relative influence of process variables on crystal size can be evaluated.

Table II shows the crystal size (mass mean diameter) and the size distribution %<10 $\mu$ m and %>40 $\mu$ m. The single largest variable to influence the crystal size is the process configuration (double-tank versus single-tank). By comparing the crystal size for runs 6 and 17, it can be seen that the mass mean diameter increased from 24 $\mu$ m with the single tank to 31.4 $\mu$ m with the double tank. In addition, the percent <10 $\mu$ m decreased from 12.9% to 5.1%. The larger crystal size obtained with the double tank configuration may solely be due to increased system residence time. As mentioned earlier, the ability to separate the influence of retention time from the two-tank configuration was not possible in this program.

The process variables had little if any influence on the resultant crystal size distribution, especially when one considers only the results from the long-term runs. When the crystal size data from the short-term run at high chloride content (run 31) are included in the analysis, it appears that the crystal size increases slightly with increasing chloride content. This would confirm earlier work<sup>3</sup> by EPRI/Radian which showed that the gypsum crystal growth rate increases with TDS levels from 30,000-240,000 mg/L. At lower TDS levels, their results indicated little dependence of crystal growth rate on TDS level.

The conclusion is that with the exception of the possible minor influence of chloride concentration on the crystal size, the process chemistry variables studied had no effect on crystal growth. This is an important observation since crystal size and shape can be expected to be stable during normal variations in FGD operation.

The typical shape of the gypsum crystal produced in the program is illustrated by Figure 6, a micrograph from run 37 material. The crystal is block-shaped as opposed

to needle-like or plate-like. A complete analysis of the by-product gypsum will be reported later. Material from all the long-term runs (6, 17, 29, 37 and 51) is available for evaluation.

A preliminary inspection of the product crystals produced during this test program showed that the crystal size and shape were typical of other by-product gypsums. In addition, a product sample was subjected to a series of batch tests to determine its suitability for producing wallboard. The results of these tests showed that a high quality board was produced from the test material. The test details will be reported at a later date. Based on these facts, the resultant crystal size and shape generated during this program should be suitable for wallboard production if the other product specifications such as moisture, chloride, purity, etc., are met.

#### Scaleup

In order for the data obtained during the testing to be more useful in projecting the operation of the Kintigh FGD converted to forced oxidation, the scaleup factor for the pilot FGD was determined. This was accomplished by comparing the performance of the pilot and Kintigh FGD systems under conditions where process chemistry was held constant.

The final testing done under this program was a series of short-term runs in the inhibited oxidation mode. Absorber slurry circulation (L/G) was the only variable changed during this test series. The other conditions for these runs are shown in Table III. Figure 7 graphically shows SO<sub>2</sub> removal as a function of L/G. As in the forced oxidation case, SO<sub>2</sub> removal plotted as NTUs is a linear function of L/G.

The SO<sub>2</sub> removal and L/G data from Kintigh are shown in Figure 7. The other conditions for the Kintigh tests are shown in Table III. Although there was some difference in the conditions between the pilot plant and Kintigh Station, the simulation was close enough to allow an estimation of the HSTC pilot plant scaleup factor. Based on the results of these tests, the L/G required at Kintigh is expected to be about 55% of the L/G required at the HSTC.

#### Summary of Results and Conclusions

The forced oxidation test program conducted at the HSTC was successfully completed. The data collected show the influence of key process variables on system performance. The results of the test work will be used to guide design efforts in

converting the inhibited oxidation FGD system at Kintigh to a forced oxidation system. Major program conclusions are presented below.

1. The test program results were positive, indicating that conversion of Kintigh to a forced oxidation system to produce salable gypsum is technically feasible. Based on pilot data and on an approximate scaleup correlation between the pilot and Kintigh absorbers, 85% SO<sub>2</sub> removal at 95% limestone utilization should be achievable at 55,000 ppm Cl<sup>-</sup>, 67% -325 mesh limestone grind, and an L/G ratio of about 95 gal/1000 acf, an achievable value at Kintigh.
2. The pilot tests generated gypsum samples at varying process conditions for characterization and by-product quality evaluation.
  - Gypsum purity has been determined for all samples. High purity was achieved by maintaining high limestone utilization.
  - Laser diffraction particle size analyses were conducted by Consol to determine the effect of process configuration and process variables on gypsum crystal size.
3. FGD performance with the double-tank configuration was somewhat better than with the single-tank configuration in the pilot tests.
  - SO<sub>2</sub> removals were slightly higher with the double-tank configuration, especially at higher limestone utilizations. For example, SO<sub>2</sub> removal was about 5% (absolute) higher at 98% utilization, but removals were essentially the same below about 92% utilization.
  - The gypsum crystals produced in double-tank testing were larger than those from single-tank testing (31 $\mu$ m versus 24 $\mu$ m mass mean diameter).
4. FGD performance was significantly impaired by increasing levels of chloride in the process liquor. Chloride was varied over a range of 15,000 ppm to 75,000 ppm, with the other species (Mg<sup>2+</sup>, Na<sup>+</sup>) held in the same ratio to Cl<sup>-</sup> as for current operating conditions at Kintigh.

--With increasing dissolved solids, SO<sub>2</sub> removals were lower at the same limestone utilization. For example, with the 89% -325 mesh limestone grind, SO<sub>2</sub> removals at 95% utilization were about 86%, 82%, and 79% at chloride contents of 15,000, 35,000, and 55,000 ppm, respectively. The decline in SO<sub>2</sub> removal was roughly linear with increasing chloride over the test data range.

5. FGD performance improved moderately with finer limestone size for three grinds tested (67%, 89%, and 94% -325 mesh).

--SO<sub>2</sub> removal increased moderately at constant limestone utilization as limestone grind size was reduced. For instance, at 55,000 ppm Cl<sup>-</sup> and 95% utilization, the SO<sub>2</sub> removal increased by about 4% (absolute) from the coarsest to the finest grind tested.

--The effect of limestone grind on performance appeared to be somewhat stronger at lower chloride concentration (15,000 ppm) than at higher Cl concentration (55,000 ppm).

6. The effect of L/G ratio on FGD performance was determined under forced oxidation conditions.

--SO<sub>2</sub> removal increased significantly with increased L/G ratio. Expressed as number of transfer units (NTU), the SO<sub>2</sub> removal was directly proportional to L/G ratio over a range of 65 to 205 gal/1000 acf. The correlation of NTU with L/G was strong, despite the use of different spray header levels and nozzle flow rates to achieve the L/G variation in the pilot absorber.

--Limestone utilization was not affected significantly by varying L/G over the range in which it was measured, 130 to 160 gal/1000 acf.

7. Pilot testing under inhibited oxidation conditions confirmed that the mass transfer capacity of the HSTC pilot plant absorber is considerably less than that of the Kintigh absorbers operated at the same L/G ratio. The results suggest that an L/G ratio of roughly 140 gal/1000 acf in the pilot plant provides about the same mass transfer capacity

as the Kintigh absorbers at current operating conditions (L/G - 79 gal/1000 acf).

#### ACKNOWLEDGEMENTS

The authors would like to recognize the operating and maintenance staffs at the EPRI HSTC for their contribution to the success of the test program. In addition, the contribution made by Greg Stevens, Radian, and Michael Delallo, Gilbert/Commonwealth, was key to the successful completion of the program.

The authors wish to acknowledge the financial support of the HSTC cosponsors: EPRI, NYSEG, ESEERCO, U.S. Department of Energy, and Consol.

#### REFERENCES

1. R. E. Moser, J. M. Burke, and S. M. Gray. "Results of Wet FGD Testing at EPRI's High Sulfur Test Center." In Proceedings of the EPA/EPRI First Combined FGD and Dry SO<sub>2</sub> Control Symposium, EPRI CS-6307, RP 982-41, St. Louis, Mo., October 1988.
2. S. M. Gray and J. M. Burke. EPRI High Sulfur Test Center Report: Wet FGD Baseline Tests, Electric Power Research Institute (RP 1031-9), Palo Alto, Calif., 1990.
3. F. B. Meserole, T. W. Trofe, and D. A. Stewart. "Influence of High Dissolved Solids on Precipitation Kinetics and Solid Particle Size," Presented at the EPA/EPRI Symposium on Flue Gas Desulfurization, New Orleans, La., November 1983.

The work reported in this paper is the result of research carried out (in part) at EPRI's High Sulfur Test Center (HSTC) located near Barker, NY. We wish to acknowledge the support of the HSTC cosponsors: New York State Electric & Gas, Empire State Electric Energy Research Corp., Electric Power Development Co., Ltd., and the US Department of Energy. The cosponsors provide valuable technical review of the work in progress as well as funding test center operations.

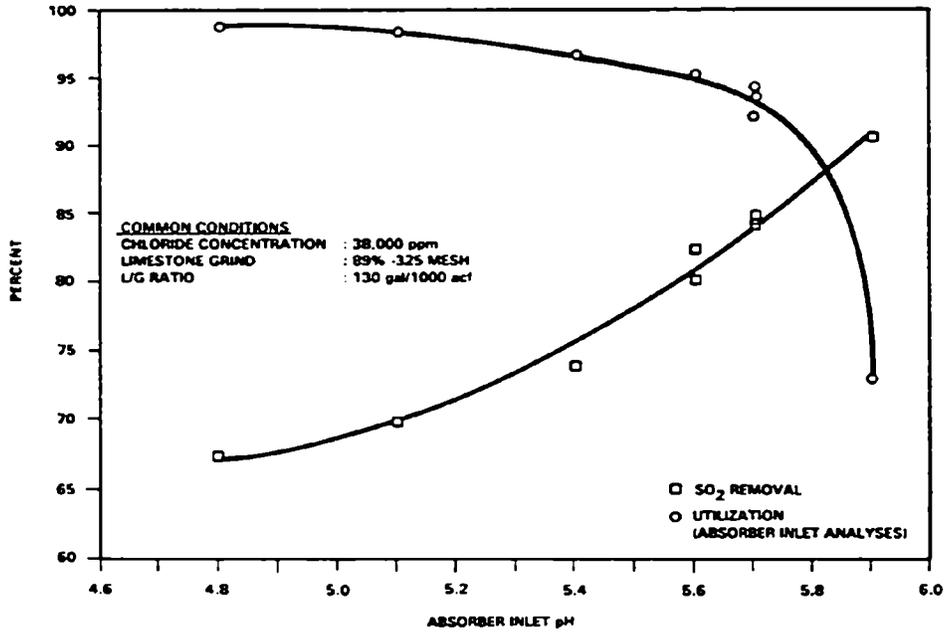


Figure 1. SO<sub>2</sub> REMOVAL AND LIMESTONE UTILIZATION AS A FUNCTION OF ABSORBER INLET PH FOR THE SINGLE-TANK MODE

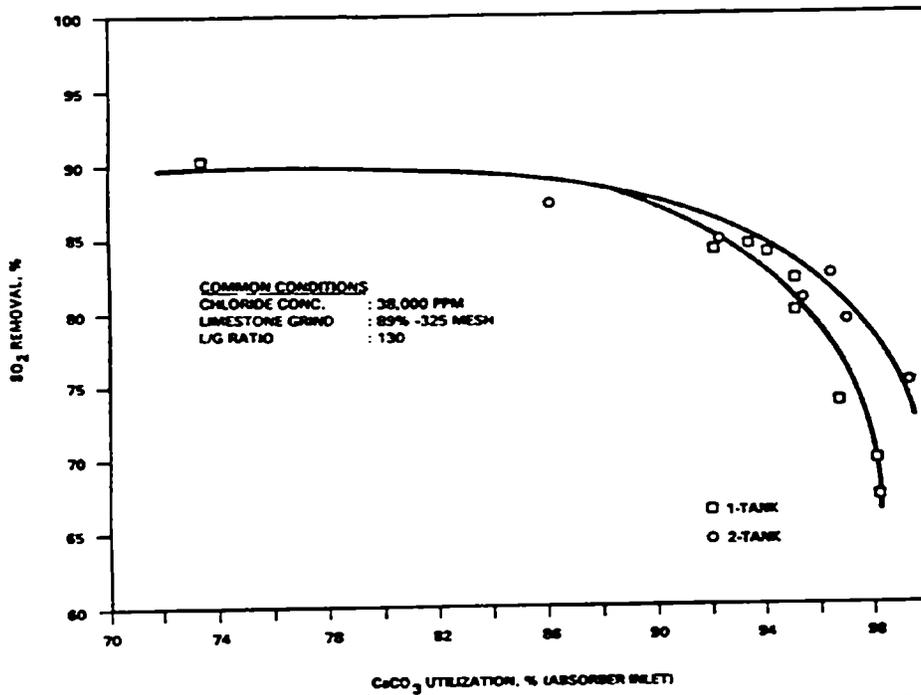


Figure 2. SCRUBBER PERFORMANCE CURVES (SO<sub>2</sub> VERSUS UTILIZATION): SINGLE TANK VERSUS DOUBLE TANK

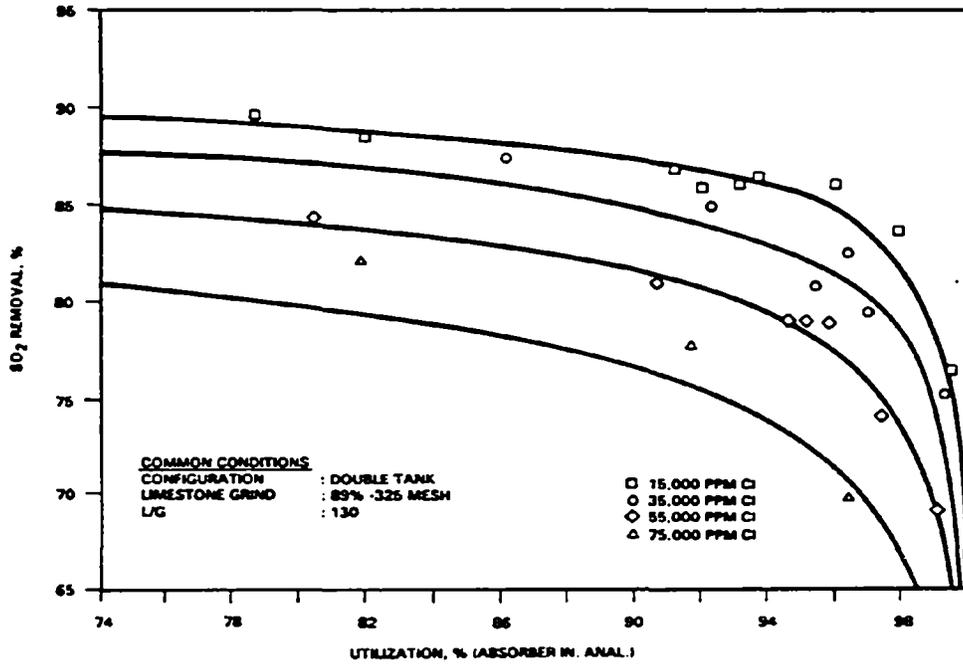


Figure 3. SCRIBER PERFORMANCE CURVES FOR FOUR CHLORIDE LEVELS

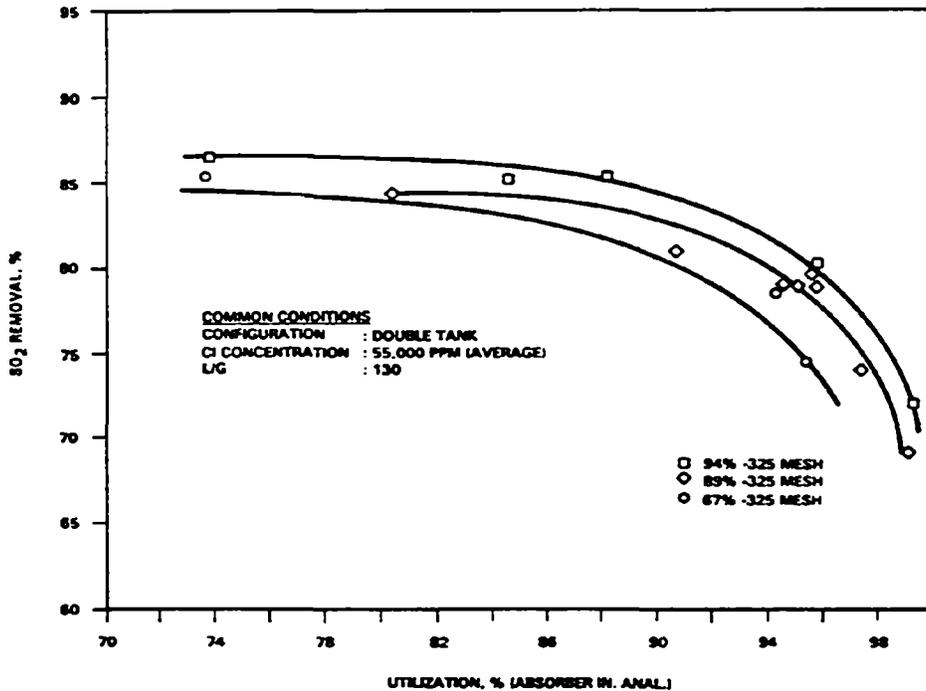


Figure 4. SCRIBER PERFORMANCE CURVES FOR THICK LIMESTONE GRINDS

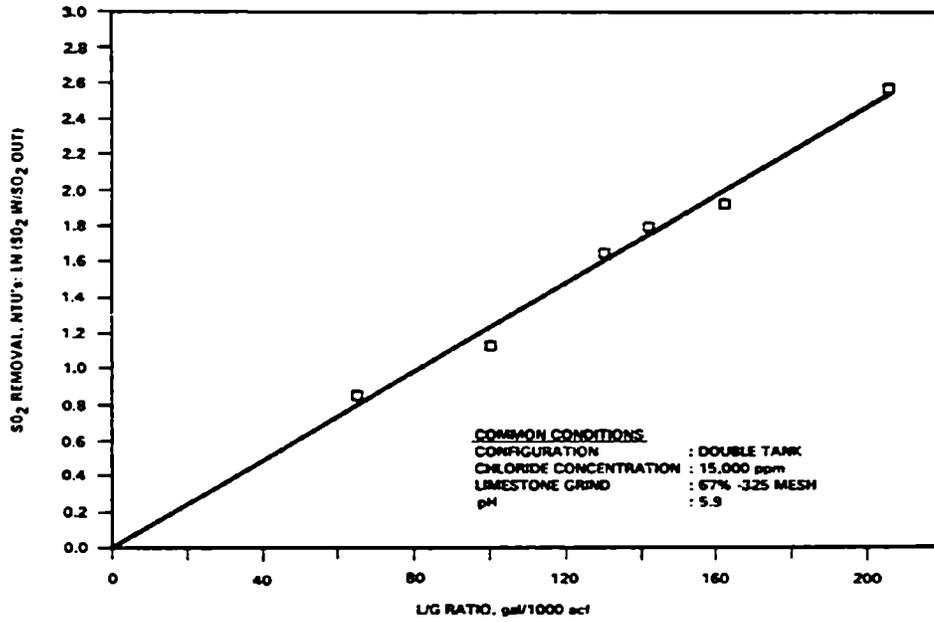


Figure 5. SO<sub>2</sub> REMOVAL IN NTU's AS A FUNCTION OF LIQUID TO GAS RATIO



Figure 6. OPTICAL MICROGRAPH (125X) OF PRODUCT GYPSUM EHS 37

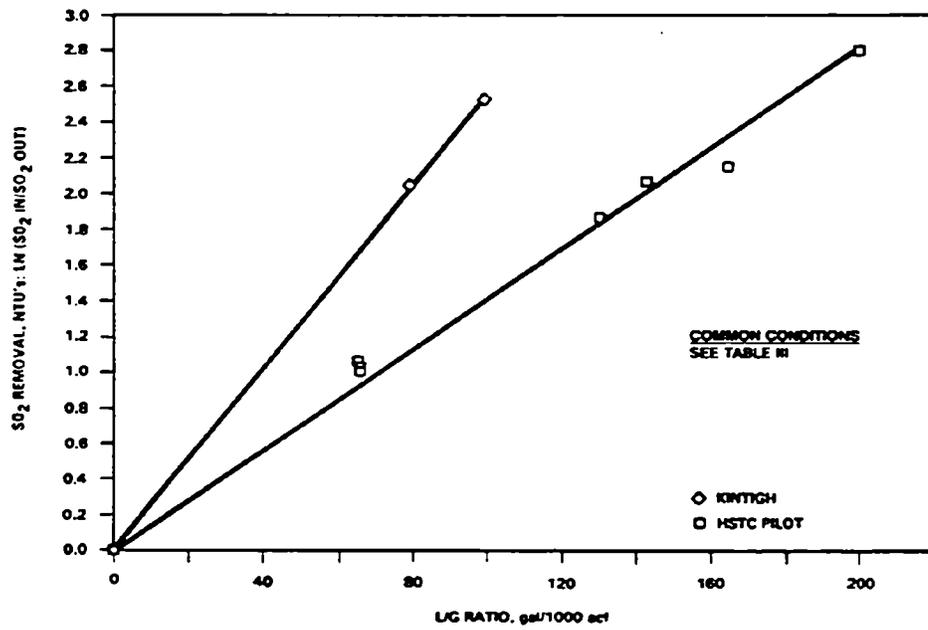


Figure 7. COMPARISON OF SO<sub>2</sub> REMOVAL VERSUS LIQUID TO GAS RATIO FOR KINTIGH STATION AND PILOT PLANT

Table I

Run <sup>2</sup>	pH <sup>3</sup>	Grind % -325 Mesh	DATA SUMMARY <sup>1</sup>				SO <sub>2</sub> Removal percent	UT <sup>4</sup> percent
			Dissolved Solids					
			Cl <sup>-</sup> ppm	Mg <sup>2+</sup> ppm	Na <sup>+</sup> ppm	Ca <sup>2+</sup> ppm		
1	4.80	88.8	43806	9062	2450	214.2	67.3	98.8
2	5.20	88.8	41015	8667	2026	211.7	69.8	98.0
3	5.40	88.8	37577	7911	1763	190.9	73.8	96.6
4	5.60	89.0	—	—	—	—	80.0	95.1
4A	5.60	89.0	36488	8044	1841	181.3	82.2	95.1
5	5.90	89.0	34140	7019	1978	170.6	90.4	73.5
6	5.70	89.0	—	7344	1983	171.2	84.0	94.1
6A	5.70	89.0	38326	7521	2168	187.6	84.2	92.0
6B	5.70	89.0	35671	7566	2096	162.8	84.6	93.4
17F	5.81	86.8	34625	7027	2137	208.8	79.4	97.0
17G	5.80	88.4	34424	7199	1895	206.0	80.8	95.4
17H	5.90	88.4	33962	7175	2018	197.1	84.9	92.3
17I	5.80	91.0	34566	6889	2188	184.3	82.5	96.4
10R	6.00	90.7	35347	7097	2019	179.9	87.4	86.1
8RR	5.42	90.7	34192	6792	1960	171.5	75.1	99.3
24A	5.59	89.7	—	3740	958	92.3	77.5	—
24B	5.60	89.4	14809	3432	803	86.6	76.4	99.5
25	5.91	89.4	14337	3171	736	84.0	83.6	97.9
26	6.11	89.4	14624	3211	751	93.0	86.0	96.0
27A	6.16	89.4	14752	3343	737	90.6	88.5	81.9
27B	6.16	89.4	14840	3514	763	90.5	89.6	78.6
28	6.06	89.7	15362	3245	898	98.6	86.4	93.7
29A	6.11	89.7	14541	3221	886	93.9	86.8	91.2
29C	6.11	89.3	15348	3038	—	—	86.0	93.1
29D	6.11	89.3	15009	3054	817	90.0	85.8	92.0
30	5.41	90.4	79412	14644	4323	424.8	69.8	96.4
31	5.60	90.4	71208	13156	4023	382.8	77.8	91.7
32	5.80	90.4	64231	12671	3730	370.2	82.2	81.8
33	5.41	89.9	53908	9332	2837	296.7	69.1	99.1
34	5.61	89.9	55007	9904	3123	279.8	74.0	97.4
35	5.81	89.4	53362	10241	3016	263.6	81.0	90.7
36	5.90	89.4	53096	10100	3014	262.4	84.3	80.4
37A	5.71	88.4	—	10449	—	256.0	78.9	95.1
37B	5.71	88.2	52217	10423	3074	277.2	78.9	95.8
37C	5.71	88.2	—	—	—	280.5	79.0	94.6
37D	5.70	88.2	54385	10899	3138	283.8	79.7	95.6
38	5.41	92.2	51585	8985	2979	246.4	72.0	99.3
39	5.70	93.7	53345	11421	3122	268.2	80.2	95.8
40	5.89	93.7	46126	9978	2724	274.4	85.3	88.2
41	5.95	93.7	48219	9962	2916	260.5	86.5	73.8
42	5.80	94.4	45951	—	—	—	85.2	84.6
43A	5.41	66.3	—	10487	—	—	73.7	—
43B	5.41	66.3	—	10173	2868	—	74.7	—
43C	5.41	66.3	56557	11033	3024	253.8	74.5	95.4
44	5.61	66.3	45878	11062	2939	276.8	78.5	94.4
45	5.80	67.0	54970	10674	2809	280.9	85.3	74.8
46	5.70	67.0	57914	11340	3046	288.7	82.0	86.9
47	5.42	66.5	11315	2733	775	75.6	75.0	99.1
48	5.72	66.5	15467	2911	817	103.7	75.6	98.1
49	5.91	66.2	14531	3047	887	109.4	80.5	94.4
50	6.00	66.2	13829	2782	752	107.4	88.6	75.7
51A	5.91	66.2	—	2540	751	—	82.4	—
51B	5.91	66.2	—	3165	—	91.5	80.8	95.1
51C	5.91	67.3	14609	3181	711	94.2	79.6	—
51D	5.91	67.3	13646	2759	746	84.4	80.9	94.4
51E	5.91	67.3	14318	3079	711	91.6	80.7	95.8

1) Slurry solids, 12%, L/G = 130, 2000 ppm inlet SO<sub>2</sub>

2) Runs 1-6B were in the single-tank configuration

3) Absorber inlet

4) Limestone Utilization

Table II  
 GYPSUM PARTICLE SIZE DISTRIBUTION<sup>1</sup>

Run <sup>2</sup>	Run Type	Liquor Cl ppm	Grind % -325 Mesh	pH <sup>3</sup>	UT <sup>4</sup> percent	Distribution		
						Mass Mean Diameter, $\mu\text{m}$	% <10 $\mu\text{m}$	% >40 $\mu\text{m}$
6	long term	35,000	89	5.7	93	24.0	12.9%	11.2%
29	long term	15,000	89	6.1	92	32.6	6.1%	25.1%
51	long term	15,000	67	5.9	95	34.2	5.0%	28.2%
17	long term	35,000	89	5.8	96	31.4	5.1%	22.5%
37	long term	55,000	89	5.7	96	34.0	7.2%	30.8%
42	short term	55,000	94	5.8	85	34.4	6.4%	32.0%
31	short term	75,000	89	5.6	92	35.6	7.9%	37.8%

- 1) L/G ratio: 130.
- 2) Run 6 was in the single-tank configuration.
- 3) Absorber inlet.
- 4) Limestone utilization.

Table III  
 COMMON OPERATING CONDITIONS FOR INHIBITED OXIDATION RUNS

<u>Operating Conditions</u>	<u>HSTC Pilot Tests</u>	<u>Kirtigh FGD</u>
Configuration	2 Tanks	2 Tanks
Dissolved Solids Concentrations, ppm		
Cl <sup>-</sup>	11300	12000-15000
Mg <sup>2+</sup>	2750	ca. 2900
Na <sup>+</sup>	805	ca. 870
Ca <sup>2+</sup>	3000	—
Limestone Grind		
% <325 mesh	67%	70%
Inlet SO <sub>2</sub> Content, ppm	1750	ca. 1500
Reaction Tank, pH	5.8	5.6-5.65
Slurry Solids, wt %	18.2%	12%
Thiosulfate (S <sub>2</sub> O <sub>3</sub> ) Concentration, ppm	498	80
Oxidation, %	17.8%	6-10%
Solids Residence Time, Hr	ca. 55	ca. 21
Limestone Utilization, %	93%	87%
CaCO <sub>3</sub> Loading, g/L	10.3	11.2

8B-66

## **Quality of FGD Gypsum**



F.W. van der Bruggen  
N.V. KEMA  
P.O. Box 9035  
6800 ET ARNHEM  
The Netherlands

**ABSTRACT**

In the Netherlands 8 large coal-fired power stations are or will be equipped with FGD installations based on the lime(stone) gypsum technology. The gypsum produced by those installations has to be marketed. To achieve this, the quality requirements specified by the gypsum industry have to be met. The gypsum quality attained by the different power stations will be assessed in relation to those standards i.e. chemical composition, crystal size and colour. The influence of the design and operation of the different FGD plants will be described. Furthermore, some remarks will be made about the trace element content, especially radioactive elements and mercury.

## INTRODUCTION

Power generation in the Netherlands is currently mainly based on natural gas and coal and it is most probable that this will remain so during the next decade. The coal-based generating capacity will even increase.

Abatement of air pollution caused by sulphur dioxide and nitrogen oxides is an important issue of the environmental policy in the Netherlands. A voluntary agreement (covenant) has been signed between the authorities and the Electricity Generating Board to limit the sulphur dioxide emissions resulting from power generation to 18,000 t/a by the year 2000. This means that by that time the full coal-fired generating capacity has to be equipped with FGD systems.

These FGD systems will be based on the lime(stone)-gypsum technology, which will mean that the output of gypsum will increase compared to the current situation.

An important factor in this respect is the quality of the gypsum. The gypsum industry has formulated requirements to ensure the quality of their products and to enable proper operation of their existing facilities.

After a short introduction to power generation in the Netherlands and its air pollution aspects, an overview will be given of the experience gained in Dutch FGD systems concerning the influence on gypsum quality of plant lay-out, operating parameters and the raw materials used. Some remarks will be made about trace elements, especially about radioactive elements and mercury.

## ELECTRICITY GENERATION IN THE NETHERLANDS

Large-scale electricity generation in the Netherlands is in the hands of four regional, publicly owned power companies. In 1990 their total installed generating capacity amounted to 15,142 MW, the net output was 57.6 TWh. At present coal and natural gas are by far the most important primary energy sources. The share of nuclear power is only modest, while the use of fuel-oil is almost negligible. This is shown in Table 1. This table also shows the division of the generating capacity, among the different fuelling possibilities.

To maintain a reliable, economic and socially acceptable power generation system, old units have to be decommissioned and replaced by new ones based on state-of-the-art technology. Furthermore, the still growing demand has to be met. In this respect, plans for the following 10 year period are published biannually in the so-called "Electricity Plan". The Electricity Generating Board "Sep", the coordinating body for large-scale electricity generation and transportation, is responsible for this plan, which has to be approved by the Minister of Economic Affairs.

According to the "Electricity Plan 1991-2000", the following new units will be built before the year 2000:

- 3 x 600 MW pulverized coal/gas firing (1993, 1994, 1997)
- 1 x 250 MW demonstration IGCC (integrated coal gasification combined cycle) (1993)
- 1 x 600 MW IGCC (1999)
- 1,700 MW natural gas fired combined cycle system (1996)
- 5 x 250 MW natural gas fired combined heat and power (1996-1999).

A number of older units will be decommissioned.

Table 2 shows a comparison between the maximum possible generating capacities for each fuel under the current situation, and as it will be in the year 2000.

The coal generating capacity will increase at the cost of fuel-oil, whereas the gas capacity remains stable. Coal and gas will remain the dominant fuels.

#### AIR POLLUTION ASPECTS OF POWER GENERATION IN THE NETHERLANDS

Abatement of air pollution caused by sulphur dioxide and nitrogen oxides is an important issue of the environmental policy in the Netherlands. It will be obvious that the electric power industry has to take its share of the often costly measures:

- since 1981 the use of natural gas sharply increased at the cost of fuel-oil. This was made possible by a change in government policy concerning the use of the domestic natural gas resources
- the existing large coal-fired power plants with a lifetime extending beyond the year 2000 were retrofitted with FGD

- the smaller units with a restricted lifetime have to fire coal with a sulphur content below 0.8%
- the new coal-fired units will be equipped with FGD.

The results achieved by those measures are shown in Figure 1. The switch from fuel-oil to natural gas had far reaching positive consequences during the early eighties. After 1985 the influence of retrofitting FGD became clear. Despite the start-up of 3 units (1,500 MW) that were converted from oil to coal firing, no increase in total annual SO<sub>2</sub> emissions occurred.

The current level of SO<sub>2</sub> emissions is 40,000 Mg/a, and has to be fully attributed to the coal-fired units. To achieve the reduction of acidification formulated in the National Environmental Plans of 1989 and 1990, a further decrease of this emission level is necessary.

One possible tool is the tightening of the emission limits stipulated in the ordinance of May 1987 in the framework of the Air Pollution Act. A draft revision has already been published with a planned date of enforcement of 1 January 1992. The current emission limit for new coal-fired power plants with a thermal capacity over 300 MW is 400 mg/m<sup>3</sup>, as well as 85% desulphurization. The value in the draft ordinance is 200 mg/m<sup>3</sup>.

However, in the meantime, a voluntary agreement, between the Federal Government, the Provinces (as licensing authorities) and the Electricity Generating Board ("Sep") has been signed in June 1990. As a result of this covenant, by the year 2000 emission levels will be achieved that are considerably lower than might be possible with revisions of the legal emission limits. On the other hand "Sep" can select the most cost-effective way of realizing the goals of this covenant.

The total yearly SO<sub>2</sub> emissions resulting from large-scale electricity generation will be limited to 18,000 Mg/a by the year 2000, with an intermediate target of 30,000 Mg/a by the year 1994. An additional 4,000 Mg/a will be allowed for possible upsets of FGD installations, in case the flue gas has to be bypassed directly to the stack. By law this bypassing is limited to 240 hours per year and may not surpass 72 hours per event.

The emission ceilings for NO<sub>x</sub> are 55,000 Mg/a by the year 1994 and 30,000 Mg/a by the year 2000, compared to the current level of 75,000 Mg/a.

#### FLUE GAS DESULPHURIZATION IN THE NETHERLANDS

Four factors will influence the SO<sub>2</sub> emissions of the electric power industry in the Netherlands during the next decade:

- the share of coal in electricity production
- the presence of flue gas desulphurization installations and their reliability
- the sulphur content of the coal
- the reliability and sulphur removal efficiency of IGCC systems.

The share of coal in electricity production is difficult to predict and will be dependent on developments in the world energy market.

In 1975 the last colliery in the Netherlands was closed. At present all coal has to be imported, mainly from the USA, Columbia, Australia and Poland. As a rule these coals are relatively low in sulphur. The mean sulphur content of the coals fired in 1989 was 0.7%.

IGCC is a new technology and to test its reliability a demonstration unit is under construction. The expectations concerning sulphur removal are very high. The expected value for the 250 MW demonstration plant is 98.5%.

Flue gas desulphurization has been introduced in the Netherlands in 1985. Table 3 gives a survey of the current situation. At present 2,686 MW or 71% of the total coal firing capacity is provided with FGD. By the year 2000 all coal-fired units, 4,486 MW in total, will be desulphurized.

All systems are based on lime(stone) scrubbing with gypsum as by-product. This technology was selected because of its high reliability, relative simplicity, acceptable costs and the applicability of the by-product.

Two basic FGD technologies are applied: the German Bischoff system, with Tebodin and Comprimo as the Dutch contractors; and the American GEESI system, with Hoogovens Technical Services (ESTS) as the contractor. The Bischoff installations currently use hydrated lime as absorbent and seawater for suspension make-up; the ESTS installations use limestone and riverwater. Major components of the FGD installations are the spray towers. The two technologies use different arrangements for the suspension spray nozzles, and different arrangements for the injection of oxidation air. It is noteworthy that Amer-8 has the largest single spray tower in the world.

A continuous purge flow from the main scrubbing loop enables the removal of gypsum. The gypsum removal process comprises two steps: concentrating and dewatering.

The concentration of gypsum in the suspension is increased either by the use of hydrocyclones or a settling tank. The concentrated suspension is dewatered.

Three methods for this final dewatering are used: batch centrifuges, continuously operating decanters and vacuum belt filters.

Finally the product has to be stored under cover. To that end, use is made of silos with loading and unloading facilities, warehouses with fixed unloading facilities and warehouses with shovels for unloading.

The marketing of FGD gypsum is in the hands of "Vliegasonie", a firm founded by the four large power companies. To date, it has been possible to sell the gypsum, mainly to the gypsum industry. With increasing coal-based generating capacity, a growth of gypsum production is expected, as is shown in Figure 2. To maintain the complete sale of gypsum it is necessary to guarantee a constant and good quality.

#### REQUIRED GYPSUM QUALITY

The major applications for FGD gypsum are: as a raw material for the production of building materials such as blocks, wallboard and plaster; and as a retarder in cement. The quality of the FGD gypsum has to meet the requirements of the industry. A major consideration of the cement industry is the handling properties. The specification of the gypsum industry has to guarantee the manufacture of products of good and constant quality as well as proper operation of the fabrication facilities, and comprises chemical composition, crystal size and shape and colour. The required gypsum quality is specified in the contracts between power plant and consumer. Table 4 summarizes several specifications used by the gypsum industry.

A and B are specifications of the gypsum industry. The VDEW/VGB specification has been drawn up in cooperation between the electric power industry and the gypsum industry in the FRG. There are only minor differences between those specifications.

The moisture content of the gypsum is codetermining for the energy use during calcining. Furthermore, a high moisture content is often accompanied by a high concentration of soluble compounds such as chloride, sodium and potassium, which is due to insufficient removal of the liquid of the scrubbing suspension.

The required  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  content is high compared to natural gypsum (normally about 80%) and is influenced by the inert content of the absorbent, the fly ash content of the flue gas and the amount of unreacted limestone. Low concentrations of those inert materials are desirable to decrease the chance of erosion in the manufacturing equipment.

The content of  $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$  is limited because of the fear of smell problems when acid reacting additives are used during manufacture of gypsum product. Furthermore, sulphite seems to have a negative influence on the hardening process. The  $\text{CaSO}_3$  content is directly coupled to the effectiveness of the oxidation in the hold tank.

The concentration of soluble halides and alkalis is closely related to the effectiveness of the dewatering. The limitations are prescribed because of a reduced fixing of the gypsum to the paper during wallboard manufacture and because of the fear of efflorescence during use of the ready product.

A much discussed subject is colour or "whiteness", which is mostly referred to BaSO<sub>4</sub> as standard. The colour is negatively influenced by the moisture content of the gypsum, so it has to be stipulated that a sample be dried at 40 °C. The colour is influenced by contaminants like iron and manganese compounds.

The presence of ammonium is of special interest for units with an SCR installation. The extremely low value is based on fear of smell problems and the possibility of the growth of micro-organisms in ready products.

The term "toxic compounds" in the VGB/VDEW specification has not been further defined, but can refer to heavy metals or certain organic compounds like "dioxines" and PAH's.

#### INFLUENCE OF OPERATING PARAMETERS OF THE FGD PLANT ON GYPSUM QUALITY

The crystal shape and especially crystal size are very important factors during the dewatering stage. The influence which the operating parameters of the scrubber loop have on the particle size and the shape of the gypsum crystals is still rather erratic. Parameters involved are concentration of solids and dissolved compounds in the scrubber liquid and the mechanical damage caused by the circulating pumps.

There is a general tendency that a reduction of the solids content in the scrubber liquid results in an increase in particle size. The influence of soluble compounds is still not clear. High sodium chloride concentrations in the seawater systems initially seemed to promote better crystal growth, but doubts remain. Influence of chloride concentrations between 4 and 30 g/l could not be established. The use of low RPM pumps largely prevents mechanical damage to the crystals.

The forced oxidation mode of operation is very satisfactory: complete oxidation is achieved without problems. In some installations it is even questionable whether injection of oxidation air is necessary at all. In those installations the oxygen concentration in the flue gas (4-4.5%) seems to be sufficient for proper oxidation.

The proper operation of the hydrocyclones is essential when vacuum belt filters are used for dewatering. Bad separation of brown mud and other fine material results in bad filtration and washing properties of the cake, which in turn can result in gypsum with a high moisture and chloride content. Regular control of the apex of the hydrocyclones is necessary. Dewatering with batch centrifuges is less sensitive to hydrocyclone separation characteristics. In this case the solids concentration in the underflow of the hydrocyclones has to be reduced with scrubber suspension to allow proper filling of the centrifuges.

One FGD plant is equipped with an oversized settling tank for thickening of the gypsum suspension. The overflow of this thickener contains less than 50 mg/l solids which means that the underflow contains all the gypsum and most of the contaminants. The underflow is fed to batch centrifuges.

For a proper functioning of the vacuum belt filters it is essential that the consistency of the feed allows rapid and even distribution across the surface of the filter cloth. Solids concentrations between 600 and 1,000 g/l are used. The cake thickness is kept between 30 and 40 mm by adjusting the belt speed. Washing of the filter cake is done with tap-water, either cold or warm. Moisture contents of 8% or better can be achieved as is shown in Table 5.

A feed with gypsum crystals of a small mean diameter is more difficult to wash and dewater. This has to be corrected in the scrubbing loop, but as already has been mentioned, the influence of operating parameters on crystal size is still rather erratic. Furthermore, the dewatering characteristics are also negatively influenced by increased amounts of brown mud and other fines. This can be improved by adjusting the setting of the hydrocyclones.

Problems have been encountered with tearing of the cloth, which was often caused by the knife fitted at the end of the belt for removal of the filter cake.

The batch centrifuges guarantee with almost 100% certainty a gypsum moisture content below 8%. Values of 6% have been reached (see Table 5). The influence of the particle size of the crystals on dewatering properties is less pronounced.

For a proper operation of the batch centrifuges attention has to be paid to the washing cycle of the centrifuge itself. This will prevent imbalance. Furthermore, a concrete foundation is preferable to a steel structure.

Because of their good performance in several German FGD installations, the relatively low price, low energy consumption and small size, one of the power companies decided to select continuous centrifuges for gypsum dewatering. The operation of these decanters turned out to be extremely sensitive to the consistency of the gypsum slurry feed. A small crystal size or a high content of fine material resulted in bad dewatering. Furthermore, the apparatus were very prone to abrasion damage, caused by contaminants of the gypsum such as fly ash and the insoluble constituents of the limestone. A large-scale effort has been made to improve the performance by testing filter cages of different designs and by increasing the wear resistance of the feed worm. The lifetime of the filter cages remained about 400 hours, whereas the lifetime of the feed worm could be extended to 3,000 hours by a plasma sprayed layer of  $\text{Cr}_2\text{O}_3$ . Changes in operation, such as using hot water for cake washing, decreasing the number of revolutions, and using acid water to flush the filter cage did not result in sufficient improvement. Because the insufficient reliability of those decanters could give rise to a decreased availability of the complete FGD installation, the power company decided to install two batch centrifuges and use the decanters as a stand-by option.

A critical item in the gypsum specification is "colour" or "whiteness". Most gypsum is faintly coloured: yellow, brown or grey. This colour can be attributed to components such as iron, manganese, fly ash and unburnt carbon, that are among the constituents of the brown mud. One utility company decreased the amount of these contaminants by changing the absorbent from limestone to hydrated lime and indeed gained some "whiteness".

Another possibility is the preferential removal of brown mud from the scrubber system. This has been done by treating part of the topflow of the gypsum hydrocyclones with specially designed purge hydrocyclones. The topflow from these purge hydrocyclones containing the brown mud is discharged to the waste water treatment plant, and the underflow is returned to the scrubber system as "seed" crystals. Marked improvements have been realized.

Brown mud removal from the FGD system with the gypsum thickener, by a twofold increase of the upward flow, did not result in an improvement of the "whiteness".

Finally the gypsum has to be stored under cover prior to transportation to the industrial consumers.

A silo has been installed in a situation where limited space was available. This Eurosilos is filled and emptied from above. Separation between good and bad quality gypsum is not possible which can lead to the deterioration of a larger amount of good quality gypsum.

An advantage of a warehouse is that a part of the floor area can be reserved for poor quality gypsum, so that mixing with good product can be avoided. A prerequisite is that a close eye is kept on the gypsum entering the warehouse. The moisture content is especially important in this respect. A method for the continuous measurement of the moisture content of gypsum on a conveyor belt is under development.

During transportation and the initial phase of the storage the gypsum is still warm (40-50 °C) and some evaporation of moisture takes place. This effect has been quantified in the Eurosilos system, where the moisture content dropped about 1%.

#### TRACE ELEMENTS

The concentration of the compounds mentioned in the gypsum specification is of the order of at least 100 µg/g, but gypsum also contains trace elements with a concentration of about 1 µg/g.

Those trace elements, such as heavy metals, are present in the flue gas (volatile as well as a constituent of the fly ash), in the lime or limestone and in the make-up water. Some of them leave the FGD plant with the gypsum. Table 6 gives a summary of

the results of the analyses of gypsum from two power plants in the Netherlands (A and B).

Table 6 also shows the results of the analyses of a limestone used in power station A, and a sample of natural gypsum from Spain, as well as the outcome of a large-scale research effort by the German power and gypsum industry [2] which comprised 15 samples from different sources. All values in the table are within the band width of the German study. The final conclusion from this study was that FGD and natural gypsum can safely be used as a building material.

Special attention has been given to radioactivity because of the unfavourable reputation of phosphogypsum in this respect. Table 7 shows a comparison of FGD gypsum with phosphogypsum, natural gypsum and several commonly used building materials in the Netherlands [1]. The specific activity of FGD gypsum is comparable to natural gypsum and is significantly lower than those of commonly used building materials. From this point of view no objections to the use of FGD gypsum exist.

The Cs-137 contamination caused by the Chernobyl accident. The high value was measured in samples taken in 1987, the low value was measured in 1989. In samples that were taken before the accident no significant amounts of Cs-137 could be detected.

Finally, attention has been given to one of the volatile trace elements, mercury. In laboratory experiments it was found that during calcining at 140 °C for 1 hour, between 5 and 30% of the mercury present in FGD gypsum samples evaporated. The mean value was 10%. This mercury evaporation can also occur in industrial calciners and may cause emission of mercury to the atmosphere. The total emission and the emission concentration will be dependent on the method of calcining, the calcining temperature and the mercury content of the gypsum. The mercury content is dependent on coal quality, efficiency of mercury removal by the scrubber and operation of the FGD plant. In the Netherlands no legal limit for mercury emissions from this type of installation exists. In Germany the TI-Air limits the emission concentration to 200  $\mu\text{g}/\text{m}^3$ .

At the Gelderland-13 power station a tentative programme has been carried out to study the behaviour of mercury in an FGD installation [4] with the intention of finding ways of reducing the mercury content of FGD gypsum by changing plant operation. This FGD plant is particularly suitable for this purpose because it has been built in two stages with two different designs for the gypsum concentration [3]. Stage 1 has a settling tank, stage 2 has hydrocyclones. The principal findings of this programme were:

- mercury removal from the flue gas in the scrubber was between 70 and 80%
- the mercury content of the coarse, rapidly settling fraction of the solid material in the scrubbing suspension was 0.3-0.7  $\mu\text{g}/\text{g}$

- the mercury content of the brown mud was 20-40  $\mu\text{g/g}$
- the amount of mercury in solution was 5-10  $\mu\text{g/l}$ .

The most obvious way of reducing the mercury content of gypsum is a sharp separation between brown mud and gypsum followed by proper washing of the filter cake. Furthermore, it is necessary to reduce the mercury content of the brown mud. This can be done by reducing the residence time of the brown mud in the installation, by taking specific measures to remove it.

It has already been mentioned that the settling tank of stage 1 is oversized, and no separation between brown mud and gypsum occurs (Figure 3). Separation occurs in the centrifuges. The centrate contains 68 g/l solids with a mercury content of about 20  $\mu\text{g/g}$ . Because the centrate is returned to the thickener, a build-up of brown mud in the loop thickener centrifuges takes place. The only outlet for the mercury-containing brown mud is the gypsum. By treating part of the centrate with purge hydrocyclones a general reduction of the brown mud, and thus mercury level, is possible in this loop and a second way out can be created in this way.

In stage 2 of the FGD plant, efficient separation between brown mud and gypsum is accomplished in the hydrocyclones (Figure 4). Part of this effect is nullified because the underflow has to be diluted with scrubbing suspension to enable proper filling of the centrifuges. Build-up of mercury-containing brown mud takes place in the whole system. One way out is again the gypsum, the second way out has been created by the installing of the purge cyclones for treatment of part of the topflow from the hydrocyclones. Indeed the presence of these purge hydrocyclones results in a lower mercury content in the gypsum produced by stage 2: 0.60  $\mu\text{g/g}$  versus 0.97  $\mu\text{g/g}$  for stage 1. Minor adaptations in the system directed at the removal of brown mud can indeed lead to a decrease in the mercury content of the gypsum. It has to be taken into account that an increased discharge of brown mud can create overloading problems in the waste water treatment plant.

#### FINAL REMARKS

Flue gas desulphurization is a common practice in the electric power industry in the Netherlands. Properly designed installations and great dedication of the power plant crews makes the availability of the FGD systems close to 100%.

In addition to  $\text{SO}_2$  removal, attention has to be paid to maintaining the gypsum quality in line with the requirements of the gypsum industry. In particular, the operation of the gypsum concentrating and dewatering steps has to be closely watched.

Batch centrifuges turned out to be least sensitive to variations in gypsum properties. Proper operation of vacuum belt filters is more sensitive to these properties, and the plant crew's close attention is required.

Colour improvements could be realized by changing from limestone to hydrated lime and by optimizing the operation of purge cyclones.

Currently it can be said that the vast majority of the gypsum produced is in line with the specifications. Trace elements such as heavy metals and radioactive elements do not interfere with the applicability.

Summing up, it can be said that the environmental measures taken in the coal-fired power stations in the Netherlands resulted in a drastic decrease in SO<sub>2</sub> emissions without creating secondary environmental problems: the gypsum produced finds its way into the building industry.

#### ACKNOWLEDGEMENT

The substance of this paper is the reflection of several years of experience in FGD operation and a number of special development efforts. We thank Mr. N.A. Doets, managing director of Amer power station, Mr. J.A. Mout, head of the chemistry department of Borssele power station, Mr. W. van der Berge, head of the chemistry department of Maasvlakte power station, Mr. H.P. Klink, head of the chemistry department of Gelderland power station, and Mr. H.W. Hoeksema, environmental engineer of the electricity production company for East and North Netherlands, for discussions about their efforts to maintain a high FGD gypsum quality standard.

#### REFERENCES

1. G. van der Lugt. "Radiation Aspects of the Firing of Coal and the Use of Fly Ash." (In Dutch.) Energiespectrum, December, 1984, pp. 270-283.
2. J. Beckert. "Vergleich von Naturgips und REA-Gips." (Comparison of Natural Gypsum and FGD Gypsum.) (In German.) VGB Conference Kraftwerk und Umwelt, Essen, April 1989.
3. F.W. van der Brugghen, J.M. Koppius-Odink, B.G. Kemper and H.P. Klink. "Operational Experience with the FGD Plant of Gelderland-13 Power Station in Nijmegen (the Netherlands)." In Desulphurisation 2, Technologies and Strategies for Reducing Sulphur Emissions, Institution of Chemical Engineers, Symposium Series No. 123, Sheffield, March 20-21, 1991, pp. 67-82.
4. H.W. Hoeksema and F.W. van der Brugghen. "Minimizing Trace Element Concentrations in FGD Gypsum." Second International Conference on FGD and Chemical Gypsum, Toronto, May 12-15, 1991.

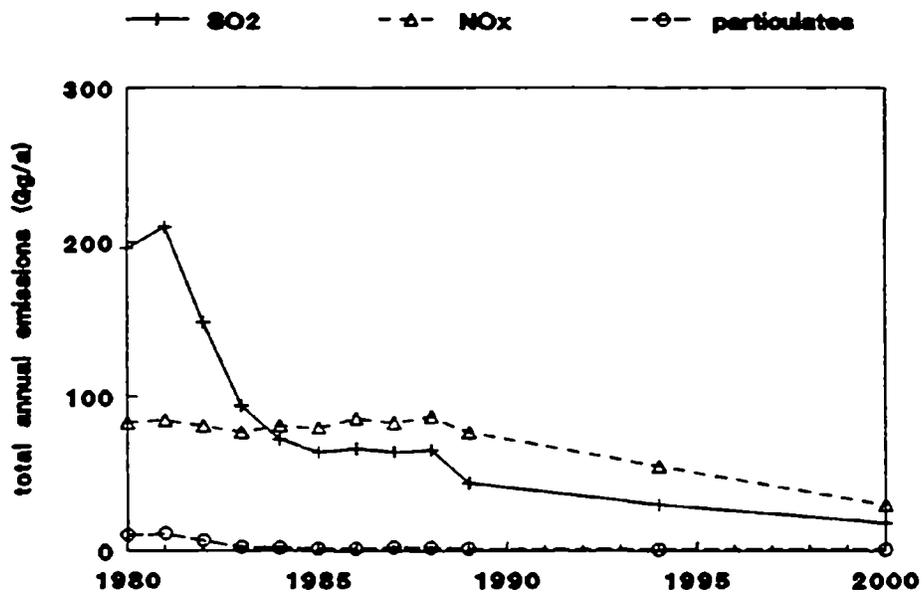


Figure 1. Total annual emissions by power stations in the Netherlands

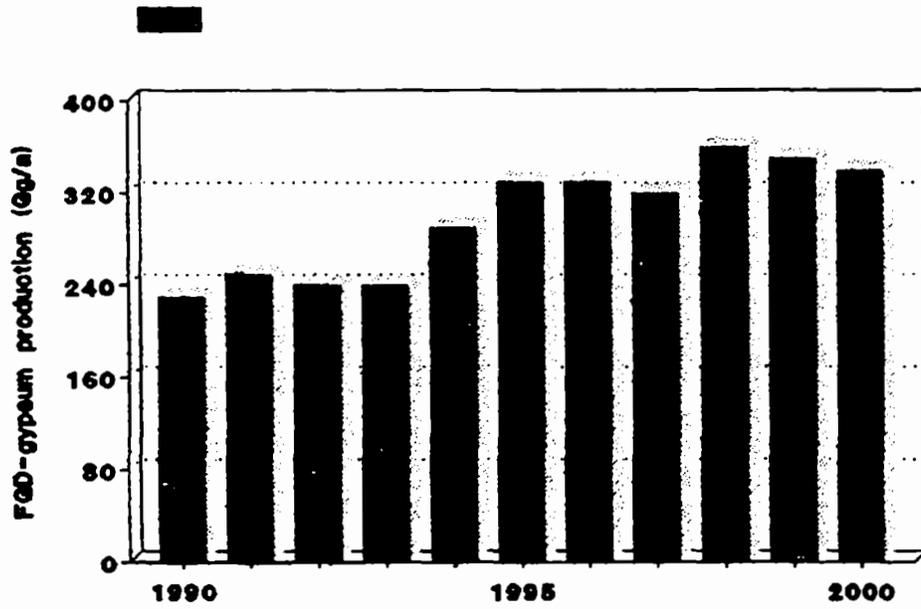
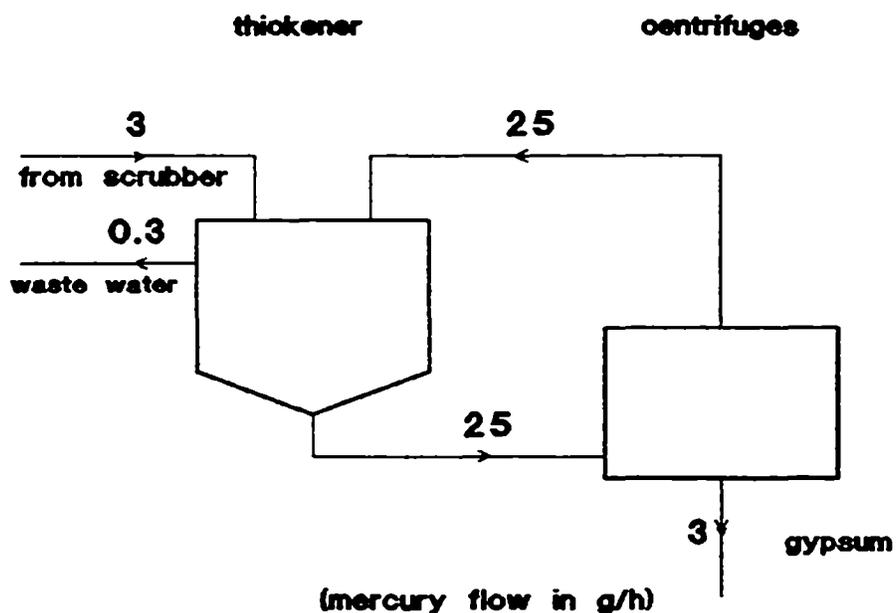
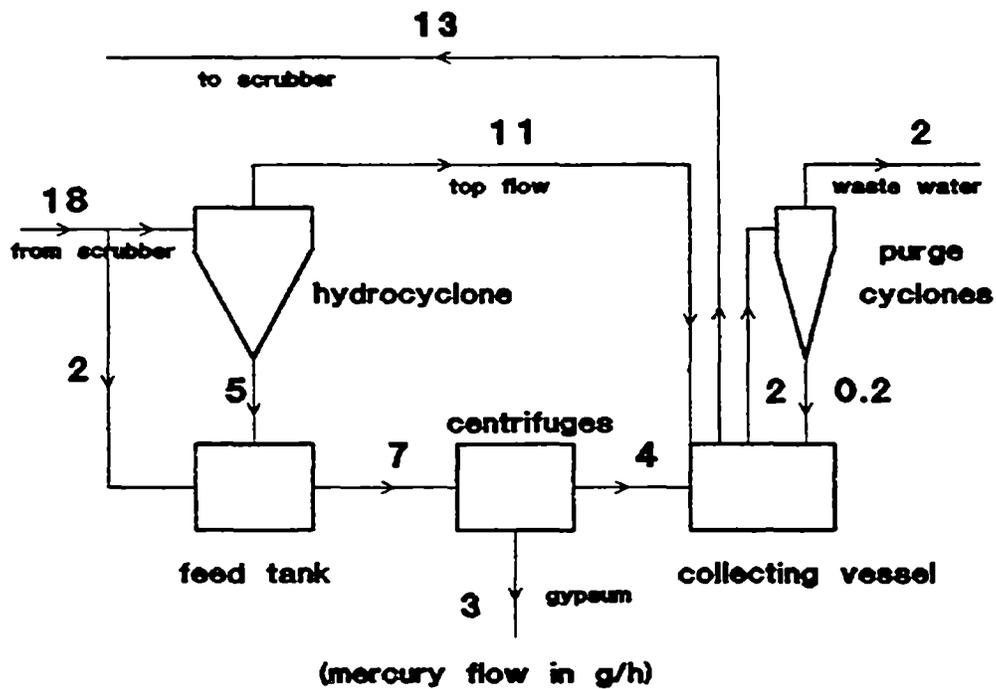


Figure 2. Expected FGD gypsum production



	<u>Solid Content</u> <u>Suspension</u>	<u>Mercury Content</u> <u>Solids</u>
from scrubber	72 g/l	1.4 µg/g
to waste water	0.2 g/l	50 µg/g
from thickener	270 g/l	7.5 µg/g
from centrifuge	68 g/l	20 µg/g
gypsum	-	0.98 µg/g

Figure 3. Mercury flow in thickener-centrifuges loop of stage 1 FGD Gelderland-13



	Solid Content of Suspension	Mercury Content of Solids
from scrubber	110 g/l	2.6 µg/g
centrifuge feed	490 g/l	1.5 µg/g
underflow	1,500 g/l	0.7 µg/g
topflow	7 g/l	39 µg/g
gypsum	-	0.6 µg/g
to purge cyclone	22 g/l	7 µg/g
to waste water	9 g/l	27 µg/g

Figure 4. Mercury flow in hydrocyclone-centrifuge area of stage 2 FGD Gelderland-13



Table 1

FINAL CONSUMPTION AND GENERATING CAPACITY  
ACCORDING TO FUELS IN 1990

Final Consumption

coal	233,640 TJ	45 %
fuel-oil	1,639 TJ	0.3%
gas	247,600 TJ	47.6%
nuclear	36,876 TJ	7.1%

Generating capacity according to fuelling possibilities

fuel-oil	37 MW
gas	3,075 MW
oil/gas	7,729 MW
oil/coal	1,705 MW
gas/coal	2,062 MW
nuclear	508 MW

Table 2

MAXIMUM POSSIBLE GENERATING CAPACITY  
FOR EACH FUEL IN THE YEARS  
1990 AND 2000

	<u>1990</u>	<u>2000</u>
coal	3,767 MW	5,336 MW
fuel-oil	9,471 MW	4,628 MW
gas	12,866 MW	12,872 MW
nuclear	508 MW	508 MW

Table 3

CURRENT STATUS OF VGD INSTALLATIONS  
IN THE NETHERLANDS

<u>Company</u>	<u>Power Station</u>	<u>Location</u>	<u>Capacity MW</u>	<u>Technology</u>	<u>Status</u>	<u>Start-up</u>
EPON	Gelderland-13-I	Nijmegen	300	Chemico/Mitsui	operational	1985
EPON	Gelderland-13-II	Nijmegen	302	GEESI	operational	1988
EPZ	Amer-8	Geertruidenberg	645	GEESI	operational	1988
EPZ	Borssele-12	Borssele	402	Bischoff	operational	1988
EPZ	Amer-9	Geertruidenberg	600	GEESI	construction	1993
EZH	Maarvlakte-1	Rotterdam	518	Bischoff	operational	1988
EZH	Maarvlakte-2	Rotterdam	518	Bischoff	operational	1987
EZH	Maarvlakte-3	Rotterdam	600	to be selected	licencing	1997
UNA	Hemweg-8	Amsterdam	600	GEESI	construction	1994

**Table 4**  
**FGD GYPSUM**  
**SPECIFICATIONS OF THE GYPSUM INDUSTRY**

		<u>A</u>	<u>B</u>	<u>VDEW/VGB</u>
moisture	weight %	<10	8-10	<10
CaSO <sub>4</sub> .2H <sub>2</sub> O	weight %	<95	<95	<95
sulphite (as SO <sub>2</sub> )	weight %	< 0.25	< 0.25	< 0.25
Cl	weight %	< 0.02	< 0.01	< 0.01
CaCO <sub>3</sub>	weight %	< 2.5	-	-
MgO (soluble)	weight %	< 0.05	< 0.05	< 0.1
Na <sub>2</sub> O	weight %	< 0.05	< 0.04	< 0.06
K <sub>2</sub> O	weight %	< 0.06	< 0.1	-
Fe <sub>2</sub> O <sub>3</sub>	weight %	< 0.5	1.5	-
SiO <sub>2</sub>	weight %	< 2.5	1.0	-
pH		5-8	5.5-7.5	5-9
colour* "whiteness"		>75**	>70	>80
NH <sub>4</sub>		-	-	0
toxic components		-	-	none

\* reference BaSO<sub>4</sub> is 100%

\*\* after calcining

**Table 5**  
**COMPOSITION OF GYPSUM PRODUCED BY**  
**POWER STATIONS IN THE NETHERLANDS**

		<u>Centrifuge/Limestone</u>	<u>Belt filter/Lime</u>
moisture	weight %	6.1 - 7.0	7.8
CaSO <sub>4</sub> .2H <sub>2</sub> O	weight %	96 - 98	97
pH		7.5 - 7.7	7.7
SO <sub>2</sub>	weight %	0.01 - 0.02	-
CaCO <sub>3</sub>	weight %	1.2 - 2.5	0.03
Al <sub>2</sub> O <sub>3</sub>	weight %	0.5 - 0.7	0.07
Fe <sub>2</sub> O <sub>3</sub>	weight %	0.12 - 0.17	0.02
SiO <sub>2</sub>	weight %	0.3 - 0.5	0.3
MgO	weight %	0.05 - 0.07	0.06
K <sub>2</sub> O	weight %	0.05	0.01
Na <sub>2</sub> O	weight %	0.005	0.04
Cl	weight %	0.002- 0.005	0.002
colour*		46 - 50	86

\* BaSO<sub>4</sub> standard as a reference

**Table 6**  
**TRACE ELEMENT CONCENTRATIONS**  
**IN FGD GYPSUM**  
**( $\mu$ g)**

	<u>A</u>	<u>B</u>	<u>Natural Gypsum</u>	<u>Limestone</u>	<u>Beckert</u>
As	1.0-1.4	< 3	1.7	2	0.21- 2.70
Cd	0.05	0.05	0.33	0.08	0.03- 0.29
Cu	0.7	7	7	1.2	1.10- 8.5
Cr	4 -8	<10	6.8	1.4	1.0 - 9.7
Hg	1.2	1.3	0.02	<0.2	0.03- 1.32
Ni	1.0-2.5	5	3	0.7	0.55-12.9
Pb	5 -7	11	3	6.5	3 -22
Zn	<7.5	<10	4.0	<5	2 -53

**Table 7**  
**RADIOACTIVITY OF GYPSUM AND**  
**BUILDING MATERIALS**  
**(Bq/g)**

	<u>Ra-226</u>	<u>Th-232</u>	<u>K-40</u>	<u>Cs-137</u>
FGD gypsum	1- 5	0.8-3	8-22	0.2-1.3
Natural gypsum	5	6	50	-
Phosphogypsum	20-110	-	5	-
Sand	8	8	250	-
Gravel	9	9	150	-
Portland cement	47	19	240	-
Sand/lime brick	8	9	270	-
Brick	45	40	600	-



**Chemical Analysis and Flowability of  
ByProduct Gypsums**



L. A. Kilpeck  
Senior Design Engineer  
Centerior Energy  
P. O. Box 94661  
Cleveland, Ohio 44101-4661

B. E. Dose, Jr.  
Associate Chemical Engineer  
B. E. Basel,  
Project Engineer  
Burns & McDonnell Engineering Co.  
4800 E. 63rd Street  
Kansas City, Missouri 64130-4696

ABSTRACT

Several forced-oxidized FGD processes produce synthetic gypsum in the U.S. Knowledge of the chemical and physical characteristics of synthetic gypsum is requisite to assess handling and disposal alternatives. Results of chemical, physical properties, and flowability testing of several representative FGD system synthetic gypsums are presented.

Physical properties of synthetic and natural gypsum samples are discussed, including freezing point, abrasion resistance of several liner materials, and particle size. Physical property data also cover a range of moisture levels and ambient and near-freezing temperature conditions. Gypsum flowability is assessed based on direct shear tests, coefficient of friction, and critical moisture content. Derived flowability results include hopper and chute slopes, arching dimensions, outlet sizes, stable rathole diameter, and rail car hopper configurations. Chemical analyses of solids and water leachate are presented for the synthetic and natural gypsum samples for selected parameters.

Test program results are compared to published literature values and are summarized in connection with material handling requirements.

## INTRODUCTION

Many utilities are considering the addition of wet limestone forced oxidized (LSFO) flue gas desulfurization (FGD) systems which will produce gypsum byproduct in the form of vacuum filter cake. This paper is based on a study which was conducted to accomplish the following primary objectives:

1. Obtain comparative chemical analyses of several natural and byproduct gypsum samples.
2. Assess flowability and related physical characteristics of byproduct gypsum for use in design of material handling equipment.

## METHODOLOGY

The study consisted of a literature search to compile information on properties of gypsum and testing of FGD byproduct and natural gypsum samples from several sources. Commercial laboratories performed chemical analysis, flowability and physical properties testing, particle size analysis, and wear testing.

Chemical analyses were performed on three natural gypsum samples and on three byproduct gypsum filter cake samples obtained from operating LSFO FGD systems as follows:

<u>Natural</u>	<u>Byproduct</u>
Iowa	Plant A
Nova Scotia	Plant B
Oklahoma	Plant C

Byproduct and natural gypsum samples were prepared and analyzed in accordance with standard analytical methods summarized in Table 1.

## CHEMICAL ANALYSIS OF SOLIDS

Chemical analyses of "as received" natural and byproduct gypsum samples are presented in Table 2.

The trace elements found in the natural and byproduct gypsum samples are compared to

literature values in Table 4. The levels of trace elements found in the gypsum samples were compared to literature values and found to be similar to those previously reported.

#### CHEMICAL ANALYSIS OF LEACHATE

Chemical analyses of the aqueous leachate from natural and byproduct gypsum samples are summarized in Table 3. Analysis results were compared to maximum contaminant levels (MCL) specified by the EPA (40CFR141 and 40CFR143) which are summarized in Table 5. Ohio standards (Table 6) require constituents in the leachates to be less than 15 times the drinking water standards. Overall, the measured concentrations in the leachates shown in Table 3 are well below the required Ohio levels.

Literature values for aqueous leachate and runoff from byproduct gypsum are compared in Table 7 to averages for the natural and byproduct gypsum samples analyzed. The values found in the gypsum samples analyzed are very similar to literature values reported in Table 7 for gypsum disposal site underdrain leachate and pond runoff. These literature data were pertinent because gypsum is similar to the samples tested.

Total water soluble salts, excluding calcium sulfate, in the leachates tested were estimated by subtracting calcium plus sulfate from TDS. Using this technique, water soluble salts for the natural gypsum samples ranged 68 to 217 mg/l compared to the byproduct gypsum samples which ranged 160 to 322 mg/l. Gypsum is soluble in water with reported solubility ranging from 2440 to 2640 mg/l at 10°C to 30°C, respectively (1).

Tables 3 and 7 indicate that natural and byproduct gypsum samples contained water soluble salts and constituents other than calcium sulfate. Reported values for water soluble salts in several natural and synthetic gypsums are listed as ranges in Table 8 (2). In natural gypsum the salts are found to be deposited evenly over the surface of crystals, resulting from the slow, near equilibrium deposition (2). Contrastingly, synthetic gypsum, which is precipitated much more rapidly from solution than the natural gypsum, could have co-precipitated salts distributed throughout the particle as well as on the surface (2).

Constituent values for leachate were used to calculate corresponding concentrations present in gypsum solids. Water soluble salts present in the natural gypsum samples analyzed ranged 1360 to 4340 mg/kg (or ppm) compared to byproduct gypsum samples which ranged 3200 to 6440 ppm. The byproduct gypsum values are within the range of literature values displayed in Table 8. Similar projections for chloride show a range of 40 to 60 ppm for the natural gypsum samples analyzed and a range of 180 to 520 ppm

for the byproduct gypsum samples tested. These ranges may be compared to the commercial-grade gypsum specifications for chloride in Table 9 which range from 100 to 400 ppm.

#### PARTICLE SIZE ANALYSIS

Particle size analysis for the byproduct gypsum samples showed the following arithmetic mean size values on a volume or mass basis compared to mean size on a frequency or counts basis.

#### Byproduct Gypsum Mean Particle Sizes

	Mass Basis <u>Size, <math>\mu\text{m}</math></u>	Frequency Basis <u>Size, <math>\mu\text{m}</math></u>
Plant A	41.28	9.804
Plant B	29.25	9.411
Plant C	43.65	26.97

To examine any potential differences in the byproduct gypsum particle morphology (structure) not revealed by the particle size analysis, optical color photomicrographs under polarized light at 100X magnification were obtained. The photomicrographs for Plant A, Plant B, and Plant C are presented in Figures 1, 2, and 3, respectively.

The photomicrographs for Plant A and Plant C show many particles of similar size while Plant B shows more particles of a smaller size range. The photomicrographs disclose significant differences in particle morphology. Plant C particles appear characteristic of gypsum and are blocky to rounded in shape and relatively uniform in size, approximately 25 to 50  $\mu\text{m}$  (3, 4, 5). The Plant A particles appear to include large gypsum needles which range in size from 25  $\mu\text{m}$  pieces to needles near 250  $\mu\text{m}$  in length (6). Numerous gypsum particles in the 25 to 50  $\mu\text{m}$  range are rounded in form. Calcium sulfite particles in the form of small platelets also appear to be present (3, 5). The presence of fly ash particles in the form of spheres is noted in all three samples, more so for Plant A and Plant B. Small calcium sulfite platelets appear to be present in the Plant B sample. The most outstanding characteristic of the Plant B sample is the visual indication of a large fraction of gypsum needles which appear to range in length from about 25  $\mu\text{m}$  to 100  $\mu\text{m}$  with proportionately varying narrow widths (6).

The chemical composition of the gypsum solids as shown in Table 2 indicates obvious differences in levels of calcium sulfate, calcium sulfite, calcium carbonate or unreacted limestone, and fly ash and inerts. Significant differences were also observed in percent oxidation levels for each byproduct; percent oxidation was 85.0, 78.8, and 99.7 percent, respectively, for Plant A, Plant B, and Plant C. The

correlation of larger mass mean particle size with increasing oxidation level is depicted graphically in Figure 4.

Many design and process related factors that can influence the shape, size, and size distribution of byproduct gypsum solids and similar materials, have been described by others (3, 4, 5, 6, 7, 8). In naturally oxidized waste materials containing a large fraction of sulfite, the presence of sulfate has not been found to affect the physical properties of the wastes (5). However, for gypsum waste, in which the major component is sulfate, laboratory tests have shown that small amounts of sulfite have an effect on the physical properties (3, 5, 7). For example, samples of completely oxidized material exhibited substantially higher unconfined compressive strength than a material containing 5 percent sulfite (5). The unconfined compressive strength of the latter material was approximately equal to that of FGD waste that is predominantly calcium sulfite (5).

Thus, oxidation level and particle size and morphology can have measurable influence on various material physical properties.

#### BYPRODUCT PHYSICAL PROPERTIES TESTING

A number of material and physical properties were determined on byproduct samples from Plant A and Plant B as summarized below.

#### Byproduct Gypsum Physical Properties

		<u>Plant A</u>	<u>Plant B</u>
Moisture			
Free (w/o hydrated water)	Percent	17.2	20.3
Total (w/hydrated water)	Percent	29.3	28.7
Angle of Repose	Degrees	35-39	33-36
Specific Gravity	--	2.68	3.08
Modified Proctor			
Optimum Moisture	Percent	23.2	28.7
Max. Dry Weight	Lb/Ft <sup>3</sup>	91.4	88.4
Freezing Point	° C	-2	-2
Permeability	Cm/Sec	4.6E-06	1.2E-05

Values for specific gravity were significantly higher than the value for pure gypsum at 2.31 (9). A contributing cause for the discrepancy may be the use of a drying temperature of 110° C which would cause loss of waters of hydration.

#### Abrasion Testing

Abrasion tests were conducted on the "as received" Plant A sample on liners of Type

304 stainless steel with a 2B finish (SS304-2B), aged carbon steel (A-36), and high density polyethylene (HDPE)(Tivar-88) with a new, smooth surface.

The results of the abrasion tests revealed that a thin coating of byproduct tended to form on the surfaces of the SS304-2B and A-36 carbon steel liners during the course of the test, and, consequently, no liner loss was measured. When compared with tests conducted on similar HDPE liners with an Eastern U.S. coal and a Western U.S. coal, the Plant A byproduct may be considered less abrasive than coal.

#### BYPRODUCT FLOWABILITY TESTING

Flowability direct shear tests and byproduct/liner friction tests were performed on the Plant A and Plant B byproduct gypsum samples. A total of 114 direct shear flowability tests and 32 wall friction tests were performed. The testing program covered several moisture levels, temperature conditions, and liner materials.

The critical strength and frictional properties measured during the flowability testing program were used to compute the minimum hopper slopes, outlet dimensions, funnel flow dimensions, and stable rathole diameters that are required for reliable flow of the gypsum byproducts.

#### Flowability Direct Shear Tests

Instantaneous and time consolidation direct shear flow tests were conducted on each gypsum byproduct under continuous instantaneous flow and three-day extended (time consolidated) storage conditions. Time consolidation testing was only performed near the critical moisture content, defined as the moisture level which results in the steepest flow function, or the least flowable condition. Instantaneous flowability tests were conducted on each "as-received" sample at a "near-freezing" temperature, defined as one degree centigrade above the freezing point (-2° C).

The Plant A sample displayed the highest overall strength at the "as-received" state with 17.2 percent free moisture. The Plant A byproduct exhibited a moderate gain in strength and cohesion after a three-day storage period under consolidating pressures. The Plant B byproduct displayed the greatest overall strength during instantaneous testing and showed substantial gain in strength after time consolidation.

#### Freeze Testing

The results of the freezing tests at minus 1° C indicate that the "as-received" byproducts gained little or no strength under the low temperature conditions as compared to the strengths at ambient room temperature conditions.

### Liner Friction Tests

Shear tests on composite byproduct/liner samples, using Plant A and Plant B byproducts, were used to determine the wall friction coefficient for SS304-2B, mild steel with a corroded surface, and HDPE with both a smooth (new) surface and abraded (in-service) surface.

The results of the tests indicated that the high density polyethylene liner, particularly the smooth polyethylene, offered the least resistance to sliding with either byproduct. For both samples, frictional resistance to sliding on the smooth HDPE liner decreased slightly with lower byproduct moisture, while resistance to sliding on the abraded HDPE liner increased slightly with lower byproduct moisture. Wall friction tests at the low temperature conditions indicated that only the SS304-2B liner exhibited any increased resistance to byproduct sliding when compared with the sliding resistance at ambient room temperature conditions.

### RAIL CAR DESIGN

#### Hopper

To promote reliable gravity flow of gypsum byproduct, the hoppers of the rail cars used to transport the byproduct should incorporate a mass flow design, described as follows:

Mass flow is a bulk material flow pattern which develops when the entire storage vessel contents are set in motion as material is withdrawn from the outlets. This flow pattern results in a first-in, first-out flow of material. The entire volume of material in the storage vessel is moving with no stagnant or dead zones. To achieve reliable withdrawal, the outlet dimension must exceed the mass flow arching dimension of the bulk material.

A mass flow design is required because the anticipated rathole diameters for both materials are significantly larger than the anticipated arching dimensions. Inhibiting the formation of stable ratholes decreases the likelihood that a steep-walled, stable material channel will form in the rail car. Formation of such stable channels would necessitate car shaking for removal of all byproduct. Hopper recommendations for gravity mass flow, based on no-arching condition, in a plane-flow hopper for Plant B byproduct in continuous flow are shown as follows.

### Hopper Recommendations for Gravity Mass Flow

Byproduct Free Moisture, %	Hopper Surface	Min. Hopper Slope, Deg	Min. Outlet Dimension, Ft	Stable Rathole Dia., Ft
20.3	SS304-2B	79	9.0 x 27.0	24.0
	HDPE-Smooth	68	9.2 x 27.6	
13.7	SS304-2B	83	4.8 x 14.4	22.7
	HDPE-Smooth	66	5.15 x 15.45	
8.5	SS304-2B	88	4.95 x 14.85	18.7
	HDPE-Smooth	64	5.35 x 16.05	

#### Liner

The entire sloping surfaces of the rail car hoppers should be lined with HDPE because flow of gypsum byproduct can be initiated on significantly shallower slopes than that possible for either of the steel liners. The HDPE has a lower moisture absorption than the steel liners, thus helping fine, wet, bulk materials slide at low temperature conditions. Based on the results of the abrasion tests, reasonable liner life is expected with hopper cars lined with HDPE.

Car liner selection should also consider the anticipated temperature environment to which the loaded rail car will be subjected. If loaded rail cars might be passed through a "thaw shed" in the winter time, then the resultant effects on any rail car liner, particularly polymeric lining materials, should be evaluated. Such concerns not exist with either Type 304 stainless steel or mild steel liners.

#### Other Liner Applications

Liners made of SS304-2B and HDPE can also be applied to the hoppers and chutes in a variety of material handling equipment and in the beds of dump trucks.

#### Rotary Dump Rail Cars

Rotary dump cars could be an alternative byproduct transportation mode using rail cars. Flow of bulk material from a rail car hopper rotated 140 to 160 degrees from vertical would be considered an asymmetric plane-flow regime. Rail cars lined with HDPE or ultra-high molecular weight (UHMW) polymer will likely promote flow of the gypsum byproduct if the rail car is rotated 145 to 155 degrees from the vertical. Cars lined with SS304-2B will likely require rotation of at least 160 degrees to evacuate the contents. In either application, additional car cleanout will likely be required.

#### CORRELATION OF RESULTS

For damp FGD gypsum (95 percent gypsum, average particle size 50  $\mu$ m) with 9 percent free moisture, instantaneous values of unconfined yield strength plotted against the major consolidation stress show that the characteristics lie in the worst flowability

zone (very cohesive and non-flowing) as defined by Jenike. This is shown in Figures 5 and 6 compared to data for Plant A and Plant B byproduct gypsums, respectively (10, 11). The flowability characteristics of damp FGD gypsum are worse than for 20 percent moisture raw coal or 10 percent moisture wet sand (10). After a period of seven days time consolidation, the FGD gypsum flowability characteristics degrade significantly (10, 11). The Plant A and Plant B byproducts significantly exceed the poor flowability characteristics of damp FGD gypsum described in the literature.

Several of the properties investigated in the study of Plant A and Plant B byproduct gypsums appear to be largely responsible for their flowability behavior in comparison to the literature. The properties having the greatest effect on flowability are free moisture, particle size, particle morphology, and percent oxidation.

#### CONCLUSIONS

The overall purity of the FGD byproduct gypsum samples tested was well below that of most high-grade or commercial-grade gypsum for which flowability characteristics are described in the literature. The presence of impurities, such as fly ash, unreacted limestone, calcium sulfite, and inerts, contributed to the poor flowability of the byproduct gypsum tested compared to "high grade" or commercial grade gypsum in the literature. The characteristics of the particles associated with these impurities in the byproduct gypsum samples tested appeared to cause significant departure in their flowability behavior from that of high-grade gypsum. The presence of moisture in any byproduct gypsum creates poor flowability characteristics.

Chemical analysis data for the byproduct and natural gypsum samples tested showed levels of trace elements which were similar to those reported in the literature. The concentrations of constituents analyzed in the aqueous leachates from the byproduct and natural gypsum samples tested were well below the required Ohio levels.

#### REFERENCES

1. GARLANGER, J.E. AND INGRA, T.S., ARDAMAN & ASSOCIATES, INC., "EVALUATION OF CHIYODA THOROUGHbred 121 FGD PROCESS AND GYPSUM STACKING, VOLUME 3: TESTING AND FEASIBILITY OF STACKING FGD GYPSUM", ELECTRIC POWER RESEARCH INSTITUTE, CS-1579, RESEARCH PROJECT 536-3, NOVEMBER 1980.
2. BARBER, J.W., ET AL, "CHARACTERIZATION OF SYNTHETIC GYPSUM", PROCEEDINGS OF A CONFERENCE PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1991; MAY 12-15:pp.26.1-26.15.
3. CROWE, J.L. AND SEALE, S.K., "FULL-SCALE SCRUBBER SLUDGE CHARACTERIZATION STUDIES", ELECTRIC POWER RESEARCH INSTITUTE, FP-942, RESEARCH PROJECT 537-1, FINAL REPORT, JANUARY 1979.

4. FEENEY, STEVE ET AL, "IN-SITU FORCED OXIDATION RETROFIT AT MICHIGAN SOUTH CENTRAL POWER AGENCY'S ENDICOTT STATION", PROCEEDINGS OF CONFERENCE PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1991; MAY 12-15: pp.10.1-10.18.
5. HURT, P.R. ET AL, "DISPOSAL OF FLUE GAS DESULFURIZATION WASTES: EPA SHAWNEE FIELD EVALUATION FINAL REPORT", EPA 600/7-81-103 (NTIS PB 81 212 482), U.S. ENVIRONMENTAL PROTECTION AGENCY, JUNE 1981.
6. MAKKINEJAD, DR. DAVID ET AL, "VARIABLES AFFECTING THE PRODUCTION OF COMMERCIAL GRADE GYPSUM FROM THE FGD PROCESS", PROCEEDINGS OF CONFERENCE PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1991; MAY 12-15: pp.11.1-11.12.
7. ROSOFF, J. ET AL, "DISPOSAL OF BY-PRODUCTS FROM NONREGENERABLE FLUE GAS DESULFURIZATION SYSTEMS: FINAL REPORT", EPA 600/7-79-046, U.S. ENVIRONMENTAL PROTECTION AGENCY, FEBRUARY 1979.
8. WILTERDINK, D.W. ET AL, "GYPSUM-AN FGD BYPRODUCT", COAL TECHNOLOGY '85, INTERNATIONAL COAL UTILIZATION EXHIBITION AND CONFERENCE, pp.187-199.
9. WIRSCHING, DR. FRANZ, "FGD GYPSUM IN RESEARCH, DEVELOPMENT, PRODUCTION AND APPLICATION", PROCEEDINGS OF CONFERENCE PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1991; MAY 12-15: pp.18.1-18.18.
10. RADEMACHER, F.J.C. ET AL, "ENVIRONMENTALLY-CONSCIOUS STORAGE AND HANDLING OF HUGE QUANTITIES OF COAL AND DAMP FLUE GAS GYPSUM AT POWER STATIONS BY MEANS OF EUROSILOS", BULK SOLIDS HANDLING, FEBRUARY 1988, pp.13-17.
11. WRIGHT, H., "LARGE SCALE HANDLING OF BULK MATERIALS", BULK SOLIDS HANDLING, FEBRUARY 1990, pp.175-179.
12. KOCHAN, VLADIMIR, "MODERN METHODS FOR THE ANALYSIS OF FLUE GAS AND BYPRODUCT GYPSUMS", PROCEEDINGS OF A SEMINAR PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1988; NOVEMBER: pp.155-164.
13. STEFFAN, PATRICIA AND GOLDEN, DEAN, "FGD GYPSUM UTILIZATION: SURVEY OF CURRENT PRACTICES AND ASSESSMENT OF MARKET POTENTIAL", PROCEEDINGS OF CONFERENCE PRESENTED BY ORTECH INTERNATIONAL, TORONTO 1991; MAY 12-15: PP.4.1-4.18.



Figure 1. Byproduct gypsum - Plant A; 100X magnification



Figure 2. Byproduct gypsum - Plant B; 100X magnification

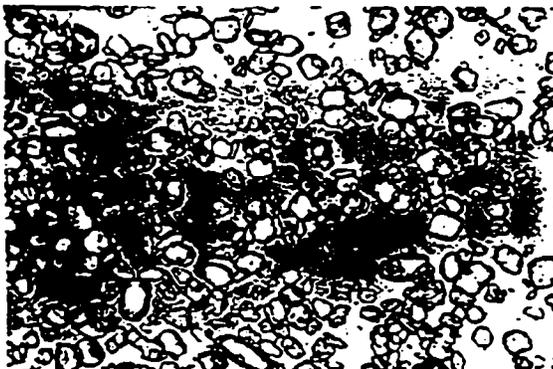


Figure 3. Byproduct gypsum - Plant C; 100X magnification

\*Please note that the illustration(s) on this page have been reduced 10% during printing

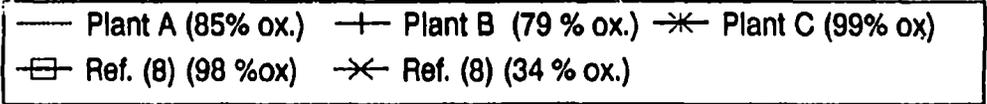
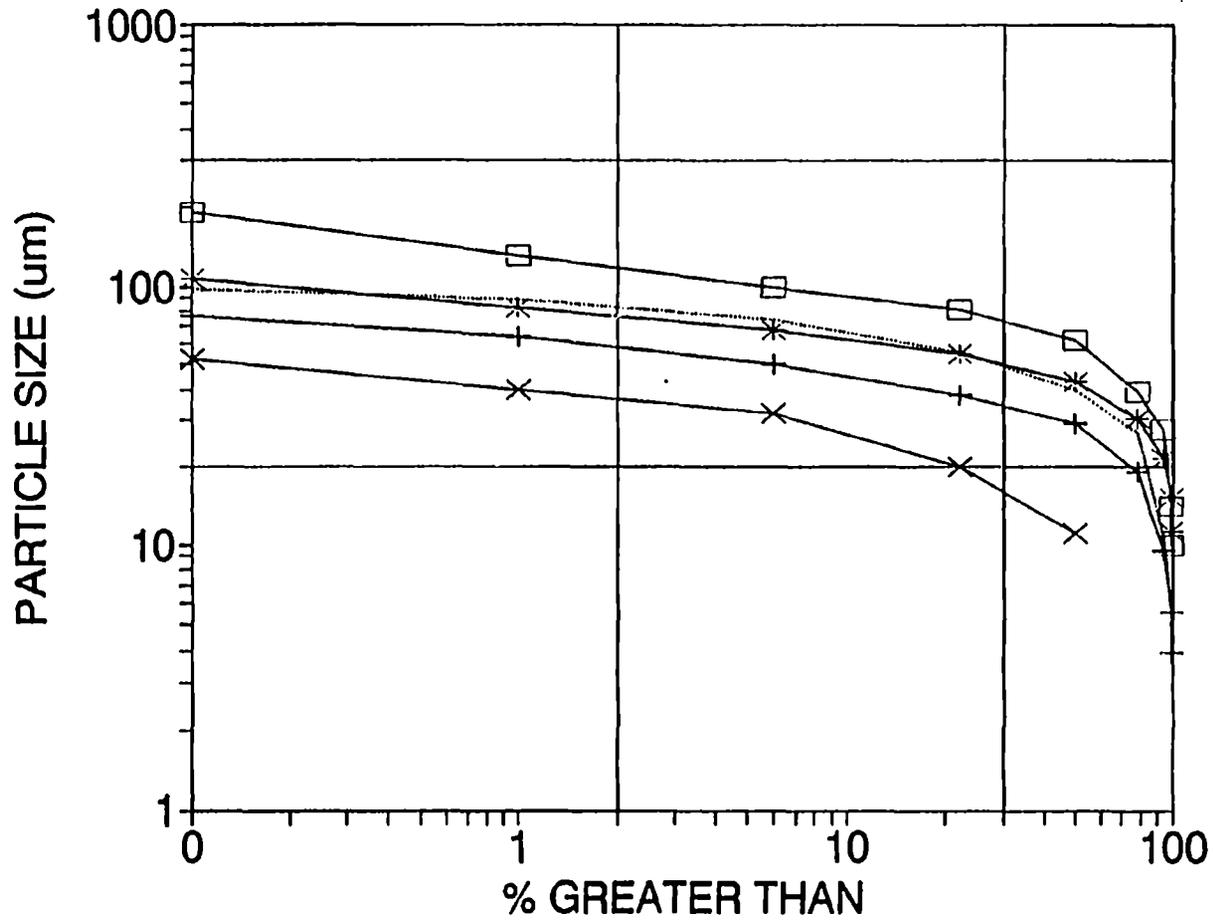


Figure 4. Oxidation state vs. particle size

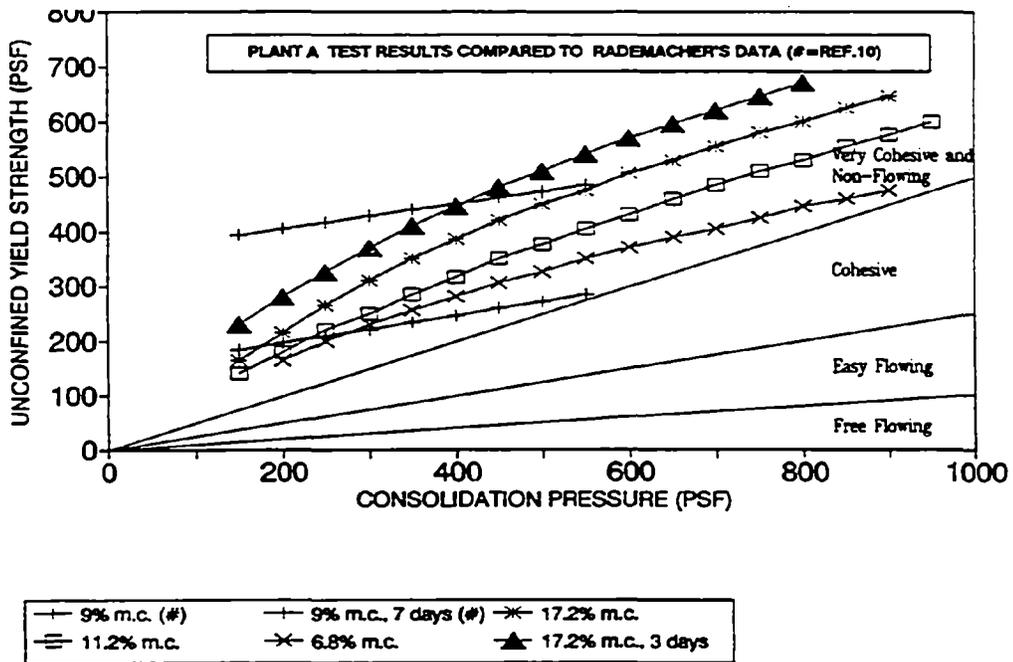


Figure 5. Flow function of byproduct gypsum; referred to Jenike's flowability zones

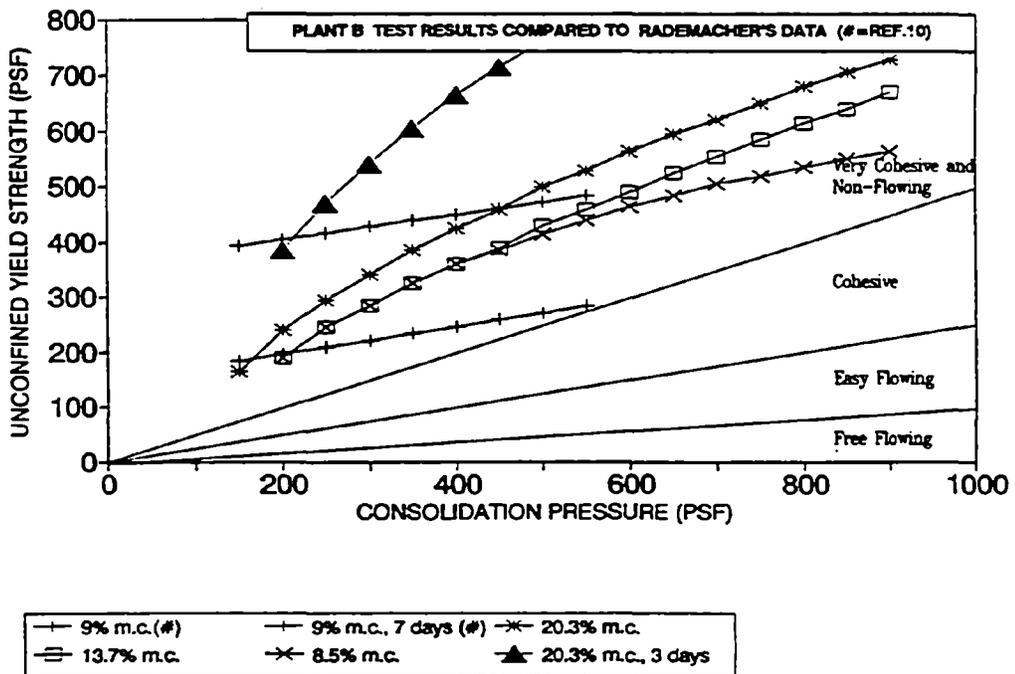


Figure 6. Flow function of byproduct gypsum; referred to Jenike's flowability zones

Table 1  
SUMMARY OF ANALYTICAL METHODS

<u>Designation</u>	<u>Source</u>	<u>Title</u>
C471-87	ASTM <sup>1</sup>	Method for Chemical Analysis of Gypsum and Gypsum Products
C471-87 (6)	ASTM <sup>1</sup>	Free Water
C471-87 (8)	ASTM <sup>1</sup>	Carbon Dioxide
C471-87 (9)	ASTM <sup>1</sup>	Silicon Dioxide and Insoluble Matter
C471-87 (13)	ASTM <sup>1</sup>	Sulfur Trioxide
D3987-85	ASTM <sup>1</sup>	Method for Shake Extraction of Solid Wastes with Water
#41	EPRI <sup>2</sup>	Analysis of Sulfite in Scrubber Liquor and Slurry Solids by Iodine-Arsenite Titration
EPA 160.1	SW-845 <sup>3</sup>	Residue, Filterable, Gravimetric, Dried at 180°C
EPA 300.0	EPA <sup>4</sup>	The Determination of Inorganic Ions in Water by Ion Chromatography
EPA 310.1	SW-846 <sup>3</sup>	Alkalinity, Titrimetric (pH 4.5)
EPA 340.2	SW-846 <sup>3</sup>	Fluoride, Potentiometric, Ion Selective Electrode
EPA 3050	SW-846 <sup>3</sup>	Acid Digestion of Sediment Sludges and Soils
EPA 6010	SW-846 <sup>3</sup>	Inductively Coupled Plasma Atomic Emission Spectroscopy
EPA 7470	SW-846 <sup>3</sup>	Mercury in Liquid Waste (Manual Cold-Vapor Technique)
EPA 9040	SW-846 <sup>3</sup>	pH Electrometric Measurement
SM303E	EPA <sup>5</sup>	Arsenic, AA Hydride (Atomic Absorption - Gaseous Hydride)

1. American Society for Testing and Materials.
2. FGD Chemistry and Analytical Methods Handbook, Volume 2: Chemical and Physical Test Methods, Revision 1, Electric Power Research Institute, EPRI CS-3612.
3. Test Methods for Evaluating Solid Waste, SW-846, EPA-600/4-79-020, EPA.
4. EPA-600/4-84-017, EPA.
5. Standard Methods for Water and Wastewater, EPA.

Table 2

Analysis	Units	Detection Limit	Gypsum Solids Analysis						Avg. Natural	Avg. Byproduct
			Natural Gypsum			Byproduct Gypsum				
			Iowa	Nova Scotia	Oklahoma	Plant A	Plant B	Plant C		
Sulfur Trioxide (SO3)	%		31.25	39.75	35.50	40.75	36.50	35.75	35.50	37.67
Free Water	%		<0.10	<0.10	<0.10	15.94	18.62	9.88	<0.10	14.75
Silicon Dioxide and Insoluble Matter	%		10.78	9.40	5.00	4.98	2.99	2.20	8.39	3.39
Carbon Dioxide (CO2)	%		1.07	0.57	0.33	3.83	6.56	0.46	0.66	3.62
Loss on Ignition (550C)	%		16.79	19.65	20.14	30.22	31.86	28.62	18.86	30.23
Sulfite (SO3)	%		0.066	0.054	0.154	7.20	9.80	0.104	0.09	5.70
Total Aluminum	mg/kg	5	824	113	176	165	282	268	371	238
Total Arsenic	mg/kg	10	<10	<10	<10	<10	<10	<10	<10	<10
Total Boron	mg/kg	5	9.99	14.4	12.4	18	52	19	12.26	29.67
Total Cadmium	mg/kg	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Total Barium	mg/kg	0.5	5.84	2.08	2.13	0.97	3.19	2.06	3.35	2.07
Total Calcium	mg/kg	1	166214	199588	172421	198724	197162	176564	179408	190817
Total Chromium	mg/kg	1	<1.0	<1.0	<1.0	<1.0	1.03	5.85	<1.0	<2.63
Total Cobalt	mg/kg	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Total Copper	mg/kg	1	1.22	<1.0	1.72	<1.0	2.25	1.52	<1.31	<1.59
Total Iron	mg/kg	1	1109	160	90	335	838	269	453	481
Total Lead	mg/kg	5	<5	<5	<5	<5	<5	<5	<5	<5
Total Magnesium	mg/kg	1	4340	714	611	245	1521	182	1888	649
Total Manganese	mg/kg	1	20	14.6	8.03	17	101	2.13	14.21	40.04
Total Molybdenum	mg/kg	1	<1.0	2.66	<1.0	<1.0	<1.0	<1.0	<1.55	<1
Total Nickel	mg/kg	1	4.19	<1	<1	<1	1.22	<1	<2.06	<1.07
Total Phosphorus	mg/kg	10	42	32.2	43	128	42	154	39.07	108
Total Potassium	mg/kg	10	433	92.4	53	67	151	39	192.8	85.7
Total Selenium	mg/kg	10	<10	<10	<10	<10	<10	<10	<10	<10
Total Silver	mg/kg	1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Total Sodium	mg/kg	1	228	111	450	107	105	246	263	153
Total Sulfur	mg/kg	25	124758	158779	141916	159828	145666	142690	141818	149395
Total Zinc	mg/kg	1	5.86	1.67	1.81	2.01	5.86	4.81	3.11	4.23

8B-105

Table 3

Analysis	Units	Detection Limit	Gypsum Water Leachate Analysis						Avg. Natural	Avg. Byproduct
			Natural Gypsum			Byproduct Gypsum				
			Iowa	Nova Scotia	Oklahoma	Plant A	Plant B	Plant C		
Total Dissolved Solids	mg/L	10	2310	2253	2182	2479	2476	2285	2248	2413
Fluoride (without distillation)	mg/L	0.1	0.2	0.3	0.1	3.6	2.5	4.0	0.2	3.4
Chloride	mg/L	1	3	3	2	26	9	18	2.7	17.7
Sulfate	mg/L	10	1451	1429	1489	1492	1503	1491	1456	1495
Nitrate Nitrogen	mg/L	0.2	5.1	8.5	1	1.2	0.5	2.3	4.9	1.3
pH	S.U.		7.28	3.32	5.75	8.28	7.94	6.01	5.45	7.41
Alkalinity	mg/L as CaCO3									
CO3	mg/L as CaCO3	0.01	0.02	<0.01	<0.01	0.35	0.17	<0.01	<0.01	<0.18
HCO3	mg/L as CaCO3	10	12	<10	<10	19	0.21	<10	<10.7	<9.7
Aluminum	mg/L	0.05	0.24	0.31	0.25	0.33	0.21	0.41	0.27	0.32
Boron	mg/L	0.05	0.21	0.38	0.36	0.54	2.60	0.66	0.32	1.27
Cadmium	mg/L	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Barium	mg/L	0.005	0.02	0.01	0.007	0.007	0.01	0.02	0.012	0.012
Calcium	mg/L	0.01	642	639	625	708	651	634	635.33	664.33
Chromium	mg/L	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cobalt	mg/L	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Copper	mg/L	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Iron	mg/L	0.05	<0.05	0.05	<0.05	<0.05	<0.05	0.26	<0.05	<0.12
Lead	mg/L	0.05	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	<0.06	<0.05
Magnesium	mg/L	0.01	1.61	0.30	0.20	2.92	18.0	0.28	0.70	7.07
Manganese	mg/L	0.01	0.01	<0.01	<0.01	0.16	0.71	0.05	<0.01	0.31
Molybdenum	mg/L	0.05	<0.05	0.12	<0.01	<0.01	<0.05	<0.05	<0.06	<0.04
Nickel	mg/L	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phosphorus	mg/L	0.10	<0.10	<0.10	<0.10	<0.10	0.18	0.16	<0.10	<0.15
Potassium	mg/L	0.10	1.54	0.73	1.29	<0.10	<0.10	0.36	1.19	<0.19
Selenium	mg/L	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Silver	mg/L	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
Sodium	mg/L	0.01	9.32	2.18	22	1.66	1.82	7.81	11.17	3.76
Sulfur	mg/L	0.10	535	527	531	570	589	514	531	558
Zinc	mg/L	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Arsenic	mg/L	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mercury	mg/L	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

Table 4

LITERATURE VALUES FOR TRACE ELEMENTS  
IN NATURAL AND BYPRODUCT GYPSUM SOLIDS  
(mg/kg or ppm)

	Avg. <sup>1</sup> Natural	Avg. <sup>2</sup> Byproduct	Range <sup>3</sup> Byproduct	Range <sup>4</sup> Byproduct	Range <sup>5</sup> Natural
Zinc	3.11	4.23	2.9 - <7	2.0	4.0 - 6.0
Cadmium	<0.5	<0.5	-	<1.0	<0.2
Chromium	<1.0	<2.63	2.2 - 11	3.0 - 10.0	<5.0 - 5.0
Nickel	<2.06	<1.07	-	<5.0	<5.0
Cobalt	<1.0	<1.0	0.05 - 0.46	<1.0	<2.0
Copper	<1.31	<1.59	0.6 - 3.2	3.0	3.0 - 6.0
Lead	<5	<5	-	<1.0	2.0
Tin	-	-	-	<5.0	<50.0
Molybdenum	<1.55	<1	0.35 - 1.74	5.0 - 6.0	<5.0
Fluorine	-	-	95 - 729	321 - 475	20.0 - 105.0
Arsenic	<10	<10	0.14 - 1.74	<5.0	1.0 - 1.4
Antimony	-	-	0.028 - 0.065	<5.0	0.8 - 1.0
Mercury	-	-	0.04 - 0.36	<1.0	<0.2
Selenium	<10	<10	<1 - 5.2	<5.0	<0.2

## Notes:

1. Analyzed for this study, Iowa, Nova Scotia, Oklahoma.
2. Analyzed for this study, Plant A, Plant B, Plant C.
3. From five FGD gypsums in Reference (12).
4. From two synthetic gypsums in Reference (2).
5. From two natural gypsums in Reference (2).

Table 5

## EPA DRINKING WATER REGULATIONS

Primary Drinking Water Regulations Maximum Contaminant Level (mg/l)*	
Arsenic (As)	0.05
Barium (Ba)	1
Cadmium (Cd)	0.010
Chromium (Cr)	0.05
Lead (Pb)	0.05
Mercury (Hg)	0.002
Nitrate (NO <sub>3</sub> as N)	10
Selenium (Se)	0.01
Fluoride (F)	4.0
Secondary Drinking Water Regulations Maximum Contaminant Level (mg/l)**	
Aluminum (Al)	0.05 to 0.2
Chloride (Cl)	250
Color	15 color units
Copper (Cu)	1.0
Corrosivity	Non-Corrosive
Fluoride (F)	2.0
Foaming Agents	0.5
Iron (Fe)	0.3
Manganese (Mn)	0.05
Odor	3 threshold odor number
pH	6.5 to 8.5
Silver (Ag)	0.1
Sulfate (SO <sub>4</sub> )	250
TDS	500
Zinc (Zn)	5

\* Maximum permissible level

\*\* These regulations control contaminants in drinking water that primarily affect the aesthetic qualities relating to public acceptance of drinking water. The regulations are not Federally enforced but are intended as guidelines for the states.

Table 6  
OHIO LEACHATE REGULATIONS

<u>Contaminant</u>	<u>Maximum Contaminant Level (ppm)</u>
Arsenic	0.75
Barium	15.0
Cadmium	0.15
Chromium	0.75
Lead	0.75
Mercury	0.03
Selenium	0.15
Silver	0.75
Cyanide	3.0
Phenolics	4.5

Table 7  
LITERATURE VALUES FOR ANALYSIS OF AQUEOUS  
LEACHATE FROM BYPRODUCT GYPSUMS  
(mg/l except as noted)

<u>Analysis</u>	<u>Avg.<sup>1</sup> Natural</u>	<u>Avg.<sup>2</sup> Byproduct</u>	<u>Underdrain<sup>3</sup> Leachate</u>	<u>Pond<sup>4</sup> Runoff</u>	<u>Pond<sup>5</sup> Runoff</u>
Total Dissolved Solids	2248	2413	4260	2400	2287
Fluoride	0.2	3.4	-	-	-
Chloride	2.7	17.7	1450	1.0	47.0
Sulfate	1456	1495	1150	1500	1450
Nitrate Nitrogen	4.9	1.3	1050	-	-
pH	5.45	7.41	6.6	7.0	7.1
Alkalinity	<1.07	<9.7	84	470	25
Aluminum	0.27	0.32	4.5	-	-
Boron	0.32	1.27	57	1.4	5.0
Cadmium	<0.005	<0.005	0.025	-	-
Barium	0.012	0.012	3.4	-	-
Calcium	635.33	664.33	580	1300	410
Chromium	<0.01	<0.01	<0.03	-	-
Cobalt	<0.01	<0.01	<0.1	-	-
Copper	<0.01	<0.01	<0.1	-	-
Iron	<0.05	<0.12	<0.1	-	-
Lead	<0.06	<0.05	0.15	0.0020	0.4400
Magnesium	0.70	7.07	372	16.0	27.0
Manganese	<0.01	0.31	1.20	-	-
Molybdenum	<0.06	<0.04	<1.0	-	-
Nickel	<0.01	<0.01	<0.1	-	-
Phosphorus	<0.10	<0.15	-	-	-
Potassium	1.19	<0.19	-	-	-
Selenium	<0.10	<0.10	0.020	0.0340	0.0070
Silver	<0.01	<0.01	<0.05	-	-
Sodium	11.17	3.76	38	2.5	2.0
Silicon (SiO <sub>2</sub> )	-	-	142	-	-
Zinc	<0.01	<0.01	0.07	-	-
Arsenic	<0.005	<0.005	<0.01	0.1560	0.0800
Mercury	<0.005	<0.005	0.006	0.0021	0.0070

Notes:

1. Analyzed for this study, Iowa, Nova Scotia, Oklahoma.
2. Analyzed for this study, Plant A, Plant B, Plant C.
3. Shawnee FGD Waste Disposal Site H in Reference (5).
4. Shawnee FGD Waste Disposal Site J in Reference (5).
5. Shawnee FGD Waste Disposal Site K in Reference (5).

Table 8  
LITERATURE VALUES FOR SOLUBLE SALTS IN SEVERAL  
NATURAL AND SYNTHETIC GYPSUMS (2)  
(ppm except as noted)

	<u>Range Natural</u>	<u>Range Synthetic</u>
K	21 - 47	22 - 1532
Na	7 - 195	18 - 2134
Mg	12 - 26	12 - 212
Cl	15 - 111	21 - 412
KCl	31.5 - 89.6	42.0 - 509.1
NaCl	0 - 112.7	0 - 233.9
MgCl <sub>2</sub>	0	0 - 37.7
CaCl <sub>2</sub>	0	0
K <sub>2</sub> SO <sub>4</sub>	0 - 9.9	0 - 3082.0
Na <sub>2</sub> SO <sub>4</sub>	21.6 - 465.4	0 - 6586.3
MgSO <sub>4</sub>	59.4 - 128.7	59.4 - 1002.0
Ca	0	0
SO <sub>3</sub>	62.0 - 417.5	197.7 - 4754.5
Sum	796.4	354.7 - 7009.5
Equiv #/Ton	1.59	0.7 - 14.0

Table 9  
COMMERCIAL-GRADE GYPSUM SPECIFICATIONS (13)

<u>Parameter</u>	<u>National Gypsum Co.</u>	<u>Georgia- Pacific Corp.</u>	<u>U.S. Gypsum Co.</u>	<u>Japan</u>	<u>West Germany</u>
Gypsum content, min %	94	90	95	95	80 - 95
Calcium sulfite content, max %	0.5	-	2.0	0.25	0.25
Total soluble salts, max ppm	-	-	600	1000	-
Sodium content, max ppm	250	200	75	-	600
Chloride content, max ppm	400	200	120	-	100
Magnesium content, max ppm	250	-	50	-	1000
Free water, max %	1	10	10	10	10
pH	6 - 8	3 - 9	6.5 - 8	6.5 - 8	5 - 9
Inerts, max %	3.0	-	1	-	-

Source: Ellison, William, and Edward Hammer. "FGD Gypsum Use Penetrates U.S. Wallboard Industry." Power, February 1988.



# **EVALUATION OF DISPOSAL METHODS FOR OXIDIZED FGD SLUDGE**

For Presentation at the  
EPRI-EPA-DOE 1991 SO<sub>2</sub> Control Symposiums  
December 3-6, 1991  
Washington, D.C.

by  
W. C. Yu  
Manager, Process Engineering

Conversion Systems, Inc.  
Horsham, PA



## Introduction

The implementation of wet flue gas desulfurization — in response to the Clean Air Act of 1990 — will cause many power generators and state regulatory personnel to face important decisions on the disposal of large volumes of resultant solid waste. Even with the selection of forced oxidation technology, it is widely recognized that the vast majority of flue gas desulfurization by-products will be disposed.

This paper analyzes the water quality issues associated with gypsum stacking, macroencapsulation of gypsum, and the stabilization/fixation of gypsum. Water quality issues include leachate quality, leachate generation, runoff management, and groundwater impact. The following analysis uses both field and literature data to measure the environmental impact of the three most discussed disposal options.

## Leachate Management

### *Comparison of Leachate Quality*

Leachate quality for each disposal option was determined by reviewing pertinent literature for reported chemical compositions of FGD waste and their corresponding leachates. The analysis focused on chemical analyses of forced oxidized gypsum sludge produced by wet limestone scrubbing of medium to high sulfur, bituminous coal. The results reported in this analysis are based on documented forced-oxidized FGD wastes from six generating stations.

The chemical composition of a leachate produced from a waste is governed by the chemical composition of the waste itself. FGD forced oxidized gypsum wastes produced by wet-limestone scrubbing consist primarily of flue gas reaction products, excess unreacted limestone, fly ash, and scrubber liquor.

Limestone contains many inert materials that do not react during the scrubbing process but become incorporated into the solid phase of the FGD waste. Magnesium ( $Mg^{2-}$ ) is a common constituent of limestone, often combining in the scrubber with sulfate ( $SO_4^{2-}$ ) to form magnesium sulfate ( $MgSO_4$ ).  $MgSO_4$  is soluble in water and may leach from the FGD waste when landfilled. Excess, unreacted limestone also becomes incorporated in the FGD waste, thereby increasing  $CaCO_3$  concentration of the sludge. Dissolution of  $CaCO_3$  from the landfilled FGD waste will result in a leachate high in  $Ca^{2-}$  with a moderately to high pH.

The coal type adds to the chemical character of the FGD waste as a source of both volatile compounds and fly ash. Volatile elements such as chlorine, lead, bromine, fluoride, and selenium are scrubbed from the flue gas, along with the sulfur, and incorporated in the FGD waste. High sulfur coals require greater quantities of limestone in the scrubber, and therefore

produce wastes and tend to produce leachates with greater concentrations of sulfur and limestone compounds. In addition, coal containing unusually high amounts of chloride produces leachates with high chloride concentrations.

Fly ash is the major source of trace elements in FGD waste. These elements often become incorporated in the FGD leachate. Although particle control devices are commonly installed prior to the FGD scrubbers, small amounts of fly ash are captured by the scrubber, and trace metals added to the FGD waste.

The composition of scrubber sludge is extremely variable, changing from station to station and hour to hour within each station (Baker 1978). In general, the unoxidized solid sludge of the FGD slurry is characterized primarily of calcium sulfate dihydrate ( $CaSO_4 \cdot 2H_2O$ ; gypsum), calcium sulfite hemihydrate ( $CaSO_3 \cdot 1/2H_2O$ ), calcium carbonate ( $CaCO_3$ ), and inert constituents (Summers et al. 1983). With oxidation, approximately all of the calcium sulfite hemihydrate is oxidized to calcium sulfate dihydrate.

Like the scrubber sludge, the chemical composition of the scrubber liquor is extremely variable. In general, the scrubber liquor is high in total dissolved solids, sulfate, chloride, calcium, magnesium, and sodium. Numerous trace elements, such as arsenic, boron, chromium, copper, iron, lead, mercury, nickel, selenium, and zinc occur at varying concentrations in scrubber liquors (Baker 1983). Typical pH values of forced-oxidized scrubber liquors produced from wet-limestone scrubbing of eastern coals range from 5 to 7.

Leachate is the result of either rain water or groundwater coming in contact with a solid waste material, and incorporating the soluble components of the waste material into the water. In the case of forced-oxidized FGD waste, the solid waste material is mainly calcium sulfate dihydrate ( $CaSO_4 \cdot 2H_2O$ ), gypsum. Rain water in contact with gypsum will dissolve the gypsum until saturation is reached.

At 25°C, the concentrations of calcium and sulfate in water saturated with respect to gypsum would be approximately 400 mg/L and 960 mg/L, respectively. Total dissolved solids (TDS) is the sum of the dissolved constituents in water. Assuming that calcium and sulfate were the only two constituents dissolved in the water as it infiltrates through the gypsum, the resulting TDS would be approximately 1,360 mg/L. However, forced-oxidized gypsum waste also contains elements associated with limestone and the fly ash; therefore, TDS of forced-oxidized gypsum waste leachates are typically higher than 1,360 mg/L.

In this analysis, the three disposal or sludge management practices evaluated have water budgets that are unique to that particular practice. This is important because leachate and runoff constituents would be expected to vary as a function of the amount of water contacting the sludge, the duration of the contact, and the initial quality of the water. Each disposal practice is evaluated below and the quality and quantity of leachate and runoff volumes are projected.

### Disposal Option 1: Wet-Impoundment/Gypsum Stacking

In this disposal option, the impounded scrubber slurry water provides a continual source of recharge for leachate generation, as opposed to the other disposal options in which leachate generation is dependent upon rainfall. The pond water is a combination of supernatant liquor from slurry and rain water. Usually, the supernatant liquor is decanted from the pond and recirculated as process water to the FGD scrubber system. As a result of the recirculating process, the supernatant liquor builds up high concentrations of ions, particularly chloride and sulfate. In turn, the pond water acquires the high ion concentrations of the supernatant liquor.

A summary of literature-reported chemical analysis of forced oxidized gypsum sludge pond water is listed in Table 1. The water is high in total dissolved solids (TDS), ranging from 6,000 mg/L to over 10,000 mg/L. The TDS consists mainly of sulfate (1,400 - 3,050 mg/L), chloride (890 - 6,600 mg/L), calcium (550 - 1,300 mg/L), and magnesium (540 - 1,100 mg/L). Numerous metals such as aluminum, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, selenium, silver, and zinc often occur at trace concentrations. Typical pH values of the pond water range between 5 and 7.4.

Published leaching studies of gypsum indicate that ion concentrations decrease in the leachate with increased pore volume displacement. The initial high leachate quality is similar to the pond water quality, and represents the release of interstitial pond water stored within the pores of the gypsum. With increased pore volume displacement, constituent concentrations in the leachate decrease to levels expected for rain water at saturation with respect to gypsum. Table 2 presents leachate concentrations which may be expected after 50 pore volume displacements from gypsum. Concentrations of TDS (2200 mg/L), sulfate (1200 mg/L) and chloride (100 mg/L) presented in Table 2 are less than the expected pond water concentrations presented in Table 1. The time required for 50 pore volumes to leach from 1 cubic meter of gypsum is approximately 50 to 100 years. Therefore, leachate concentrations similar to the pond water should be expected from this disposal option for a long time following its closure.

### Disposal Option 2: Macroencapsulation of Gypsum Filtercake

In this option, dewatered gypsum filtercake is placed in clay lined cells and capped with clay. The results of ASTM and EP Toxicity leaching tests of dewatered gypsum filtercake are listed in Table 3. Leachate compositions produced from the gypsum filtercake are similar to the leachates produced from the wet-impoundment/gypsum stacking option. The leachates are high in TDS (2,000 mg/L to 10,500 mg/L), with the TDS consisting mainly of calcium (1,420 - 2,220 mg/L), chloride (3330 - 3930 mg/L), sulfate (788 - 1800 mg/L) and magnesium (465

- 740 mg/L). Reported pH values of gypsum filtercake leachate vary from 5.0 to 6.6. Although the results in Table 3 are reported for gypsum containing no fly ash, the metals aluminum, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, and silicon can be expected to leach from the gypsum filtercake at trace concentrations. The occurrence of these metals may indicate that some fly ash escapes the particulate control devices, that the metals are inherent at trace concentrations in the limestone, or that the metals are a combination of both fly ash and limestone sources.

The analysis presented in Table 4 are results of leachate collected from a macroencapsulated test cell. The TDS concentrations presented in Table 4 are significantly higher than the results reported from standard leaching tests (Table 3) and range from 2,000 mg/L to 46,000 mg/L. The dominant ion contributing to the high TDS is chloride with concentrations ranging from 272 to 38,145 mg/L (Table 4). As mentioned earlier, the facility shows the impact of a tight water loop and a coal high in chloride content, thereby producing a leachate high in chloride.

### Disposal Option 3: Disposal of Stabilized/Fixated Gypsum

Table 5 presents a compilation of literature-reported values of leachates produced from standard leaching tests, as well as from leachate collected from a field disposal site of stabilized/fixated gypsum. In all cases, the gypsum was treated with the addition of fly ash and small quantities of lime to produce a stabilized/fixated material using CSI's Poz-O-Tec<sup>®</sup> technology. Leachate concentrations produced from the stabilized/fixated material are significantly lower than the leachates produced from dewatered gypsum. TDS values of leachates from stabilized/fixated gypsum range from 177 to 2372 mg/L, an order of magnitude lower than the leachates produced in the previous three options (2,000 to 10,000 mg/L). Expected chloride concentrations (40 to 80 mg/L) are one to three orders of magnitude lower in the leachate from the stabilized/fixated gypsum, as compared to the dewatered gypsum. Sulfate and calcium concentrations are somewhat lower in leachates from the stabilized/fixated material, as well. In addition, leachate produced from stabilized/fixated gypsum has a higher pH than leachate from dewatered gypsum, ranging from 6.6 to 10.5. Similar to leachate from dewatered gypsum, the metals arsenic, boron, cadmium, chromium, lead, mercury, nickel, selenium, and silver are still expected to leach from the stabilized/fixated gypsum at trace concentrations.

### Predicting Leachate Quality

Although laboratory leaching tests are more commonly used to determine leachate compositions, the test results often do not adequately characterize the leachate produced from coal combustion by-products. The reason for the discrepancy is that

the standardized leaching tests (EP, TCLP, and ASTM) are designed to mimic the biological decomposition conditions typical of disposed hazardous wastes or municipal wastes in a sanitary landfill. FGD waste, however, is composed of inorganic constituents which, for the most part, do not undergo active biological decomposition.

In an attempt to predict the leachate quality from oxidized-gypsum, the Electric Power Research Institute (EPRI)-developed computer model Fossil Fuel Combustion Waste Leaching Code (FOWL) was utilized (Hostoetler et al. 1988). The FOWL model is the result of numerous EPRI studies conducted for the purpose of predicting leachate compositions from fossil fuel combustion by-products.

The model is designed to calculate quantities, aqueous concentrations, and release durations of selected inorganic constituents released from fossil fuel combustion by-products. Given an initial waste composition, rainwater infiltration rate, and physical characteristics of the waste form, the FOWL model estimates leachate compositions as a function of time by combining a geochemical model with a water balance model.

Constituents considered by the model include Al, As, B, Ba, Ca, Cd, Cr, Mo, S, Si, Sr, Cu, Fe, Mg, Na, Ni, Se, and Zn. The model assumes that the concentrations of each of these constituents are controlled by the solubilities of particular solids. Constituent concentrations are determined for deionized water at equilibrium with respect to the solids phases at various values of pH.

A major limitation of the model is that the pH of the waste is assumed to be constant. Although this may be the case for the solid waste material, the pH of the leachate will most probably vary; this is not considered in the model. The model also assumes that the rainwater infiltrating through the waste is similar in composition to deionized water. In many regions of the U.S., particularly in the eastern U.S., rainwater is more acidic than deionized water. Some of the leachate constituents are modeled based on empirical relationships as opposed to mechanistic thermodynamic data. The model also does not consider redox reactions which govern the leachability of redox-sensitive constituents such as iron and sulfur. Finally, the model does not consider some elements, such as chloride, which are significant in FGD wastes.

The input parameters required for the model include physical characteristics of the waste material including its landfill geometry, bulk density, and initial and saturated moisture contents. Chemical characteristics of the waste material input to the model include its solid composition, leachable fractions of individual constituents, and its pH. Net infiltration through the waste material is also input to the model.

For this exercise, two disposal scenarios were considered: First, the disposal of gypsum filtercake alone; and second, the disposal of stabilized/fixated gypsum filtercake. For the gypsum filtercake alone the solid material was assumed to contain 90 percent  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and 10 percent other constituents. The pH of the gypsum filtercake was assumed to be 5.5, the mean literature-reported value (Table 3). The solid material of the stabilized/fixated gypsum filtercake was assumed

to have a 0.5 to 1 ratio of fly ash to filtercake on a dry weight basis.

The leachable fractions of each constituent listed in Table 1 correspond to the fraction of the total amount of that particular constituent expected to leach from the solid waste material. The model assumes leachable fractions for each of the elements based upon laboratory leaching tests performed by Ainsworth and Rai (1987). Use of Ainsworth and Rai's (1987) data in this modeling exercise is limited for two reasons. First, the leachable fractions calculated by Ainsworth and Rai (1987) were obtained in nitric acid solutions and are considered in the model even though the model assumes that deionized water is the leaching solution. Second, Ainsworth and Rai (1987) did not conduct leaching tests of forced oxidized FGD wastes, the subject of this analysis. The leachable fractions considered in the model are for unoxidized FGD wastes only. Conveniently, the user of FOWL has the option to use alternative value for the leachable fractions. In this analysis, only the leachable fraction for calcium was changed to a value of 1.0, since calcium is reported as a major ion in leachates of forced oxidized FGD wastes.

The FOWL estimated leachate concentrations of almost all of the constituents for the gypsum filtercake are significantly lower than literature-reported values (Table 3). In particular, calcium (393 mg/L), sulfur (315 mg/L), and TDS (756 mg/L) produced by FOWL are an order of magnitude lower than those reported by the literature (Table 3). Even if a chloride concentration of 3,600 mg/L were added to the leachate composition expected by FOWL, the resultant TDS would still be half of the mean value reported by the literature (Table 3). Leachate compositions expected for the stabilized/fixated gypsum filtercake are closer, but still lower than the literature-reported value (Table 5).

The consistent underestimation of leachate constituents by the FOWL model, as compared to literature sources, is a result of the model's limitations. By assuming that only deionized water is in contact with the solid waste material, the model ignores that most disposed FGD waste contains residual process water in its pore spaces. This process water is typically high in major ions and TDS which dominates the leachate characteristics when released. By ignoring pH changes and redox processes, the model is not also considering geochemical processes which highly influence the concentrations of many constituents. Finally, by ignoring major ions such as chloride and potassium, the model will always underestimate the TDS of the resilient leachate.

### ***Comparison of Leachate Generation Rates***

The volume of leachate potentially produced from each disposal option was estimated using the Hydrologic Evaluation of Landfill Performance (HELP) computer model. The HELP model, developed by the United States Environmental Protection Agency (US EPA) and The Army Corp of Engineers (Schroeder et al., 1984), uses climatologic, soil, and design data to produce volume estimates of runoff, drainage, and

leachate expected from various landfill designs. Inherent to the model is a detailed data base of climatological data for 102 cities in 45 states, enabling the estimation of leachate and runoff volumes from landfill designs located in each of the eight states of interest.

As is the case for all models, HELP is based on many simplified assumptions which can produce results quite different from actual values. In particular, the climatological data inherent to the model consists of daily rainfall data for only five years, from 1974 to 1978. This data may not be representative of unusually wet or dry conditions. In addition, the model can not be used to estimate the large volumes of runoff expected from high intensity rain storms, typical of five-year, ten-year or greater storm events.

The HELP model is additionally restricted in that it can not estimate the volume of leachate and runoff generated from a pond. For disposal Option 1- wet-impoundment/gypsum stacking method, leachate generation from beneath the pond was estimated using the following modified Darcy equation:

$$Q = KAT \cdot H/L \quad (1)$$

In Equation (1), Q is the volume of leachate generated, K is the hydraulic conductivity of the soil layer underlying the pond, A is the area of the pond, T is time, H is the head of standing water in the pond, and L is the thickness of the soil layer beneath the pond. The pond was assumed to have a constant head of 15 feet of water, and was underlain by a one foot layer of low permeability ( $1 \times 10^{-7}$  cm/s) clay. For a pond area of 100,000 square feet, a leachate generation rate of 165,610 ft<sup>3</sup>/yr was estimated. Similarly, a pond area of 50 acres (2,180,000 ft<sup>2</sup>) would produce an estimated 3,610,298 ft<sup>3</sup>/yr of leachate.

Input parameters required for the model included climatological data, soil characteristics, and the landfill design. Climatological data were utilized from the model's internal data base. This data included daily rainfall amounts, mean monthly temperatures, mean monthly solar radiation, leaf area indices, and winter snow cover. Physical characteristics (permeability, porosity, field capacity, and wilting point) typical of clay liners and soil covers are also taken from the model's internal data base. The physical parameters for each disposal option including permeability, initial water content, porosity, and thickness of the waste material were input manually.

Initially, all of the model simulations were conducted under the assumption that each landfill design option was located in one city: Cleveland, Ohio. This assumption allows for direct comparison of leachate volumes produced between disposal options. Two simulations were conducted for each disposal option, the first assuming the landfill was actively being filled and contained no cover (Active/Open), and the second assuming that the landfill was closed with some type of cover (Closed/Inactive). For the Active/Open simulation, the landfill thickness was assumed to be half of the total thickness, while for the Closed/Inactive simulation, the total landfill thickness was used.

### **Disposal Option 1: Wet-Impoundment/Gypsum Stacking**

Although the HELP model could not be used to simulate leachate generation from the pond, it was used to estimate leachate and runoff generation rates from the gypsum stacks. For this disposal option, it was assumed that the gypsum stacks were underlain by a one foot sand drain and a one foot layer of compacted clay.

Table 6 presents expected leachate generation rates assuming the gypsum stacks are underlain by both a sand drain and compacted clay while the pond is underlain by compacted clay only. From 2 to 30 years, leachate expected from this disposal scenario increases from 3,600,000 ft<sup>3</sup>/yr to 4,600,000 ft<sup>3</sup>/yr. Comparing this result to a case with a liner and no sand drain, the inclusion of the sand drain cuts the expected leachate volume in half during the active years of the disposal facility. Upon closure, leachate generation is expected at 970,000 ft<sup>3</sup>/yr. This estimate is one order of magnitude less than the leachate volume estimated for the closed facility lined only with compacted clay.

### **Disposal Option 2: Macroencapsulation of Gypsum Filtercake**

The expected leachate generation rates from the macroencapsulation of gypsum filtercake without fly ash are included in Table 7. This option includes a one foot clay liner, a sand drain, and ultimately, a clay cap. Leachate generation from this option increases from 72,000 ft<sup>3</sup>/yr for the first five years of operation to 420,000 ft<sup>3</sup>/yr by the end of 30 years. Upon closure, 420,000 ft<sup>3</sup>/yr of leachate is expected to be generated from the macroencapsulation of gypsum filtercake. Approximately half the amount of leachate is expected from macroencapsulation of the gypsum filtercake as compared to the wet-impoundment/gypsum stacking method.

### **Disposal Option 3: Disposal of Stabilized/Fixated Gypsum**

This disposal option is expected to produce the lowest volumes of leachate as compared to the other disposal options. Leachate generation rates expected to be produced from disposal of stabilized/fixated gypsum ranged from 0 ft<sup>3</sup>/yr in the first five years of operation to 61 ft<sup>3</sup>/yr by the end of thirty years (Table 8). This disposal option, due to the impermeability of the fixated material, includes neither a liner nor a cap. Upon closure, 73 ft<sup>3</sup>/yr of leachate is expected from the disposal of stabilized/fixated gypsum. The leachate generation rates expected from this disposal option are three orders of magnitude lower, less than 0.1%, of the leachate generation expected from disposal Option 2 (the second lowest leachate producer). The low leachate volumes expected from this option are directly attributable to the low permeability ( $1 \times 10^{-7}$  cm/sec) of the stabilized/fixated gypsum.

### ***Leachate and Runoff Generation by Geographic Area***

The leachate generation rates discussed above were determined assuming that a landfill representative of each disposal option was located in one central city: Cleveland, Ohio. To determine the effect of geographic region on leachate generation rates, the eight states were grouped into four of the US EPA designated rainfall zones. New York, Pennsylvania, northern Ohio, northern Indiana, and northern Illinois are located in rainfall zone 1. Southeastern Illinois, southern Indiana, southern Ohio, Kentucky, and Tennessee are located in rainfall zone 2. Florida and southwestern Illinois are located in rainfall zone 3 and 4, respectively. HELP model simulations were conducted for one city considered to be centrally located within each rainfall zone. The cities chosen for zones 1 through 4 included Cleveland, Ohio; Lexington, Kentucky; Orlando, Florida; and East St. Louis, Illinois, respectively.

Simulations were conducted assuming that landfill Option 2 - disposal of gypsum filtercake (alone) in an unlined landfill - was constructed in each central city. For best comparison of expected leachates generated in each city, all landfills were assumed to occupy a 100,000 square foot area. In addition, model simulations were conducted for both an active and closed landfill.

The expected leachate volumes did not vary between cities, but were all approximately 62,000 ft<sup>3</sup>. These results suggest that leachate generation rates should be similar for landfills located anywhere within the US EPA designated rainfall zones 1 through 4, given similar conditions as assumed in this study. Although rainfall amounts are expected to vary from region to region, so do other climatic factors such as evaporation, temperature, solar radiation, and snow cover — all factors which affect infiltration. The net effect of all these factors results in similar leachate generation rates for each rainfall zone.

### ***Assessment of Relative Potential for Groundwater Impact***

The potential for groundwater impact is determined by both the quality and quantity of the leachate expected from each disposal option. Typically, the potential for leachate to impact groundwater is determined by comparing the chemical character of the leachate to drinking water standards. Therefore, the US EPA regulated drinking water standards are included on the tables listing the leachate chemical analysis. However, even if the leachate quality exceeds the drinking water standards, it may have no measurable impact on the groundwater if the amount of leachate generated is low. Work is currently underway to integrate the above findings with the US EPA's vertical/horizontal spread model (VHS) to measure groundwater impact.

### **Disposal Option 1: Wet-Impoundment/Gypsum Stacking**

As illustrated in Table 1, the leachate expected from disposal of gypsum by wet-impoundment/gypsum stacking may exceed the maximum contaminant levels (MCLs) for fluoride, arsenic, cadmium, chromium, lead, and selenium. In addition, the secondary maximum contaminant levels (SMCLs) for chloride, sulfate, TDS and pH may be exceeded. Assuming that long-term leaching of the gypsum waste produces leachates similar in chemical character to that illustrated in Table 2, SMCLs for sulfate, TDS, and pH may still be exceeded. Combining the poor quality of leachate with the large volumes expected suggests that the potential for groundwater to be impacted from this disposal option is quite high.

### **Disposal Option 2: Macroencapsulation of Gypsum Filtercake**

As mentioned previously, leachate quality for disposal of gypsum filtercake with and without fly ash is expected to be similar (Table 3). These leachates may exceed the MCLs for arsenic, cadmium, chromium, lead, and selenium. In addition, the SMCLs for chloride, sulfate, manganese, TDS, and pH may be exceeded. Long-term leaching of the gypsum filtercake can produce leachates that no longer exceed the MCLs, but do exceed the SMCLs for sulfate and TDS. The volume of leachate expected to be generated from this option is less than for Option 1; however, it still has the potential to impact groundwater. The potential for groundwater to be impacted from this disposal option is considered to be moderate.

### **Disposal Option 3: Disposal of Stabilized/Fixated Gypsum**

The leachate quality for the disposal of stabilized/fixated gypsum may exceed the MCLs for cadmium, chromium, lead, and selenium, and silver (Table 7). In addition, the SMCLs for sulfate, TDS, and pH may be exceeded. However, the leachate volumes estimated from this disposal option are extremely low. With such low volumes of leachate released, the leachate constituents have the potential to become diluted to background levels upon mixing with the groundwater. The potential for groundwater impact from this disposal option is considered to be low.

## **Runoff Management**

### ***Comparison of Runoff Quality***

Runoff from each disposal option is a combination of rain water and the soluble components of the gypsum. The concentration of constituents in the runoff is dependent upon the contact time of the runoff water with the gypsum. Typically, the

contact time of the runoff with the gypsum is quite low; therefore, ion concentrations in the runoff water are expected to be less than ion concentrations reported in leachates. Table 4 lists leachate and runoff concentrations from disposed gypsum filtercake. Runoff concentrations are significantly less than the leachate concentrations. TDS of the runoff was 10,000 mg/L as compared to 37,000 mg/L in the leachate.

Although there is a lack of runoff water quality reported in the literature, the following generalizations can be made. Since leachate compositions for disposal Options 1 and 2, without co-disposal of fly ash, are similar, then runoff produced from these options are expected to be similar. The runoff is expected to have less metals, less total dissolved solids, and only comparable levels of the more soluble constituents such as sulfate and chloride as compared to their leachate results. Given the low ion concentrations expected in leachates from the stabilized/fixated gypsum, the runoff concentrations are also expected to be even lower and the lowest of all disposal options.

### ***Comparison of Controlled Discharges***

In this report, controlled discharges are considered to be the combined discharges of runoff and discharges from a sand drain if present beneath the landfilled gypsum. Addition of both runoff and collection from the sand drains provides a total estimate of the volume of water requiring management and treatment for each disposal option. Discharge estimates from runoff and from the sand drain for each disposal option were estimated using the HELP model. In general, disposal practices producing the largest volumes of uncontrolled discharges (leachate) produce the lowest volumes of controlled discharges. Upon closure of a facility, runoff is expected to contact the cover material and not the gypsum; therefore, treatment of runoff from a closed/inactive facility is not expected to be needed. As a result, controlled discharges estimated for each disposal option upon closure considers discharges estimated from the sand drain only and not runoff.

### **Disposal Option 1: Wet-Impoundment/Gypsum Stacking**

The wet-impoundment/gypsum stacking option considering both the pond and the gypsum stacks that are lined with compacted clay but without a sand drain produce the lowest controlled discharges. No runoff is anticipated to leave the pond. Therefore, during this facility's first year of operation, zero controlled discharges are estimated. Runoff, however, is expected from the gypsum stacks and is estimated at 83,000 ft<sup>3</sup>/yr for the second year of operation and at 420,000 ft<sup>3</sup>/yr at the end of thirty years. Beyond thirty years, runoff generated from the closed gypsum stacks will not require treatment, and therefore, controlled discharges requiring treatment at that time are considered to be zero.

Upon addition of the sand drain, the estimated controlled discharges triples for this disposal option and ranges from 260,000 ft<sup>3</sup>/yr after the first two years of operation to 4,300,000 ft<sup>3</sup>/yr after 30 years. Beyond thirty years, controlled discharges from the sand drain are estimated at 3,700,000 ft<sup>3</sup>/yr. Without the sand drain, the 3,700,000 ft<sup>3</sup>/yr would have been released as uncontrolled leachate to the groundwater.

### **Disposal Option 2: Macroencapsulation of Gypsum Filtercake**

Macroencapsulation of gypsum filtercake produces moderate amounts of controlled runoff as compared to the other disposal options. Controlled discharges are estimated at 1,000,000 ft<sup>3</sup>/yr during the thirty active years of the facility. Beyond thirty years, approximately 76,000 ft<sup>3</sup>/yr is anticipated as discharge from the sand drain.

### **Disposal Option 3: Disposal of Stabilized/Fixated Gypsum**

Controlled discharges estimated from the disposal of stabilized/fixated gypsum are similar to the controlled discharges estimated for macroencapsulation of gypsum filtercake (1,100,000 ft<sup>3</sup>/yr); however, field data to date shows that this controlled discharge can be reused or discharged without treatment. Upon closure of a stabilized/fixated FOS landfill, zero controlled discharges requiring treatment are anticipated. These results combined with the low anticipated leachate discharges with low constituent concentrations shows that this disposal option is clearly superior in terms of lowest potential for groundwater and surface water impacts.

## **Conclusions**

The above data clearly set forth the potential impact to groundwater quality by each of the most widely considered gypsum disposal options. Physical properties of materials and disposal economics for each option are important considerations and will be presented in subsequent papers.

Given the above modeling results, only the stabilization/fixation option can provide assurance of little or no groundwater degradation, even on sites with little available existing groundwater dilution for leachate. Similarly, stabilization/fixation offers wider operating choices to the management of surface runoff — an increasingly complex problem in today's power plants.

Finally, it is believed that the superior results in all the areas of water quality management studied for stabilization/fixation demonstrate that this technology can meet the tightening groundwater protection requirements that are integral to generator compliance.

**Table 1  
Literature Reported Values of  
Forced Oxidized FGD Pond Water (a)**

<i>Constituent/ Parameter</i>	<i>Range (mg/L)</i>	<i>Mean (mg/L)</i>	<i>Drinking Water Standards</i>
<u>Major Cations</u>			
Calcium	550 - 1300	946	
Magnesium	540 - 1100	775	
Sodium	62 - 116	89	
Potassium	5.9 - 43	27	
<u>Major Anions</u>			
Chloride	890 - 6600	2500	250
Sulfate	1438 - 3050	2500	250
Fluoride	2.4 - 6.5	4	2 - 4
<u>Trace Constituents</u>			
Aluminum	0.2 - 0.6	0.4	
Antimony	1.4	1.4	
Arsenic	<0.003 - 0.09	0.04	0.05
Barium	1		
Beryllium	0.004 - 0.05	0.025	
Boron	95 - 140	115	
Cadmium	0.003 - 0.009	0.004	0.01
Chromium (total)	0.09 - 0.51	0.23	0.05
Cobalt	0.1	0.1	
Copper	0.01 - 0.4	0.15	1
Iron	0.02	0.02	0.3
Lead	<0.01 - 0.67	0.27	0.05
Manganese	0.05		
Mercury	<0.0002 - 0.002	0.001	0.002
Molybdenum			
Nickel	0.33 - 0.5	0.42	
Selenium	0.035 - 0.14	0.09	0.01
Silicon			
Silver	0.005	0.005	0.05
Tin			
Vanadium			
Zinc	0.02 - 27	6.4	
<u>Parameters</u>			
TDS	6694 - 10756	9012	500
pH	5.8 - 7.4	6.57	6.5 - 8.5

(a) Sources: Aerospace Corporation. 1977. Disposal of By-Products from Nonregenerable Flue Gas Desulfurization Systems Second Progress Report. Prepared for Industrial Environmental Research Lab., Research Triangle Park, N. C. PB-271 728.

USEPA. 1980. Disposal of Flue Gas Desulfurization Wastes Shawnee Field Evaluation — EPA 625/2-80-028.

Morasky, et al. 1981. Evaluation of Gypsum Waste Disposal By Stacking. In Proceedings: Symposium on Flue Gas Desulfurization - Houston, October 1980; Volume 2.

**Table 2**  
**Literature Reported Values of Leachate from Forced Oxidized FGD Waste (a) after 50 Pore Volumes**

<i>Constituent/ Parameter</i>	<i>Concentration (mg/L)</i>	<i>Drinking Water Standards</i>
<b>Major Cations</b>		
Calcium	100	
Magnesium		
Sodium		
Potassium		
<b>Major Anions</b>		
Chloride	100	250
Sulfate	1200	250
Fluoride	0.08	2 - 4
<b>Trace Constituents</b>		
Aluminum		
Antimony		
Arsenic	0.005	0.05
Barium	1	
Beryllium	<0.005	
Boron		
Cadmium	0.002	0.01
Chromium (total)	<0.003	0.05
Cobalt		
Copper		1
Iron		0.3
Lead	0.01	0.05
Manganese		0.05
Mercury	<0.0005	0.002
Molybdenum		
Nickel		
Selenium	0.006	0.01
Silicon		
Silver		0.05
Tin		
Vanadium		
Zinc	0.04	
<b>Parameters</b>		
TDS	2200	500
pH	5.5	6.5 - 8.5

(a) Source: USEPA (1979) Disposal of By-Products from Non-Regenerable Flue Gas Desulfurization Systems: Final Report, EPA 600/7-79-046.

**Table 3**  
**Literature Reported Values of Leachate From Forced Oxidized FGD Filtercake (a)**

<i>Constituent/ Parameter</i>	<i>Range (mg/L)</i>	<i>Mean (mg/L)</i>	<i>Drinking Water Standards</i>
<b>Major Cations</b>			
Calcium	1420 - 2220	1788	
Magnesium	440 - 740	528	
Sodium			
Potassium			
<b>Major Anions</b>			
Chloride	3330 - 3930	3630	250
Sulfate	788 - 1800	1136	250
Fluoride			2 - 4
<b>Trace Constituents</b>			
Aluminum	1	1	
Antimony			
Arsenic	<0.01 - 0.02	0.02	0.05
Barium	0.05 - <0.5	0.15	1
Beryllium	0.05	0.05	
Boron			
Cadmium	<0.01 - 0.02	0.01	0.01
Chromium	<0.05 - 0.06	0.05	0.05
Cobalt			
Copper	0.07	0.07	1
Iron	0.07 - 0.2	0.01	0.3
Lead	0.12 - 1.43	0.45	0.05
Manganese	0.12	0.12	0.05
Mercury	0.0008 - 0.001	0.0009	0.002
Molybdenum			
Nickel	0.06	0.06	
Selenium	0.02 - 0.065	0.04	0.01
Silicon	<0.05 - 0.05	0.05	
Silver			0.05
Tin			
Vanadium			
Zinc			
<b>Parameters</b>			
TDS	2138 - 10490	6000	500
pH	5 - 6.6	5.4	6.5 - 8.6

(a) Source: USEPA (1979) Disposal of By-Products from Non-Regenerable Flue Gas Desulfurization Systems: Final Report, EPA 600/7-79-046.

**Table 4  
Chemical Composition of Leachate and Runoff  
from Forced Oxidized FGD Filtercake**

<i>Constituent/ Parameter</i>	<i>Leachate</i>		<i>Runoff</i>		<i>Drinking Water Standards</i>
	<i>Range (mg/L)</i>	<i>Mean (mg/L)</i>	<i>Range (mg/L)</i>	<i>Mean (mg/L)</i>	
<b><u>Major Anions</u></b>					
Chloride	272 - 38145	21770	560 - 19203	6138	250
Sulfate	390 - 1018	678	544 - 1590	1111	250
Fluoride	0.98	0.98	0.59 - 1.2	1	2 - 4
<b><u>Trace Constituents</u></b>					
Aluminum					
Antimony					
Arsenic	<0.01 - <0.05	<0.05	<0.01 - 0.53	0.26	0.05
Barium					1
Beryllium					
Boron					
Cadmium	<0.01 - 0.07	0.01	<0.1 - 0.3	0.175	0.01
Chromium	<0.05 - 0.10	0.05	<0.05 - 0.05	0.03	0.05
Cobalt					
Copper	<0.05 - 0.5	0.07	<0.05 - <0.5	0.14	1
Iron	<0.1 - 5.2	0.88	<0.1 - 0.3	0.1	0.3
Lead	<0.05 - 1.2	0.09	<0.05 - 0.40	0.21	0.05
Manganese	<0.05 - 0.87	0.43	<0.05 - 0.37	0.2	0.05
Mercury	<0.001 - <0.002	<0.002	<0.001 - <0.002	<0.001	0.002
Molybdenum					
Nickel	<0.05 - 0.6	0.09	<0.05 - 0.26	0.14	
Selenium	<0.01 - <0.05	<0.05	<0.01 - <0.02	<0.01	0.01
Silicon					
Silver					0.05
Tin					
Vanadium					
Zinc	<0.05 - 0.12	0.05	<0.05 - <0.1	<0.1	
<b><u>Parameters</u></b>					
TDS	2096 - 46588	36811	2716 - 18700	10708	500
pH	6.0 - 7.4	6.4 (d)	6.4 - 8.1	6.7	6.5 - 8.5

**Table 5  
Literature Reported Values of Leachate From  
Stabilized/Fixated Forced Oxidized FGD Waste (a)**

<i>Constituent/ Parameter</i>	<i>Range (mg/L)</i>	<i>Mean (mg/L)</i>	<i>Drinking Water Standards</i>
<u>Major Cations</u>			
Calcium	67 - 647	520	
Magnesium			
Sodium			
Potassium			
<u>Major Anions</u>			
Chloride	40 - 80	60	250
Sulfate	85 - 1356	886	250
Fluoride			2 - 4
<u>Trace Constituents</u>			
Aluminum			
Antimony			
Arsenic	0.005 - 0.032	0.014	0.05
Barium	<0.5 - <1	<1	1
Beryllium			
Boron	0.25 - 1.6	0.925	
Cadmium	<0.01 - 0.10	0.04	0.01
Chromium	<0.05 - 0.20	0.09	0.05
Cobalt			
Copper	<0.1	<0.1	1
Iron	<0.1	<0.1	0.3
Lead	<0.05 - 0.56	0.15	0.05
Manganese			0.05
Mercury	0.0008 - 0.0052	0.0014	0.002
Molybdenum			
Nickel	0.05	0.05	
Selenium	0.002 - 0.043	0.018	0.01
Silicon	<0.05	<0.05	
Silver	<0.01 - 0.05	0.03	0.05
Tin			
Vanadium			
Zinc	<0.1	<0.1	
<u>Parameters</u>			
TDS	177 - 2372	1865	500
pH	6.6 - 10.5	7.6	6.5 - 8.5

(a) Source: Conversion Systems, Inc.

Source: Golden, D.M. 1981. EPRI FGD Sludge Disposal Demonstration and Site Monitoring Projects; In Proceedings: Symposium on Flue Gas Desulfurization Houston, October 1980; Volume 2. EPA-0600/9-81-09b.

**TABLE 6**

**Option 1 - Wet-ponding of FGD Sludge and Stacking of Settled Material**

				Average Annual Discharge Rate (Cubic feet per year per 100,000 square feet disposal area)		Peak Daily Discharge Rate (Cubic feet per day per 100,000 square feet disposal area)	
				Controlled	Uncontrolled	Controlled	Uncontrolled
Pond area lined with 1 foot of compacted clay							
Leachate					165,610		453.4
Lined FGD Stack Area - Open/Active							
Runoff				33,647		5,640	
Drainage from drain layer				69,556		797	
Leachate					12,999		49.9
Lined FGD Stack Area - Closed/Inactive							
Runoff (Does not need to be treated)							
Drainage from drain layer				49,357		222	
Leachate					12,999		37.2
				Average Annual Discharge Rate (Cubic feet per year)		Peak Daily Discharge Rate (Cubic feet per day)	
				Controlled	Uncontrolled	Controlled	Uncontrolled
Year	Pond Area (Square feet)	Open Stack Area (Square feet)	Closed Stack Area (Square feet)				
1	2,180,000	0	0	0	3,610,298	0	9,884
2	2,180,000	248,520	0	256,480	3,642,603	15,998	10,008
5	2,180,000	994,080	0	1,025,920	3,739,518	63,992	10,380
10	2,180,000	1,242,600	1,242,600	1,895,711	3,933,349	82,748	10,966
15	2,180,000	1,242,600	2,485,200	2,509,021	4,094,875	85,507	11,429
20	2,180,000	1,242,600	3,727,800	3,122,331	4,256,400	88,266	11,891
25	2,180,000	1,242,600	4,970,400	3,735,641	4,417,926	91,024	12,353
30	2,180,000	1,242,600	6,213,000	4,348,951	4,579,451	93,783	12,815
>30	0	0	7,455,600	3,679,860	969,153	16,551	12,658

**TABLE 7**

**Option 2 - Macro-encapsulation of dewatered FGD sludge**

				Average Annual Discharge Rate (Cubic feet per year per 100,000 square feet disposal area)		Peak Daily Discharge Rate (Cubic feet per day per 100,000 square feet disposal area)	
Case 1				Controlled	Uncontrolled	Controlled	Uncontrolled
Lined FGD disposal area - Open/Active							
Runoff				143307		7882	
Drainage from drainage layer				12348		91	
Leachate					10864		32
Lined FGD disposal area - Closed/Inactive							
Runoff (Does not need to be treated)							
Drainage from drainage layer				1838		10	
Leachate					10367		29
				Average Annual Discharge Rate (Cubic feet per year)		Peak Daily Discharge Rate (Cubic feet per day)	
				Controlled	Uncontrolled	Controlled	Uncontrolled
Year	Open Area (Square feet)	Closed Area (Square feet)					
5	667,080	0		1,038,343	72,472	53,186	213
10	667,080	667,080		1,050,604	141,628	53,253	407
15	667,080	1,334,160		1,062,865	210,784	53,320	600
20	667,080	2,001,240		1,075,126	279,940	53,386	794
25	667,080	2,668,320		1,087,387	349,096	53,453	987
30	667,080	3,335,400		1,099,648	418,252	53,520	1,181
>30	0	4,002,480		73,566	414,937	400	1,161

**TABLE 8**

**Option 3 - Unlined disposal of stabilized/fixed FGD sludge**

			<i>Average Annual Discharge Rate (Cubic feet per year per 100,000 square feet disposal area)</i>		<i>Peak Daily Discharge Rate (Cubic feet per day per 100,000 square feet disposal area)</i>	
<i>Case 1</i>			<i>Controlled</i>	<i>Uncontrolled</i>	<i>Controlled</i>	<i>Uncontrolled</i>
Unlined FGD disposal area - Open/Active						
	Runoff		185.123		9.950	
	Leachate			0		0
Unlined FGD disposal area - Closed/Inactive						
	Runoff (Does not need to be treated)			2		0.1
	Leachate					
			<i>Average Annual Discharge Rate (Cubic feet per year)</i>		<i>Peak Daily Discharge Rate (Cubic feet per day)</i>	
			<i>Controlled</i>	<i>Uncontrolled</i>	<i>Controlled</i>	<i>Uncontrolled</i>
Year	Open Area (Square feet)	Closed Area (Square feet)				
5	610,400	0	1,129,991	0	60,735	0
10	610,400	610,400	1,129,991	12	60,735	1
15	610,400	1,220,800	1,129,991	24	60,735	1
20	610,400	1,831,200	1,129,991	37	60,735	2
25	610,400	2,441,600	1,129,991	49	60,735	2
30	610,400	3,052,000	1,129,991	61	60,735	3
>30	0	3,662,400	0	73	0	4

**COMMERCIAL AGGREGATE PRODUCTION  
FROM FGD WASTE**

**Charles L. Smith  
Conversion Systems, Inc.  
200 Welsh Road  
Horsham, Pennsylvania 19044**



#### ABSTRACT

A commercial quality aggregate can be made from flue gas desulfurization wastes. This aggregate is capable of meeting American Society for Testing and Materials specifications for construction aggregate -- even the stringent Los Angeles Abrasion Test for toughness. The result of a 12 year development program, this aggregate can be lightweight or normal weight.

The rationale behind this development is two fold, the first reason is that FGD is expensive, an added cost to power generation. Any possible byproduct that can reduce overall costs, including minimizing landfill space consumed, is a benefit.

A second fact that lent emphasis to the program is that although the United States consumes over one billion tons of aggregate per year, aggregate is in scarce supply in many parts of the country. It is becoming increasingly more expensive as regulatory constraints cause the opening of new sources to replace exhausted old ones, to be extremely difficult, if not impossible.

The paper presents test data on aggregate and aggregate end uses focusing on concrete masonry units. A strong advantage is the ability to use either forced oxidation or unoxidized FGD waste in aggregate production.

## INTRODUCTION

Our reason for being here today is elementary; the Clean Air Act Amendments have initiated another surge of pulverized coal electric generating facility scrubbing. The logical sequence of events, comparable to the early wave of scrubbing in the 1970's and early 1980's, is that we clean up the air and produce substantial quantities of solid waste; this, in turn, must be dealt with in an environmentally safe manner. Similar to that earlier period, there are applications where coal cleaning or coal switching are the answers to CAAA compliance, but for the overwhelming majority of power plants, scrubbing is the most cost effective answer. Scrubbers come in several general classes, as we all know. Regenerative processes have been built in limited numbers, dry scrubbers have been well proven for limited SO<sub>2</sub> reduction levels, but the bulk of past and future scrubbers appear to be wet throw-away processes producing either calcium sulfite hemihydrate or calcium sulfate dihydrate (gypsum). Historically, disposal of throw-away scrubber sludges was a problem. The solution most commonly used is fixation by dewatering followed by fly ash and lime interblending.

## REUSE

There have been many efforts to make constructive use of the cementitious character of fixated scrubber sludge, beyond its initial purpose as an environmentally safe landfill disposal method. Significant success has been achieved in utilizing this material as a roadbase medium, with somewhere in excess of a quarter million tons sold for that purpose. This tends to be an erratic market; road construction is not a continuous demand.

Focusing on potential usages that are more continuous and uniform in quantity demanded, the search quickly narrows in on aggregate as a promising market.

## AGGREGATE IN THE UNITED STATES

This nation consumes over one billion tons of aggregate annually. In many areas of the country, aggregate is in scarce supply and must be transported from significant distances. The difficulty is enhanced as regulatory constraints tighten on existing sources. Permitting for new aggregate sources, to replace exhausted quarries, has become extremely difficult.

Following this rationale, production of an aggregate from the pozzolanically cementitious scrubber sludge - fly ash - lime composition was selected as a desirable target. It has taken twelve years work to bring this concept to the commercial level achieved as of this symposium.

Simple economics will point out that the cost of extracting a natural aggregate, as opposed to the cost of manufacturing one, is low. However, aggregates are transportation sensitive; that is, hauling costs are large in relationship to the actual value of the aggregate. Note specifically that aggregate uses are predicated upon volume, not weight. In concrete, concrete block, and in highway construction, the aggregate fills a volume; as long as it has sufficient strength and durability, the weight of that volume is not of importance. If available at a comparable price, a 60 pound per cubic foot aggregate (with adequate physical properties) can substitute for a 120 pound per cubic foot aggregate. The cost of hauling is significantly less.

## CHEMISTRY OF THE PROCESS

The Poz-O-Tec process or comparable processes, are in operation at over 35 locations in the U.S., production of lightweight aggregate can be carried out on wastes from wet scrubbing by lime, limestone, or dual alkali scrubbers. The scrubbing can be with or without forced oxidation, as long as the general waste composition falls largely within the ranges given in Table I.

It should be obvious that the demand for a commercial aggregate product is greater than those for a hardening landfill disposal process; quality control constraints for the process are more demanding.

#### LIGHTWEIGHT AGGREGATES

Until the 1970's, when energy costs jumped drastically, there were many lightweight aggregates produced in this country by heat processes. Hundreds of heat expanded clay, shale, slate, and perlite sources were spread throughout the county. Because of energy costs, few are left. There are a very few plants producing no-heat or low-heat, cementitiously set aggregate.

The majority of lightweight aggregate is utilized in the production of concrete masonry units, where there are specific advantages to lightweight aggregate:

- Lower transportation costs,
- Lower block laying costs,
- Superior insulating characteristics,
- Superior acoustical characteristics,
- Superior fire resistance.

To achieve acceptability as a lightweight aggregate, the potential product must comply with American Society for Testing and Materials requirements. The largest market for a lightweight aggregate is in concrete masonry units, therefore compliance with ASTM C-331 STANDARD SPECIFICATION FOR LIGHTWEIGHT AGGREGATES FOR CONCRETE MASONRY UNITS is critical.

Table II provides these requirements along with typical values for the new FGD waste-derived aggregate. In examination of this Table, it is

noted that there are five particle size gradations listed in the specifications; these are a function of the physical crushing and screening, and are not relevant to the material itself. Table III indicates that the vital characteristics, with given specifications, are met by the new aggregate. Figure I shows the material.

#### Greater Yield

Typical aggregates for block making are siliceous or calcareous in nature. When sized for concrete masonry unit production, the new product has from about 50 to 75% of the bulk density of conventional types. It is obvious that an increase in blocks produced per ton of aggregate of up to 75% can be obtained. This advantage has been readily understood by users. Figures II and III show blocks being produced, and ready for shipment, respectively.

#### Labor

If the concrete masonry units produced are substantially lighter, then they are less taxing for the mason to handle. The result is more blocks laid per day per man. Or, in the areas in the United States that have very specific union rules, the difference can reduce the number of men required for placement.

#### Improved Insulating Characteristics

Insulation in building materials is a function of density, or entrapped air. Historically, lightweight concrete masonry units have substantially superior insulating characteristics, as delineated in Table VI. Air conditioning, or home heating, efficiency is increased, resulting in a distinctive economic advantage.

#### Improved Fire Resistance

Along with improved insulating characteristics, the thermal flow in these concrete masonry units provides resistance to degradation by fire. A University of Ohio fire wall test gave a superior, two hour

rating to concrete blocks produced from the new lightweight aggregate (Figure 4).

#### Acoustical Insulation

Another clear advantage of lower density block is acknowledged to be lower sound transmission characteristics.

#### THE NEW AGGREGATE

The new FGD waste-derived lightweight aggregate (Poz-O-Lite) required many years to fully develop. Final block producer plant trials were completed in mid 1991. Test data given in Tables IV and V are on concrete masonry units produced at two commercial facilities, using Poz-O-Lite. The tests were by independent testing laboratories. Compare the data with Table III which gives ASTM C-90 SPECIFICATION FOR HOLLOW LOADBEARING CONCRETE MASONRY UNITS.

Concrete masonry units produced from the new Poz-O-Lite aggregate meet ASTM C-90.

#### COMMERCIAL PRODUCTION FACTORS

Those pulverized coal burning power stations whose wet scrubbers produce an oxidized or unoxidized waste have the raw material for commercial production. Although all testing has not been completed, the indications are that nearly every FGD lime or limestone scrubber waste can be used in the Poz-O-Lite process. Oxidized wastes seem to give a superior product.

#### CONCRETE AGGREGATE TESTS

The previous discussion has focused upon the largest market for lightweight aggregate, in concrete masonry units. Developmental scale tests on Poz-O-Lite for concrete usage have been promising. There seems to be full capability for meeting ASTM C332 LIGHTWEIGHT AGGREGATE FOR STRUCTURAL CONCRETE. Similarly, laboratory tests have indicated the

ability to meet even ASTM C33 STANDARD SPECIFICATION FOR CONCRETE AGGREGATE, including the rigorous Los Angeles Abrasion Resistance requirement.

#### STATUS

The commitment in shifting from a landfill disposal to a commercial product requires caution. The developmental program that generated the new concept was begun over 12 years ago. Since long term durability is an essential in building materials, the first concrete block test walls and test buildings were constructed nearly 10 years ago. Figure 5 shows the first building, constructed in 1982, still standing today with no degradation of the concrete masonry units utilized in its construction. A decade of performance testing would seem promising. As of this writing, full scale commercial production of Poz-O-Lite has begun.

**TABLE I**

**RANGE OF CONSTITUENTS: FGD WASTE SOLID PHASE**

Calcium Sulfite Hemihydrate	1 to 98%
Calcium Sulfate Dihydrate	1 to 99%
Calcium Carbonate	0 to 30%
Fly Ash	0 to 65%
Magnesium Sulfate Hexahydrate	0 to 4%
Calcium Hydroxide	0 to 3%
Sodium Chloride	0 to 3%

**TABLE II**  
**FGD WASTE - DERIVED AGGREGATE FOR MASONRY**

ASTM C-331	SYNTHETIC AGGREGATE
● FIVE GRADATIONS	CONTROLLED BY SCREENING OPERATION
● UNIT WEIGHT (LB.FT <sup>3</sup> ) Coarse Sizes 55 Maximum Fine 70 Maximum Combined Sizes 65 Maximum	54 62 60
● ORGANIC IMPURITIES "Little or None"	NONE
● STAINING None	NONE
POPOUTS None	NONE
CLAY LUMPS AND FRIABLES 2% Maximum	<1%
Drying Shrinkage 0.1% Maximum	0.074%

TABLE III

CONCRETE MASONRY UNITS FROM FGD WASTE - DERIVED AGGREGATE

ASTM C-90	CONCRETE MASONRY UNITS TEST DATA
COMPRESSIVE STRENGTH (PSI)	1000 MIN (AVERAGE)
GROSS AREA	800 MIN (INDIVIDUAL)
UNIT WEIGHT (LBS/FT <sup>3</sup> )	
LIGHT WEIGHT	< 105
MEDIUM WEIGHT	105 TO 125
NORMAL WEIGHT	> 125
ABSORPTION (LB/FT <sup>3</sup> )	
LIGHT WEIGHT	18 MAX
MEDIUM WEIGHT	15 MAX
NORMAL WEIGHT	13 MAX
DRYING SHRINKAGE (%)	0.065 MAX

**TABLE IV**  
**CONCRETE MASONRY UNITS: PRODUCER B**

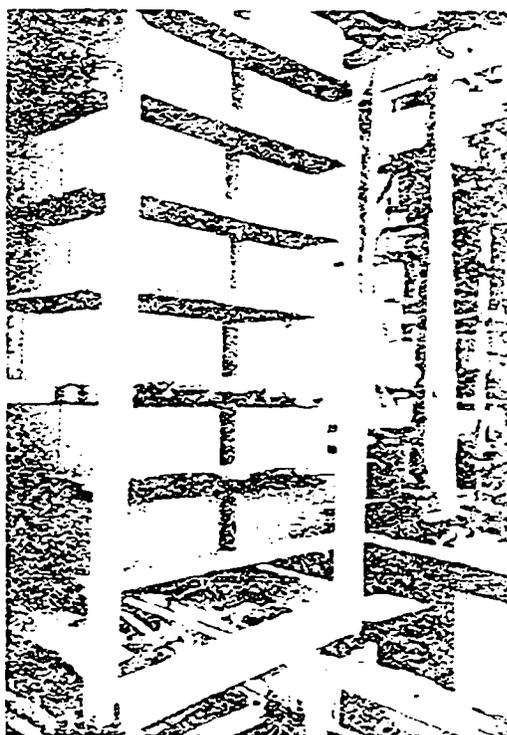
	<u>Run #1</u>	<u>Run #2</u>
STRENGTH (psi)	1466	1155
BLOCK WEIGHT (LBS)	34.2	32.5
DENSITY (LB/FT <sup>3</sup> )	118.5	114.8
ABSORPTION (LB/FT <sup>3</sup> )	12.65	12.77
DRYING SHRINKAGE (%)		
MAX:0.065%	0.0440	0.0597

**TABLE V**  
**CONCRETE MASONRY UNITS: PRODUCER C**

	Run #1	Run #2	Run #3	Run #4	Run #5	Run #6
COMPRESSIVE STRENGTH (PSI)	1259	1397	1294	1388	1154	1242
BLOCK WEIGHT (LBS)	32.2	32.0	32.0	32.1	31.8	31.3
UNIT WEIGHT (LB/FT <sup>3</sup> )	115.6	114.4	113.4	114.8	111.5	111.4
ABSORPTION (LB/FT <sup>3</sup> )	15.7	16.1	16.5	15.7	17.2	17.2
(%)	13.6	14.1	14.6	13.6	15.5	15.5
DRYING SHRINKAGE (%)	0.057	0.025	0.033	0.045	0.045	0.039

**TABLE VI**  
**INSULATING CHARACTERISTICS OF CONCRETE MASONRY UNITS**

	RESISTANCE (°F/BTU/HR/FT <sup>2</sup> )	CONDUCTIVITY (BTU/HR/FT <sup>2</sup> /°F)
8 x 12 x 16"		
Conventional Aggregate	1.28	0.78
Lightweight Aggregate	2.63	0.38
8 x 8 x 16"		
Conventional Aggregate	1.11	0.90
Lightweight Aggregate	2.27	0.44



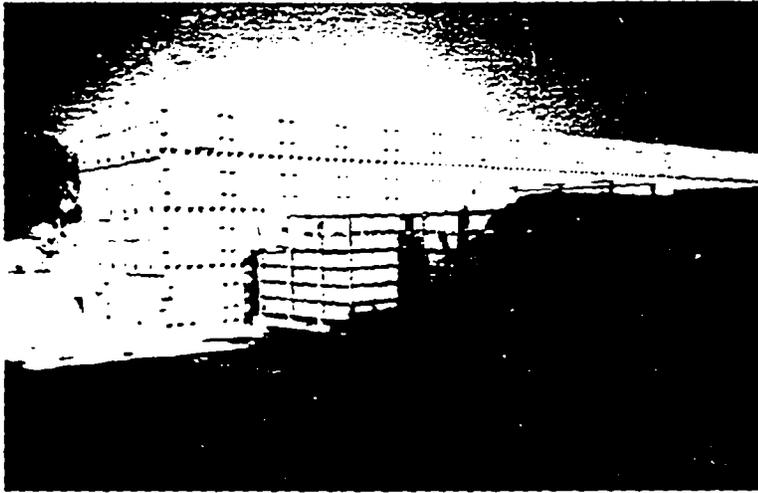


Figure 3. FGD Lightweight Aggregate Block  
Ready For Shipment

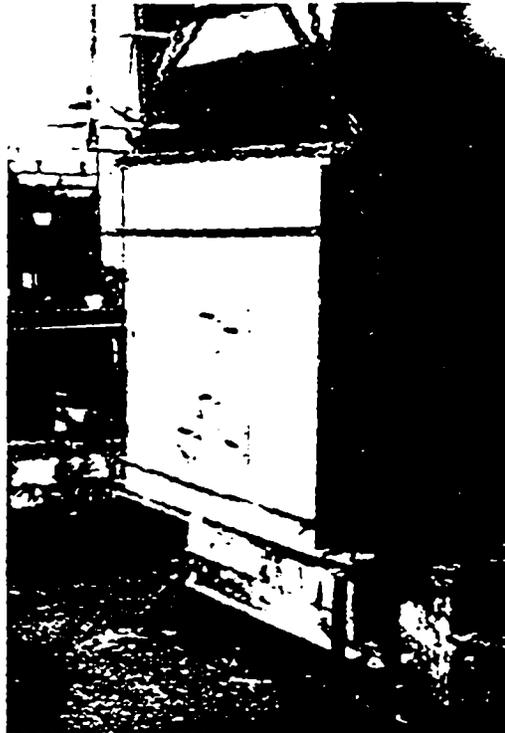


Figure 4. Block Fire Wall Testing  
At University Of Ohio

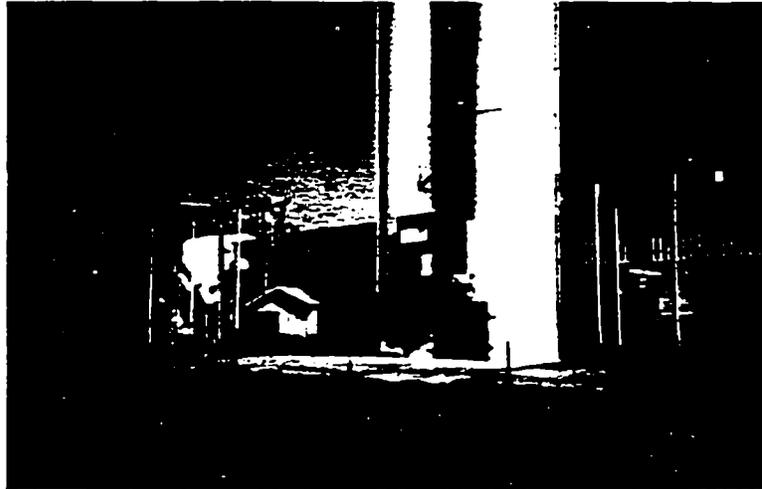


Figure 5. Initial Building Using FGD  
Byproduct Aggregate Stands Without Flaw  
After Nearly Ten Years.