Dry Scrubbing Technologies for Flue Gas Desulfurization

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Sponsored by

Ohio Coal Development Office
Ohio Department of Development
Jacqueline F. Bird, Director

KLUWER ACADEMIC PUBLISHERS
Boston / Dordrecht / London

Distributors for North, Central and South America:
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101 Philip Drive
Assinippi Park
Norwell, Massachusetts 02061 USA
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Distributors for all other countries:
Kluwer Academic Publishers Group
Distribution Centre
Post Office Box 322
3300 AH Dordrecht, THE NETHERLANDS
Telephone 31 78 6392 392
Fax 31 78 6546 474
E-Mail <services@wkap.nl>

Electronic Services <http://www.wkap.nl>

Library of Congress Cataloging-in-Publication Data

A C.I.P. Catalogue record for this book is available
from the Library of Congress.

Printed on acid-free paper.

Printed in the United States of America

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Preface

The State of Ohio has long encouraged the use of its vast reserves of coal. Support has come primarily through the Ohio Coal Development Office (OCDO), an entity within the Ohio Department of Development. Among other things, OCDO is charged with the development of technologies and processes that can use coal in an economical, environmentally sound manner. Although primarily focused at the demonstration end of the research and development continuum, OCDO is also directed to ". . . ensure that an adequate portion [of its funds] be used for conducting research on fundamental scientific problems related to the utilization of Ohio coal . . .." [Ohio Revised Code, Sec. 1555.03(B)]

Since its inception in 1984, OCDO has cofunded over 100 projects, the majority of them at the research level. Early on, OCDO noticed that many of the colleges and universities were performing similar but varied types of coal research. As Professor L. Douglas Smoot of Brigham Young University notes in his review of directions in coal research (*Energy and Fuels*, Vol. 7, page 689, 1993), six pertinent areas that merit further attention include: (1) boiler-efficiency, (2) carbon carry over, (3) fouling, (4) SO_x removal, (5) NO_x control, and (6) coal gasification. OCDO, recognizing its charge to hasten the development, installation and use of clean coal technologies, concentrated its research efforts on Item 4, SO_x removal.

OCDO created and funded the Ohio Coal Research Consortium (OCRC) in 1990. Its broad objective was to "improve the efficiency of 'dry' high-sulfur-coal flue gas SO_2 removal processes using calcium-based sorbent injection." The consortium was comprised of four universities—Case Western Reserve University, Ohio University, The Ohio State University, and University of Cincinnati. It was designed to support useful and relevant fundamental research to improve existing processes and to develop new ideas and improved process technologies. The consortium members worked very closely with an industrial and governmental advisory committee representing researchers and experts from U.S. DOE, U.S. EPA, EPRI, utilities, private research institutions and companies.

The consortium was organized into several focus areas, such as dry sorbent processes at high temperature (upper furnace), dry and wet/dry sorbent processes at medium temperature (economizer region), and low temperature processes (in-duct/spray dryer). The technical objectives of the consortium included reaction engineering issues, such as identifying and quantifying fundamental chemical/physical mechanisms of dry and wet/dry SO_2 removal processes, and formulating rate models for these processes. In addition to the above fundamental studies, the consortium identified applied areas of research that needed attention, such as the development and evaluation of chemical additives, better sorbent production, and mechanistic models for enhancement processes. The four universities shared these projects based on their expertise and experience.

Dry desulfurization processes offered significant advantages of low capital and low operating costs when compared to wet desulfurization. It held great economic potential for economically reducing the sulfur emissions from power utilities using high-sulfur coal such as that in the State of Ohio. However, the technology still had not matured sufficiently and was achieving lower-than-desired SO_2 removal efficiencies, and sorbent under-utilization. Hence the consortium served to bring together a specific group of scientists and researchers who were interested in and capable of pursuing research in these areas. The consortium dedicated itself to the common goal of improving the state-of-the-art of dry sorbent processes. Promoting high-sulfur Ohio coals by developing efficient sulfur removal technologies provided the motivation for OCDO to undertake this massive and challenging task.

In the fourth year of the consortium, the scope of work expanded to include hazardous air pollutants and dry processes to control their emissions. The Title III trace toxics were likely to be regulated by the EPA as hazardous emissions from power utilities so the consortium decided to investigate the fundamental characteristics of their formation and control.

The efforts of the consortium members have led to a number of significant scientific breakthroughs, major advancements in our knowledge, and new ideas for process development. Throughout the last five years, a number of fundamental research findings have had a significant and lasting impact in terms of scientific understanding and the development of new and improved processes. A few are worth highlighting:

- The experimental investigation of the upper-furnace sulfur capture obtained time-resolved kinetic data in less than 100 ms time-scales for the first time ever, revealing the true nature of the ultrafast and overlapping phenomena. This was accomplished through the development of a unique, first-of-its-kind entrained flow reactor system.
- Mechanistic investigations of the CaO/SO_2 reaction showed conclusively for the first time the true mechanism of outward ionic diffusion of Ca^{++} and O_2-ions through the product $CaSO_4$ layer.
- Work on the influence of sorbent internal pore structure and size distribution on SO_2 reactivity has led to identification of criteria that can lead to great improvements in reactivity.

- Heavy metals research led to the identification of the true mechanism of selenium interaction with sorbents under the high temperature flue gas conditions.
- The role of chemical additives in SO_2 capture efficiency was elucidated and modeled in the dry scrubbing process.
- Research on the spray dryer for desulfurization resulted in the development of methods and additives that allow these devices to achieve >95% SO_2 removal, along with a discovery that would allow them to reach >99% removal rates of SO_2 in the future. This work is currently undergoing patent review.
- Research into attrition and reaction kinetics of wet/dry gas-sorbent reactions has led to the development of a circulating fluidized bed absorber system that is undergoing demonstration and commercialization.
- Work on the advanced sorbents has resulted in the development of a porous lime-silica sorbent and a mixed portland cement-lime sorbent. These low cost, mixed sorbents are prepared from readily available raw materials and have shown remarkably high SO_2 reactivity. The sorbent and its preparation technique have been patented by researchers. These sorbents are also being developed for selenium and other trace toxics.
- Research into the sorbent dispersion phenomena has led to the identification of optimum particle loading that results in good mixing between particles and cocurrent flue gas flow in ducts. An improved nozzle design, requiring no extra energy, has been suggested for more efficient sorbent injection.
- Research work in the granular limestone scrubbing process resulted in the scale-up and development of a continuously operating pilot plan. This work provided design data for scale-up and operation on a commercial scale.

These major achievements earned the consortium members a number of prestigious awards and honors.

The researchers have contributed to the education and training of graduate students to become skilled researchers and innovators. The four universities granted a total of 19 M.S. and 17 Ph.D. degrees, with 17 more working toward the completion of their degrees. The group has published more than 40 peer-reviewed journal articles and made over 54 presentations at various national and international meetings. The OCDO funds helped generate additional research funds from other government and industrial sources. These efforts have resulted in approximately $3,200,000 in external support from federal agencies and industrial sources between 1990 and 1995.

Another important purpose of the consortium was the training of skilled scientific personnel in the State of Ohio that would continue the development of environmental technologies for the safe and efficient use of the nation's fossil resources.

Funding from OCDO for the entire program was nearly five million dollars, or approximately one million dollars per year. Each year, the projects were reviewed by the Consortium Review Committee, experts from private research institutions, the electric power production sector, the coal production sector, the federal government, and others. Based on these yearly progress reviews, the suite of funded projects evolved. The scope of research was expanded in 1993 to include a number of basic trace metal studies. These are not included in the present document.

The Consortium Review Committee evaluated individual project proposals and recommended broad program direction. The OCRC Steering Committee, comprised of one individual from each school, fine tuned program direction. The OCDO provided program oversight, management, and funding.

Dr. Michael Prudich (Ohio University) served as program manager of the OCRC from 1990 to 1992. His role was to review and edit OCRC publications, to perform other administrative functions, and to arrange meetings. These meetings were often held at Ohio power plants hosting various clean coal technology demonstration projects that the OCRC toured and evaluated. Dr. Prudich was succeeded by Dr. Kendree Sampson (Ohio University) from 1992 through 1996.

Most of the research produced by the OCRC in the 5-year program is presented in this monograph. Each of the chapters is a complete body of work with detailed literature survey, description of the work undertaken, the results obtained, and the significance of the results to dry desulfurization technologies.

Chapter 1, "Flue Gas Desulfurization (FGD) for Acid Rain Control," serves as a general introduction and provides a critical literature review of the state-of-technology of dry, calcium-based sorbents and processes. It contains the original position paper that defined the scope of the consortium.

Chapter 2, "New Calcium-Based Sorbents for Flue Gas Desulfurization." Proceeding from early findings that $Ca(OH)_2$-fly ash sorbents showed a special reactivity related to the silicates in fly ash, a series of "C-S-H" (CaO-SiO_2-H_2O) sorbents was developed and evaluated for SO_2 uptake.

Chapter 3, "Fundamental Studies Concerning Calcium-Based Sorbents." This study responded to the need for advances in sorbent materials, both in terms of the chemistry and the processing methods. This work focused on the role of additives for enhancing SO_2 removal. The lowering of water vapor pressure may be the primary cause for enhancement.

Chapter 4, "Sorbent Transport and Dispersion." This study examines the cohesive nature of powders and its influence on powder dispersion due to shear stress in nozzles to simulate flow structure in a nozzle. A model that simulates flow structure in a nozzle is also discussed in this chapter.

Chapter 5, "Transport Process Involved in FGD," along with Chapter 4, considers the characteristics and optimization of transport and dispersion of sorbents in ducts and the interactions between sorbent physical characteristics and dispersibility. In this program Doppler interferometry/laser Doppler velocimetry are used to develop nonintrusive procedures for examination of flow reversal zones in ducts.

Chapter 6, "High Temperature Desulfurization of Flue Gas Using Calcium-Based Sorbents." High-temperature, fast reaction kinetics are used to examine internal structural properties such as pore structure and surface area. The results are also applied to the development of a model.

Chapter 7, "Kinetic Studies on the Medium Temperature $Ca(OH)_2$ Sorbent Injection FGD Process." Medium temperature (600-1100°F) kinetics are developed for dehydration, sulfation and carbonation processes.

Chapter 8, "Advances in Spray Drying Desulfurization for High-Sulfur Coals." In this work sorbent properties are related to hygroscopicity. Additives are employed which increase dissolution rate and oxidation potential. A model is developed which examines the drying of slurry droplets, mass transfer, and reaction in the droplet.

Chapter 9, "Low Temperature Dry Scrubbing/Limestone Emission Control (LEC) Support," along with Chapter 8, investigates sorbent reactivity in three temperature regions of interest. Chapter 8 reports on low temperature kinetics in spray drying systems and Chapter 9 considers low temperature kinetics in a granular limestone process. Effects of temperature on limestone solubility and dissolution rates show that only the latter is significant.

Chapter 10, "Simulation and Optimization of a Granular Limestone FGD Process," along with Chapters 8 and 9, advances the understanding of particular desulfurization processes. Based on a computer simulation of the Limestone

Emission Control (LEC) system, optimum operating conditions are predicted. LEC appears best suited for high-sulfur coal, small scale applications.

As noted, the consortium has been successful in advancing the dry sorbent processes from their initial, not yet mature state in 1990, to a more evolved and mature technology. The consortium efforts have led to some major improvements that mark the beginning of the next generation of advanced dry sorbent processes. The consortium has also played a significant role in developing dry processes for other pollutants such as trace heavy metals which now represent an entirely new area of application for dry sorbent processes. It also sets the stage for Consortium II efforts which began in September 1996 with the objective of examining advanced dry technologies for acid gas and trace toxics characterization and emission control for Ohio coal. The theme for Consortium II reflects the emphasis on the state-of-the-art processes impacting the utilities' industries and the energy sector in general. Specifically, the advanced low-NO_x pulverized combustors and combined cycle generation systems, such as integrated gasification combined cycle and pressurized fluidized combustors, represent the processes that are of significant interest to the State of Ohio and the U.S. today. These processes will dominate power generation in the future. Consortium II represents the commitment of the State of Ohio to remain at the forefront of research and development in this crucial area of national interest.

The OCRC members wish to gratefully acknowledge the contributions of the Consortium Review Committee, and the funding, support and guidance of the Ohio Coal Development Office. Jacqueline Bird has served as Director of OCDO since 1989.

Kendree J. Sampson,
Program Manager
Ohio University

Acknowledgments

OHIO COAL DEVELOPMENT OFFICE (OCDO), OHIO DEPARTMENT OF DEVELOPMENT

The OCDO supports the research, development and deployment of technologies that can economically use Ohio coal within environmental limits. OCDO was the primary funder of the Ohio Coal Research Consortium (OCRC), providing program oversight, management, and guidance to the project. OCDO staff involved in the OCRC effort were Jacqueline Bird, OCDO Director, Richard Chu, P. E., Howard Johnson, P. E., and Arthur Levy, OCDO consultant.

THE OHIO COAL RESEARCH CONSORTIUM (OCRC)

The consortium was comprised of four universities—Case Western Reserve University, Ohio University, The Ohio State University, and University of Cincinnati. It was designed to support fundamental research to improve the efficiency of flue gas SO_2 removal processes and to develop new ideas and improved process technologies.

Dr. Michael Prudich (Ohio University) served as program manager of the OCRC from 1990 to 1992. Dr. Prudich was succeeded by Dr. Kendree Sampson (Ohio University) from 1992 through 1996, whose strong and active guidance was instrumental in bringing this project to a successful conclusion.

OCRC STEERING COMMITTEE

The OCRC Steering Committee, comprised of one individual from each school, was responsible for program direction. Members were:

Dr. L. S. Fan, Ohio State University
Dr. Jaikrishnam R. Kadambi, Case Western Reserve University
Dr. Ken Sampson, Ohio University
Dr. Timothy C. Keener, University of Cincinnati

CONSORTIUM REVIEW COMMITTEE

The Consortium Review Committee evaluated individual project proposals and recommended broad program direction. Members included:

Manny Babu, Dravo Lime Company
Howard Couch, Ohio Edison

Dr. Brian Gullet, U.S. Environmental Protection Agency
Dr. Joseph Oxley, Battelle Memorial Laboratories/Columbus
Dr. James Porter, Energy and Environmental Engineering
Charles Schmidt, U.S. Department of Energy/Pittsburgh
Dr. Robert Statnick, Consolidation Coal Company
William Downs*, Babcock & Wilcox
Barbara Toole-O'Neil**, Electric Power Research Institute
* Chair, 1990-1992; **Chair, 1992-1996

PRINCIPAL INVESTIGATORS

Case Western Reserve University
Adler, Dr. R. J. (deceased)
Kadambi, Dr. Jaikrishnam R.
Kenney, Dr. Malcolm E.

THE OHIO STATE UNIVERSITY

Fan, Dr. L. S.

OHIO UNIVERSITY

Bayless, Dr. Dave
Prudich, Dr. Michael E.
Sampson, Dr. Kendree

UNIVERSITY OF CINCINNATI

Biswas, Dr. Pratim
Keener, Dr. Timothy C.
Khang, Dr. Soon-Jai
Lin, Dr. Jerry

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We thank Meredith Angwin, President of Fourth Floor Databases, and Katherine Clay and Laura J. Rinaldi, consultants, for their efforts in the final editing and design of this document.

Jacqueline (Jackie) F. Bird, Director
Ohio Coal Development Office/OCDO
PHN: 614/466-3465; FAX: 614/466-6532
e-mail: jbird@odod.ohio.gov

Table of Contents

CHAPTER 2 New Calcium-Based Sorbents for Flue Gas Desulfurization 115

Ray-Kuang Chiang, Gwanghoon Kwag and Malcolm E. Kenney
Department of Chemistry
Case Western Reserve University

CHAPTER 3 Fundamental Studies Concerning Calcium-Based Sorbents 207

D. Mandal, R. Venkataramakrishnan, K.J. Sampson, M.E. Prudich
Department of Chemical Engineering
Ohio University

CHAPTER 4 Sorbent Transport and Dispersion 255

L.-S. Fan, E. Abou-Zeida,
S.-C. Liang, X. Luo
The Department of Chemical Engineering
The Ohio State University

CHAPTER 5 Transport Processes Involved in FGD 343

J.R. Kadambi, P., Chinnapalaniandi
C.U.Yurteri, V.P. Kadaba, M.A. Assar
Mechanical and Aerospace Engineering
Case Western Reserve University