



OHIO DEPARTMENT OF DEVELOPMENT  
Ohio Coal Development Office

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**OHIO COAL  
RESEARCH  
CONSORTIUM**

**1994  
SUMMARY REPORT**

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State of Ohio  
George V. Voinovich, Governor

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**OHIO COAL RESEARCH CONSORTIUM**

**FOURTH YEAR  
FINAL SUMMARY REPORT**

**for the period**

**September 1, 1993 through August 31, 1994**

**on projects funded by the  
Ohio Coal Development Office  
Ohio Department of Development**

**Ohio Coal Development Office  
Ohio Department of Development**

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**May, 1995**

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## PREFACE

As a part of its efforts to improve the use of high-sulfur Ohio coal within environmental limits, the Ohio Coal Development Office, an entity within the Ohio Department of Development (OCDO/ODOD), in late 1988 established a consortium of four Ohio universities. The purpose of the Ohio Coal Research Consortium is to conduct a multi-year fundamental research program. The Consortium research work is to represent an integrated, cooperative program among all of the members and not a group of unrelated research projects. The "charter" university members are Case Western Reserve University, The Ohio State University, the University of Cincinnati, and Ohio University. Ohio University is the managing member of the consortium.

The OCDO is providing this status, in summary form, of the project work completed in the Consortium's fourth year. Anyone with questions regarding the Consortium or its specific projects may contact Richard Chu or Art Levy of OCDO at 614/466-3465, or Dr. Ken Sampson of Ohio University at 614/593-1503. Additionally, those interested should also feel free to contact the individual principal investigators associated with each project.

When it first formed, the Consortium selected the subject of dry, calcium-based sorption processes for removing SO<sub>2</sub> from combustion gases produced by burning high-sulfur Ohio coal. The goal is to develop a base of fundamental knowledge to complement practical expertise gained from demonstration projects already underway in the State of Ohio. OCDO wished to determine whether dry, calcium-based sorption processes ultimately can prove to be more advantageous than wet sorption processes. Dry methods may be especially suitable in Ohio for retrofitting existing power plants because of their low space and capital requirements. The scope of the consortium was increased at the beginning of the fourth year to include research in the area of air toxics. Hence the two broad objectives of the Consortium are:

- ♦ Enhancement or development of dry sorption processes for the economical removal of high levels of SO<sub>2</sub> and other pollutants from combustion gases produced by the burning of high-sulfur Ohio coal. This includes in-furnace (above the flame zone) and post-furnace injection processes, and the use of additives in existing technologies. Projects focus on optimizing existing processes as opposed to starting from scratch.
- ♦ Increased understanding of methods for reduction in air toxics emissions from combustion gases produced by burning high-sulfur Ohio coal. Air toxics are defined to include the hazardous air pollutants listed in Title III of the Clean Air Act Amendments of 1990. This area includes but is not limited to coal cleaning techniques, new sorbent development, enhancement of existing wet or dry scrubbing processes, processes using fly ash to assist

in removal, methods for disposal of solid waste streams containing captured air toxics, the chemistry of air toxics formation and conversion in combustion processes, the chemistry and mass transfer processes, and the quantification of emitted species from processes using Ohio coals.

Copies of full technical reports are available upon written request to the OCDO at the address noted on the title page of this document or from the principal investigators. There may be a small charge for copying and shipping.

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OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC/93-1.1

OCDO Grant No. CDO/R-87-2C/B

**KINETICS AND STRUCTURAL EVOLUTION OF SORBENTS AT HIGH  
TEMPERATURES**

Final Report for the Period  
September 1, 1993 to August 31, 1994

by

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February 1995

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This project was funded in part by the Ohio Coal Development Office, Department of  
Development, State of Ohio.

## EXECUTIVE SUMMARY

The focus of this project is on furnace sorbent injection technology using dry, calcium-based sorbents for flue gas desulfurization. The goal is to provide fundamental research kinetics and the effects of sorbent properties, aimed at improving SO<sub>2</sub> removal and increasing sorbent utilization in a cost-effective fashion.

The fourth year work has been carried out in three phases: 1) structural evolution of sorbent, 2) modified sorbent studies, and 3) development of mathematical model. The results, their interpretation, and discussions are the primary focus of this report.

Sorbent structural evolution studies have helped vastly in understanding the role of internal structure and the influence of calcination, sintering and sulfation. Surface area, porosity and pore size distribution changes were studied with calcination and sintering at two temperatures, 1273 K and 1353 K. Pore size distribution shows the effect of sintering in closing the smaller pores and shifting the distribution to higher sizes.

Structural evolution studies during sulfation were carried out at 1353 K. The porosity shows a decreasing trend right from the start unlike calcination which shows a increasing porosity initially. In addition to sintering, which causes coalescence of smaller pores into larger ones, deposition of higher volume reaction product (CaSO<sub>4</sub>) fills up the CaO pores and reduces the overall porosity. The pore size distribution curves for the partially sulfated sorbent lie below the parent hydrate curve and show the decreasing contribution of the smaller pore sizes and shifting of the entire distribution to the higher sizes.

Modified sorbent studies have yielded results leading to improved understanding

of the mechanism of promotion. Studies were conducted with lignosulfonate as the modifier at a concentration of 1.5 mass% at 1353 K. The modified hydrate possesses higher surface area (about 45 m<sup>2</sup>/g) as well as internal porosity (32%). Results indicate superior capturability in the initial 50 milliseconds, the extent of sulfation is about 30% more than that of the unmodified hydrate. At higher residence times, the rate of capture attenuates and becomes similar to that of the unmodified hydrate. The initial edge is preserved at the higher residence times studied. The porosity as well as surface area of the partially sulfated lignohydrate drop drastically in the first 50 milliseconds and become similar to that of the unmodified hydrate. The very high surface area leads to high sintering rates (since sintering has been shown to be proportional to the square of surface area) causing rapid reduction of surface area. Calcination and sintering studies will be carried out to probe into this phenomena and gain a better understanding.

Modeling work has yielded results which match very well with the experimental data. The model has been developed for simultaneous calcination and sintering of Ca(OH)<sub>2</sub>. The model is based on a modified form of the simple grain model. The model visualizes these phenomena taking place on a single grain of Ca(OH)<sub>2</sub> with surrounding micrograins of product CaO which undergo sintering. The model matches the experimental data of calcination kinetics very well. It predicts the two characteristics exhibited by the reaction; very high initial rate followed by sharp attenuation and subsequent 'die-off' at higher residence times. The surface area evolution predictions also match closely with the experimental data. The modeling work will continue and will involve incorporating the following: intraparticle transport effects for larger particle sizes, sulfation reaction modeling and the structural changes accompanying sulfation, and finally, model the simultaneous calcination, sintering and sulfation of the sorbent.

# **OHIO COAL RESEARCH CONSORTIUM**

## **FOURTH YEAR FINAL SUMMARY REPORT**

**for the period  
September 1, 1993 through August 31, 1994**

### **ABSTRACT**

As a part of its efforts to improve the use of high-sulfur Ohio coal within environmental limits, the Ohio Coal Development Office, an entity within the Ohio Department of Development (OCDO/ODOD), in late 1988 established a consortium of four Ohio universities. The purpose of the Ohio Coal Research Consortium is to conduct a multi-year fundamental research program focused on 1) the enhancement or development of dry sorption processes for the economical removal of high levels of SO<sub>2</sub> and other pollutants and 2) an increased understanding of methods for reduction in air toxics emissions from combustion gases produced by burning high-sulfur Ohio coal. This report contains summaries of twelve studies in these areas.

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-1.2**

**OCDO Grant No. CDO/R-87-2C/B**

**HANDLING, TRANSPORT AND DISPERSION OF SORBENT POWDER  
FOR IN-FURNACE INJECTION**

**Final Report for the Period  
September 1, 1993 to August 31, 1994**

**by**

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**February 1995**

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**This project was funded in part by the Ohio Coal Development Office, Department of  
Development, State of Ohio.**

## EXECUTIVE SUMMARY

In the fourth year, the overall charging tendency and the charge polarity of three sorbent powders have been examined. It was found that  $\text{CaCO}_3$  and lignosulfonated hydrate are charged positively during transport and lignosulfonated hydrate exhibits the highest charge pick-up ability. All sorbent materials exhibit a decrease in specific surplus charge with increasing powder mass flow rate but an increase with increasing gas flow rate. An increase in humidity was found to result in less charge build-up on powder. A comparison of the charge pick-up ability of  $\text{Ca}(\text{OH})_2$  for three tube materials shows that the powder acquires charges the lowest when transported through carbon steel tubes. Theoretical calculations of the attraction forces demonstrate that the electrostatic force dominates at larger separation distances. Also, mechanical testing equipments have been used to measure and analyze the flow properties of calcium carbonate, hydrate, and lignosulfonated hydrates under different handling and transport conditions. The tests performed showed that calcium carbonate has low flowability and dispersibility compared to the hydrates. Results proved also that increasing the lignosulfonate percentage improves the flow properties of the modified hydrates. Presence of moisture was shown to affect badly the flowability of the tested sorbents because of bonding between adjacent water layers which increases the cohesive strength of the sorbents.

One of the major accomplishments in the fourth year is the development of an integral model for powder dispersion. Previous studies on powder characterization and powder handling have been integrated to establish a mathematical model, in which both hydrodynamic forces and interparticle forces have been taken into account. The agglomerate size distribution is dependent on two simultaneous processes, i.e., coalescence and break-up of agglomerates. Both processes are controlled by hydrodynamic forces and interparticle forces in the system.

The turbulent flow in the sorbent conveying system is simulated by  $k-\epsilon$  model. Simulation results show that turbulence intensity is very high in the nozzle and drops rapidly along the nozzle. It is found that under conditions in previous experimental studies, most agglomerates are smaller than energy dissipation eddies (Kolmogorov eddies) in the turbulent flow and therefore, viscous shear stress is dominant.

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-1.8**

**OCDO Grant No. CDO/R-87-2C/B**

**NEW HIGH-CAPACITY, CALCIUM-BASED SORBENTS - CALCIUM  
SILICATE SORBENTS**

**Final Report for the Period  
September 1, 1993 to August 31, 1994**

**by**

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**This project was funded in part by the Ohio Coal Development Office, Department of  
Development, State of Ohio.**

## EXECUTIVE SUMMARY

### Aim

A search is being carried out for new calcium-based  $\text{SO}_2$  sorbents for induct injection. More specifically, a search is being carried out for induct injection calcium silicate sorbents that are highly cost effective.

### Current Year Objectives

The objectives for the current year include the study of sorbents made from  $\text{Ca}(\text{OH})_2$ , from mixtures of  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$ , and from portland cement. They also include the study of sorbents made from model compounds.

During this year, sorbents prepared from  $\text{Ca}(\text{OH})_2$  and from mixtures of  $\text{Ca}(\text{OH})_2$  and fumed  $\text{SiO}_2$  were investigated. The results show that very good  $\text{SiO}_2$ -modified  $\text{Ca}(\text{OH})_2$  sorbents in which the Si-to-Ca reactant ratio is low can be prepared from  $\text{Ca}(\text{OH})_2$  and fumed  $\text{SiO}_2$ . This is significant because in some cases it could be economically advantageous to use  $\text{SiO}_2$ -modified  $\text{Ca}(\text{OH})_2$  sorbents in which the Si-to-Ca reactant ratio is low rather than high. Sorbents prepared from  $\text{Ca}(\text{OH})_2$  and natural  $\text{SiO}_2$  or natural  $\text{SiO}_2$  sources were also studied. The results obtained show that very good  $\text{SiO}_2$ -modified  $\text{Ca}(\text{OH})_2$  sorbents and calcium silicate hydrate sorbents, C-S-H sorbents, can be prepared from  $\text{Ca}(\text{OH})_2$  and diatomite, pumice or perlite, minerals that are readily available.

In addition, sorbents prepared from  $\text{Ca}_3\text{SiO}_5$  and  $\beta\text{-Ca}_2\text{SiO}_4$  and from mixtures of these compounds and  $\text{SiO}_2$  were studied. This model work was done in

support of the work on the cement-derived sorbents. The results secured demonstrate that very good C-S-H rich sorbents can be prepared from these compounds and from mixtures of them with SiO<sub>2</sub>. They also provide information useful for interpreting the cement sorbent results.

Sorbents prepared from cement and from mixtures of cement and natural SiO<sub>2</sub> or SiO<sub>2</sub> sources were investigated as well. The results secured show that cement and mixtures of it with diatomite, pumice or perlite rapidly yield excellent sorbents with the proper reaction conditions. They further suggest that such sorbents are attractive for practical use.

In sum, the project proceeded as anticipated to the extent a research project can be expected too, and it provided valuable results.

### **Work To Be Done**

In the coming year, work will be done in an effort to find ways to make C-S-H type sorbents that have still better combinations of SO<sub>2</sub> uptake, Ca utilization and projected cost. Work will also be done in an effort to find C-S-H type adsorbents and absorbents for Se in flue gas. The work is designed to yield highly effective sorbents that can be made by means that are fast, cheap and reliable. Work on pure compounds will be done when necessary to provide base-line data.

### **Collaborations**

During the course of the year, collaborative work with other members of the consortium was done. A sample of a cement-derived sorbent and data on it were

given the Professor T. C. Keener of the University of Cincinnati. A visit to his laboratories was made and discussions on his scale-up work on cement-derived sorbents were carried out. In addition, a sample of a cement-derived sorbent and data on it were given to Professor L.-S. Fan of Ohio State University for use in his Sorbent studies. Also, infrared analysis of samples from the air toxics studies of Professor P. Biswas of the University of Cincinnati was carried out for Professor Biswas.

OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC/93-2.1

OCDO Grant No. CDO/R-87-2C/B

INVESTIGATION OF TRANSPORT PROCESS INVOLVED IN FGD

Final Report for the Period  
September 1, 1993 to August 31, 1994

by

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This project was funded in part by the Ohio Coal Development Office, Department of  
Development, State of Ohio.

## EXECUTIVE SUMMARY

This report describes the work done in the fourth year of the project "Investigation of Transport Processes Involved in FGD". The objectives of this five year plan of study are to experimentally obtain a basic understanding of (1) turbulent flow structure of the mixing zone and its influence on particle dispersion, (2) the effect of particle loading on turbulent properties and mixing, (3) the effect of jet entrainment, (4) water spray-sorbent interaction, sorbent wetting and mixing, (5) investigate the flow field where certain ratios of jet velocity to flue gas velocity result in regions of negative flow and define onset of negative flow, and (6) sorbent reactivity in immediate mixing zone.

In the first two years of the project a sorbent injection facility which can simulate the conditions encountered in COOLSIDE set up was designed and built. Non-intrusive laser based diagnostic tools PDA/LDA were used for flow characterization of particle laden jet in cocurrent flows. In the third year a new technique called TTLDV which combines particle transit time in measurement volume of LDV and LDV velocity measurements to simultaneously obtain non-spherical lime particle size and velocity was developed. Better sorbent injection schemes were investigated. Spray cocurrent flow tests were conducted.

During the fourth year the spray cocurrent flow interaction data was analyzed. A criterion was developed for predicting the flow reversal which results in deposition of water droplets on the duct wall (Table 3). The flow reversal occurs when the spray has entrained all the cocurrent flowing stream. The criterion is based upon the mass flow rate of the two phases. The criterion successfully predicted the flow reversals encountered in the experiments and will be a very useful

practical tool.

Lime laden jet cocurrent flow interactions tests were completed . Tests on the swirling nozzle have been conducted. The single phase data have been analyzed while the two phase glass particle laden jet data is being analyzed . Based upon the analyses of the results , the swirl plate axial length , height and twist angle can be varied . No extra energy is required to enhance the mixing . The results indicate that the mixing is enhanced and the turbulence intensities in the radial direction show an increase of 10 to 30 %.

Tests indicate that the spray droplet size obtained from SS 1/8 JJ nozzle are the proper size for studying particle water droplet interactions . Initial tests with water and glass bead slurry to ascertain the capacity of the multiphase software to differentiate between water droplet , glass particles and water coated glass particles indicate that the technique can be used . However to obtain cocurrent air flow at temperatures of 160 degree F as suggested by the project monitor to simulate the flue gas temperature , a heating system was ordered . The heating system is being installed .

The equipment needed for modification of the facility to simulate sulfur dioxide laden flue gas and for removal of the sulfur dioxide prior to releasing the simulated flue gas was investigated. Safety concerns raised by the environmental safety department implied a substantial and costly modification of the facility. This was brought up during the July OCRC meeting and it was suggested that the spray dryer facility at University of Cincinnati (PI Dr. T. Keener) may be utilized for this purpose. The PI and the graduate student visited Dr. Keener's laboratory . It was decided that sulfur dioxide tests will be carried out

at the spray dryer facility . A test set up to fit in the spray dryer facility conveniently has been designed.

Satisfactory progress has been made in the project during the fourth year . However , the PI , Dr. J.R. Kadambi underwent open heart surgery in April 1994 and that had some effect on the project . The PI has recovered from the surgery and is deeply involved with the project . In spite of this setback all the tasks associated with the fourth year, were addressed.

One of the graduate students , Mr. V.P. Kadaba successfully defended his M.S. thesis and graduated in May , 1994.

#### Publications:

The following publications and presentations resulted from the fourth year work.

1." A New Approach Using Transit Time for Simultaneous Measurement of Size and Velocity of Non-spherical Particles," C.Yurteri, V.Kadaba and J.R. Kadambi, Laser Anemometry : Advances and Applications , ASME Symposium. FED vol 190, June, 1994.

2. " Spray Cocurrent flow Interactions and Flow Reversal," V.Kadaba, C.Yurteri and J.R. Kadambi, accepted for ASME Solid -Liquid Flow Symposium to be held at Hilton Head, August, 1995.

3." A Simultaneous Measurement of Irregular Particle Size and Velocity using Transit Time and LDV," M.Assar, C.Yurteri, V.Kadaba and J.R.Kadambi . Flow Instrumentation Forum, FED vol. 161, ASME , New York, NY . 1993.

A poster session presentation of the TTLDV work was also made at NASA Lewis research Center sponsored Advanced Subsonic Transport Workshop held at Cleveland , Ohio in August 1994.

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-4.1**

**OCDO Grant No. CDO/R-87-2C/B**

**SELENIUM EMISSION CONTROL AT HIGH TEMPERATURES WITH  
MINERAL SORBENTS**

**Final Report for the Period  
September 1, 1993 to August 31, 1994**

**by**

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**February 1995**

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**This project was funded in part by the Ohio Coal Development Office, Department of  
Development, State of Ohio.**

## EXECUTIVE SUMMARY

The focus of this project is on toxic heavy metal removal by sorbent injection in the upper-furnace region of a coal-fired boiler. Selenium is chosen as the candidate heavy metal to be studied because of its high volatility and associated difficulty in removal. Mercury being the most volatile of all the heavy metals, has already been singled out for extensive studies by different research programs, funded by EPA, DOE, and EPRI. However, results of the proposed work can be suitably extended to tackle emission problems of other heavy metals.

The preliminary sorbent screening experiments were performed in a differential reactor, built in the first year of this project. A host of sorbents, such as, alumina, kaolinite, limestone and also hydrated lime were tested at a reaction temperature of 900°C, and for reaction duration of 4 hrs. The reason for choosing these minerals was because of their proven moderate to high capability of lead and cadmium capture, and also for moderate selenium capture at high temperatures, reported by recent studies. The sorbent screening experiments have used selenium dioxide as the Se source, since in the oxidizing atmosphere of the furnace, that is reported to be the existing form of selenium species.

The preliminary sorbent screening experiments have shown that  $\text{Ca(OH)}_2$  is the most promising sorbent for selenium capture out of all the sorbents tested. A careful review of the sorption results for  $\text{Ca(OH)}_2$  has also revealed the strong possibility for occurrence of a chemical reaction. Since Se belongs to group VI of the periodic table along with sulfur, and shares many common properties with the latter, formation of a calcium selenite ( $\text{CaSeO}_3$ ) or selenate ( $\text{CaSeO}_4$ ) compound is likely by the reaction of CaO with  $\text{SeO}_2$ . The captured selenium has exhibited poor leachability in water, a property which is also shared by  $\text{CaSeO}_4$ . The presence of  $\text{CaSeO}_4$  is confirmed by the X-ray diffraction analysis of the sorbent sample. Preliminary

studies for investigating the effect of temperature on  $\text{SeO}_2/\text{Ca}(\text{OH})_2$  reaction have shown that the percent of water-leachable selenium increases with decreasing reaction temperature. This strongly suggests an enhancement of physical adsorption with decreasing temperature, since  $\text{SeO}_2$  is characterized by its high solubility in water. However, sorption results show a greater capture at  $900^\circ\text{C}$ , than for  $800$  and  $1000^\circ\text{C}$ . Further examination of the temperature effect and proper characterization of the reaction product is required before drawing a reasonable conclusion.

Following up on first year's work, second year of the project will initially concentrate on performing more reaction studies with  $\text{Ca}(\text{OH})_2$  sorbents in the differential reactor. The objective for this work will be to determine the most favorable temperature window for selenium capture by chemical reaction. Moreover, the duration of reaction time will be shortened to few minutes instead of hours for a preliminary feasibility testing of whether calcium hydroxide will be effective in capturing sufficient amount of selenium during its short stay in the high-temperature window of the upper-furnace region.

Once the fundamental information about product compound, and optimum temperature range are obtained from the differential reaction results and X-Ray Diffraction study, the reaction will be carried out in a flow reactor to simulate the entrained-flow condition of above-the-flame region of the furnace. A high-temperature, flow reactor will be built in the second year for carrying out such studies. The typical residence time of the hydroxide sorbent in the entrained-flow reactor will vary between less than 100 milliseconds to few seconds. Rate of selenium capture by chemical reaction at high temperature, and for sorbent flow conditions will be the primary focus of the study.

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-4.2**

**OCDO Grant No. CDO/R-87-2C/B**

**ROLE OF FLY ASH IN HEAVY METAL REMOVAL FROM FLUE GAS**

**Final Report for the Period  
September 1, 1993 to August 31, 1994**

**by**

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## EXECUTIVE SUMMARY

The primary objective of this work is to study the fundamental phenomena involved in the sorption of trace chalcophilic elements by fly ash at high and medium temperatures. Chalcophiles are the low-boiling trace elements that are volatilized during pulverized coal combustion and are transferred to the gas phase, e.g., As, Pb, Cd and Se. Fly ash acts as a sink for some of these volatile trace toxics and a great deal of chemical interaction is speculated to take place under furnace conditions. This fly ash-chalcophiles interaction, though crucial to the control of chalcophilic emissions, is still very poorly understood. This is due, in part, to the lack of experimental studies and data on the behavior of fly ash and chalcophiles.

The main focus of this work is investigating the sorption phenomena of a representative chalcophile, arsenic (As) on fly ashes at temperatures representative of the upper-furnace region (850-1200°C) and the economizer section (375-600°C). Arsenic is chosen because it is a highly toxic chalcophile and shows some affinity for fly ash but is also emitted from the stack as vapor and aerosol particles. The two temperature zones have been chosen because most of the dry-sorbent injection technologies are being developed for application in these two regions. Also, various fly ash samples from different sources are being studied because their chemical composition and subsequently their chemical sorption characteristics would show a great deal of variation depending on their source.

In the first year of this project, it was proposed to conduct isothermal sorption experiments in a differential reactor system. The first year's work was divided into two phases; namely 1) design, construction, testing and trouble-shooting of the differential reactor assembly and the analytical instrumentation, and, 2) designing experiments and conducting sorption studies in the differential reactor system. The first phase was completed, not before encountering a number of challenges and making quite a few design modifications to tackle them. The two most important challenges were: the need to generate reactant gas containing a fixed and low (order of 1-10 ppm) concentration of the arsenic species, and the need to prevent or minimize condensation of the arsenic species in the transport lines and tubes (for achieving mass balance).

The second phase of first year's work has yielded some interesting results which are discussed here. Two fly ashes, NIST Certified fly ash and from Zimmer utility station near Cincinnati have been tested. Both the fly ashes exhibit high levels of arsenic capture, a significant portion of which is not water leachable. The fraction that is not leached with water is believed to be captured by some chemical reaction. NIST shows increased capture by chemisorption at 900°C compared to 500°C, which indicates an activated chemical reaction as the primary sorption mechanism. Zimmer seems to exhibit little effect of temperature on the amount of arsenic captured by chemisorption.

Differential reaction studies were also carried out at a higher concentration of  $As_2O_3$  in order to explore the effect of concentration. Zimmer fly ash showed increased capture after 2 hours of exposure at 1173 and 773 K, with majority of the capture being water leachable. Increased concentration of arsenic will lead to increased physisorption and thereby water leachability.

XRD studies have shed more light on the chemical nature and structure of the captured species and have confirmed chemical interaction. In addition to  $As_2O_3$  itself (which may be physically adsorbed), XRD results show the presence of Ca-arsenate as well as Al-arsenate. These compounds could only have been formed by some chemical interaction.

**OHIO COAL RESEARCH CONSORTIUM**

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**DEVELOPMENT OF NEW SORBENTS TO REMOVE MERCURY AND  
SELENIUM FROM FLUE GAS**

**Final Report for the Period  
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**by**

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## EXECUTIVE SUMMARY

Mercury (Hg) and selenium (Se) are two of the volatile trace metals in coal, which are often not captured by conventional gas clean up devices of coal-fired boilers. An alternative is to use sorbents to capture the volatile components of trace metals after coal combustion.

In this project sorbent screening tests were performed in which ten sorbents were selected to remove metallic mercury in N<sub>2</sub>. These sorbents included activated carbon, char prepared from Ohio No. 5 coal, molecular sieves, silica gel, aluminum oxide, hydrated lime, Wyoming bentonite, kaolin, and Amberlite IR-120 (an ion-exchanger). The sorbents were selected based on published information and B&W's experience on mercury removal. The promising sorbent was then selected and modified for detailed studies of removal of mercury and selenium compounds.

The sorbents were tested in a bench-scale adsorption facility. A known amount of each sorbent was loaded in the column as a packed bed. A carrier gas was bubbled through the mercury and selenium compounds. The vaporized species were carried by the gas and went through the sorbent beds. The amount of mercury and selenium compounds captured by the sorbents was determined by atomic absorption.

The results of the sorbent screening tests indicated that activated carbon removed 200 µg Hg/gm of sorbent at 100°C and a flow rate of 0.63 liter of N<sub>2</sub>/minute in 6 hours. Except for Wyoming bentonite which removed 28.8 µg Hg/gm of sorbent, the other mineral-based sorbents had mercury removal less than 3 µg Hg/gm of sorbent. The activated carbon was the best-performing sorbent for mercury capture among the 10 selected sorbents. Adsorption of metallic mercury on the activated carbon was performed at different reaction times. The results indicated that the reaction still occurred after two days.

The activated carbon was then impregnated with inorganic salts, i.e., KCl, CaCl<sub>2</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, and K<sub>2</sub>S. The activated carbon and its impregnated samples were evaluated by performing bench-scale adsorption tests under different conditions. The test variables included the type of inorganic salt additives, reaction temperature, type of the carrier gas, and the chemical species of mercury and selenium compounds. Two types of carrier gases were used: pure N<sub>2</sub> and a premixed gas of 3000 ppm SO<sub>2</sub> and 10% CO<sub>2</sub> in N<sub>2</sub>. Metallic mercury and mercuric chloride (HgCl<sub>2</sub>) were used as the representatives for mercury compounds. Selenium dioxide was used as the representative for selenium compounds.

Capture of metallic mercury and mercuric chloride by the activated carbon samples was generally higher in the premixed gas than in pure N<sub>2</sub>. Adsorption of metallic mercury increased as the reaction temperature was decreased.

Some of the inorganic salts in the impregnated activated carbon enhanced mercury capture. The degree of increasing adsorption of metallic mercury was dependent on temperature, the carrier gas, and other test conditions. Some other impregnated inorganic salts reduced the amount of metallic mercury. The reduction in adsorption might be attributed to plugging the fine pores of the activated carbon by the inorganic salts.

Adsorption of mercuric chloride ( $\text{HgCl}_2$ ) on the activated carbon samples was much higher than that for metallic mercury under comparable test conditions. Adsorption of mercuric chloride on the activated carbon was  $1546 \mu\text{g/gm}$  of sorbent at  $60^\circ\text{C}$  and  $0.63$  liter of  $\text{N}_2/\text{min.}$  in 6 hours, as compared to  $254 \mu\text{g/gm}$  of sorbent for mercury under similar conditions. Impregnation of the activated carbon with inorganic salts reduced the amount of adsorption of mercuric chloride.

Although  $\text{SeO}_2$  is more volatile than metallic mercury, adsorption of  $\text{SeO}_2$  on the activated carbon samples was much less than that for metallic mercury. Adsorption of  $\text{SeO}_2$  on the activated carbon was  $11 \mu\text{g/gm}$  of sorbent at  $60^\circ\text{C}$  and  $0.63$  liter/minute of  $\text{N}_2$  in 6 hours, as compared to  $254 \mu\text{g/gm}$  of sorbent for mercury under comparable conditions.

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-4.8**

**OCDO Grant No. CDO/R-87-2C/B**

**EVALUATION OF OHIO FLY ASH/HYDRATED LIME SLURRIES AND  
TYPE I CEMENT SORBENT SLURRIES IN THE U.C. PILOT SPRAY  
DRYER FACILITY**

**Final Report for the Period  
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## EXECUTIVE SUMMARY

### Objectives.

The objectives of this year's work included an evaluation of the performance of fly ash/hydrated lime as well as hydrated cement sorbents for spray drying absorption (SDA) of SO<sub>2</sub> from a simulated high-sulfur flue gas. These sorbents were evaluated for several different hydration methods, and under different SDA operating conditions. In addition, the physical properties of surface area and porosity of the sorbents was determined.

### Conclusions.

The most reactive fly ash/hydrated lime sorbent studied was prepared at room temperature with milled fly ash. Milling fly ash prior to hydration with lime did have a beneficial effect on calcium utilization. No benefit in utilization was experienced either by hydrating the slurries at a temperature of 90°C as compared to hydration at room temperature, or by increasing hydration time. While the surface areas varied greatly from sorbent to sorbent, the pore size distributions indicated "ink bottle" pores with surface porosity on the order of 0.5 microns. No correlation could be drawn between the surface area of the sorbents and calcium utilization. These results suggest that the composition of the resulting sorbent might be more important than its surface area.

The most effective sorbent studied this year was produced by hydrating cement for 3 days at room temperature. This sorbent provided a removal efficiency and a calcium utilization over 25 percent higher than baseline results at an approach to saturation

temperature of 30°F and a stoichiometric ratio of 0.9. A maximum SO<sub>2</sub> removal efficiency of about 90 percent was experienced with this sorbent at an approach to saturation temperature of 20°F.

The hydrated cement studies indicate a clear benefit in milling the cement slurry during hydration. As in the fly ash/hydrated lime studies, no clear relationship between surface area and reactivity was exhibited. The pore size distribution of the reactive sorbent indicates a bimodal pore size on the order of 1 micron and 0.1-0.2 microns. The larger surface pore size may contribute to the enhanced reactivity.

#### **Future Objectives.**

In the following year the performance of hydrated cement in the spray dryer will be more fully investigated. Bench scale experiments at elevated temperatures will be performed. Sorbent reactivity will be related to spray dryer operating parameters, as well as to ball mill hydration conditions. Surface area and porosity will continue to be evaluated. Also, the effect of additives such as fumed silica and diatomaceous earth will be determined.

A wet chemistry procedure for determining the calcium content of cement will be evaluated. The procedure, from ASTM C 114, consists of removing silicon, aluminum, iron, titanium, phosphorus, and manganese from a sample of cement through a series of precipitations and filtrations. Calcium is then precipitated as an oxalate. After filtering, the oxalate is redissolved and titrated with potassium permanganate (KMnO<sub>4</sub>).

**OHIO COAL RESEARCH CONSORTIUM**

**SUBCONTRACT AGREEMENT NO. OCRC/93-4.9**

**OCDO Grant No. CDO/R-87-2C/B**

**KINETIC STUDIES OF DRY SORBENTS FOR MEDIUM TEMPERATURE  
APPLICATION**

**Final Report for the Period  
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## EXECUTIVE SUMMARY

The purpose of this project is to study the fundamental nature of the sorbent reactivity and reaction kinetics in the medium temperature range from 600°F to 1200°F available in the convective pass of a boiler upstream of the economizer, where dry sorbents are injected to remove SO<sub>2</sub> from the flue gas. Research focus is on the fundamental mechanisms of sorbent-flue gas interaction under economizer and hot baghouse conditions utilizing the experimental setup and the results of the first three years of research.

During the first year study, it was found that a significant portion of unused sorbent was reacted with carbon dioxide in a simulated flue gas (~14%) and produced calcium carbonate. This behavior had not been actively reported in the literature, and thought to be one of the important factors that limit the eventual utilization of calcium based sorbents. During the second year study, it was found that the majority of gas-solid reactions with small sorbent particles are practically reached its final conversions within the first 1 second of reaction time. Furthermore, dolomitic hydrate was found to have better reactivity because its magnesium carbonate has a lower equilibrium temperature than that of pure calcium carbonate, thus increasing the total amount of available lime for better utilization of sorbent material. During the third year study, the experimental techniques were refined to measure the sorbent kinetics within the first 100 milliseconds. Although the sulfation reaction of hydrated lime levels off below 1 second of reaction time, the sulfation reaction of dolomitic hydrate continues beyond 1 second of reaction time. Based on the preliminary test results, it was found that the temperature range of 900°F to 1000°F appeared to be favorable zone for the injection of dolomitic sorbent while the range of 1000 to 1200°F was favorable for lime

sorbent under the tested flue gas conditions in the ductwork. During the fourth year, the interference of carbonation reaction to sulfation reaction was studied as well as the concentration dependency of the sulfation reaction. The data to date showed that the carbonation did not interfere the sulfation reaction rate for reactions taking place less than 1 second. However, there was significant decrease in carbonation conversion when the sulfation reaction took place simultaneously. The levels of SO<sub>2</sub> concentration had negligible effects on reaction rates when the concentration was maintained above 3000ppm. An n-th order deactivation kinetic model was also developed during the fourth year to model the kinetics of various reactions. This model is particularly useful for the dry sorbent reactions, since the apparent rate constants rapidly decrease during the first 1 second of exposure to various gaseous reactants.

OHIO COAL RESEARCH CONSORTIUM

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## THE EFFECT OF ADDITIVES ON LIME DISSOLUTION RATES

Final Report for the Period  
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## EXECUTIVE SUMMARY

In spray dryer flue gas desulfurization, lime slurry is injected into a spray dryer where it contacts with the hot flue gas and desulfurization occurs. This process is complex owing to the heat and mass transfer which must take place. One of the most important fundamental steps in the scrubbing process is the rate at which lime dissolves from the solid particle in the slurry drop and becomes available for reaction with the absorbed sulfur dioxide. This dissolution rate to a large extent controls the degree of reactivity and is the rate controlling step for this process. However, studies on this dissolution rate have been very few and its magnitude under a variety of operating conditions is not well known. This research has as its objective, the study and understanding of the lime dissolution rate. This understanding should lead to a better method of predicting and optimizing spray dryer performance for flue gas desulfurization.

The lime dissolution rate has been successfully measured by means of a spinning disc experimental method. It was found that lime dissolution rate was dependant on the disk rotating speed when the rotating speed was below 300rpm. When the disk rotating speed was greater than 300rpm, lime dissolution rate become constant. Lowering the solution pH increased lime dissolution rate, and lowering the solution temperature reduced lime dissolution rate.

Two groups of additives have been tested for their effects on lime dissolution rate. Among the organic chemicals, sugar and phenol were the most effective in enhancing lime dissolution rate. Glycerin slightly increased the lime dissolution rate, and ethyl-alcohol depressed the lime dissolution.

The most prominent chemical tested was in the inorganic chemicals group. In its 20% by weight solution at 50° C, the  $\text{NH}_4\text{Cl}$  solution increased lime dissolution rate more than a hundred times compared with dissolution in pure water. The other two inorganic chemicals,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCl}_2$ , just slightly increased lime dissolution rate.

**OHIO COAL RESEARCH CONSORTIUM**

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**CONTROL OF TOXIC METALLIC EMISSIONS FORMED DURING THE  
COMBUSTION OF OHIO COALS**

**Final Report for the Period  
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## **EXECUTIVE SUMMARY**

The objective of the project "Control of toxic metallic emissions formed during the combustion of Ohio coals" was to characterize metallic emissions from representative coals and develop strategies for their control. Though metallic emissions from coal combustors have been extensively studied, more studies need to be performed to better characterize the interaction of various species which is required for the selection and design of sorbents for effective control of these emissions. Furthermore, this characterization is important as the 1990 Clean Air Act Amendments (CAAA) have targeted a list of air toxics for further regulation under Title III. Eleven metallic species and their compounds - antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel and selenium are in this list, and most of them are prevalent in coal. Major sources (industries emitting 10 tons per year of any single air toxic or 25 tons per year of any combination) will be initially targeted, and many utilities and industrial facilities using coal fall in this category. The other feature of the 1990 CAAA is that USEPA has been instructed to set stringent technology based standards, and therefore control techniques have to be developed. Some coals are rich in sulfur, and utilities using these coals will have to use some form of Flue Gas Desulfurization (FGD). A technique for FGD is the use of calcium based sorbents, and the degree of metals capture of these sorbents under different conditions will be researched.

The objective of the first year of the study was to understand the evolution of metallic aerosol size distributions and the capture characteristics of various sorbents. Also, the metallic emissions resulting from the combustion of two seams of Ohio coals were to be characterized. Studies on the evolution of the metallic aerosol size distributions have been completed and the use of silicon and calcium based sorbents for capture of lead species has been examined. Co-injection of metallic compounds along with organometallic silicon indicated a high degree of capture of lead in a certain

temperature regime. Preliminary results with Calcium based sorbents also indicate capture of metallic species. To gain a further understanding of the capture processes, in situ optical diagnostic studies were performed in collaboration with researchers at the National Institute of Standards and Technology. Spectroscopic studies (laser induced fluorescence coupled with particle scattering) were performed to help understand the mechanisms of metallic species capture. Characterization of metallic emissions from the combustion of Ohio coals is in progress. Several modeling efforts have also been initiated. A detailed thermodynamic equilibrium model to predict metallic species capture rates has been developed and a number of simulations have been carried out to establish conditions for optimal removal of metallic species. As several competing mechanisms determine metallic species behavior in combustion systems, a detailed model accounting for competing effects of chemical reaction, nucleation, condensation and coagulation is being developed for comparisons with controlled experiments and to help develop design criteria. The results of some of the studies described above are discussed in some detail later. Publications and conference presentations resulting from the first year study are also listed.

Due to the novelty of the approach, the use of vapor phase sorbent materials, a patent was filed for the control of metallic emissions. This was done after a review of the existing patents. Several industries are also being contacted for further development and commercialization.

In the upcoming year, the capture characteristics of mercury species on calcium and silicon based sorbents are being determined. The capture rate of mercury by these sorbents will be compared to that by activated carbon. Several industrial calcium sorbents will also be tested. Results from the first year of the study have indicated that there are narrow temperature ranges over which the capture efficiency is the highest. It is also clear that several competing effects establish the capture characteristics. Optical diagnostics will be used to firmly establish the dominant mechanisms and develop a comprehensive predictive model. Based on all the results, a summary of metallic species

emissions from utilities using Ohio coals will be provided. This will include the impact vis a vis the 1990 Clean Air Act Amendments, and recommendations for potential capture technologies to prevent emission of metallic species.

The results of the proposed study will enable characterization of metallic species during the combustion of Ohio coals. The results of the controlled tests will provide information and data to determine the impact of these emissions from Ohio coals and allow a comparison to results of previous studies on coals from other locations in the United States. The results of the metals capture studies will demonstrate the use of potential technologies for reducing metallic emissions. Operating conditions wherein sorbents for FGD can be potentially used for metals control will be established, providing for cost effective solutions.

OHIO COAL RESEARCH CONSORTIUM

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ADSORPTION AND DESORPTION OF SULFUR DIOXIDE ON NOVEL  
ADSORBENTS FOR FLUE GAS DESULFURIZATION

Final Report for the Period  
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## Executive Summary

Dry regenerative sorption processes have recently attracted increasing attention in flue gas desulfurization (FGD) because of their several advantages over the conventional wet-scrubbing processes. Dry sorbents are usually made by coating a transition or alkaline earth metal precursor on the surface of a porous support. Major disadvantages of these sorbents prepared by the conventional methods include relatively poor attrition resistance and low SO<sub>2</sub> sorption capacity. The physical and especially chemical attrition (associated with the sulphation-oxidation-reduction cycles in the process) deteriorates the performance of the sorbents. The low SO<sub>2</sub> sorption capacity is primarily due to the small surface area of the support. Materials with a high surface area are not used as the supports for FGD sorbents because these materials usually are not thermally stable at high temperatures.

In the past year, the research supported by OCDO was focused on synthesis and properties of sol-gel derived alumina and zeolite sorbents with improved properties for FGD. The sol-gel derived alumina has large surface area, mesopore size and excellent mechanical strength. Some alumina-free zeolites not only possess the basic properties required as a sorbent for FGD (hydrophobicity, thermal and chemical stability, mechanical strength) but also have extremely large surface area and selective surface chemistry. The major objectives of this research program were to synthesize the sol-gel derived sorbents and to explore the use of the zeolites either directly as adsorbents or as sorbent support for FGD. The research was aimed at developing novel FGD sorbents possessing better sorption equilibrium and kinetic properties and improved physical and chemical attrition resistance.

The original objectives of the research proposed for year four were to investigate the SO<sub>2</sub> sorption and desorption regeneration, properties of a sol-gel derived CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sorbent and zeolite silicalite. Improvement on the synthesis conditions of the CuO/

$\gamma$ - $\text{Al}_2\text{O}_3$  sorbent, and study on the thermal and chemical stability of these two sorbents were also included in the research proposed for year four. During the course of the investigation in year four, the research was extended to include sol-gel derived  $\text{CaO}/\gamma$ - $\text{Al}_2\text{O}_3$  sorbents and another hydrophobic and thermal stable zeolite (the DAY zeolite). Therefore, the research in year four was specifically aimed at (1) synthesis of  $\text{CuO}/\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{CaO}/\gamma$ - $\text{Al}_2\text{O}_3$  sorbents by the sol-gel method; (2) test of the thermal and chemical stability of these sorbents and (3) measurements of  $\text{SO}_2$  sorption and desorption (regeneration) equilibrium and kinetics on  $\text{CuO}/\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{CaO}/\gamma$ - $\text{Al}_2\text{O}_3$ , silicalite and the DAY zeolite sorbents.

Two sol-gel methods were developed to synthesize  $\text{CuO}/\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{CaO}/\gamma$ - $\text{Al}_2\text{O}_3$  sorbents. In both methods, the support  $\gamma$ - $\text{Al}_2\text{O}_3$  was synthesized by hydrolysis and condensation of an aluminum metal oxide. The acceptor was coated to the support by, in the first method, mixing a solution containing precursor of the acceptor into the alumina (boehmite) sol, and, in the second method, wet-impregnating the calcined sol-gel derived  $\gamma$ - $\text{Al}_2\text{O}_3$  with a precursor containing solution. The sorbent synthesized have surface area, pore volume and average pore size of about  $250 \text{ m}^2/\text{g}$ ,  $0.4 \text{ ml/g}$  and  $40 \text{ \AA}$ , respectively. XRD data suggest that acceptor amounting up to 40 wt% can be coated on the grain surface of the alumina support. The acceptor appears to be present in a form of two dimensional layer on the grain surface of the support.

The sol-gel derived alumina sorbents have a good thermal and chemical stability. The surface area of these sorbents, after treatments under conditions much more harsh than those encountered in practical use of these sorbents, is still larger than that of sorbents commercially used for FGD. As these alumina sorbent particles consist of fine grains of  $\gamma$ - $\text{Al}_2\text{O}_3$  strongly bound by necks of the same material formed through sintering, these sol-gel derived sorbents appear to be mechanically very strong. The zeolites studied also exhibit extremely good chemical and thermal stability.

The sol-gel derived  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  can take 5.66 mmol  $\text{SO}_2$  per gram of sorbent, larger than the CuO sorbents prepared by other method (1.03 mmol/g). The sol-gel derived  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  can be completely regenerated using  $\text{H}_2/\text{N}_2$ .  $\text{SO}_2$  sorption and regeneration rates on the sol-gel derived  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  sorbent are also greater than those on the CuO sorbents prepared by other method.  $\text{SO}_2$  sorption and regeneration properties of the sol-gel derived  $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$  sorbent are not as good as those of the  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  sorbent in terms of equilibrium sorption capacity and sorption/regeneration rate.

The adsorption isotherms of  $\text{SO}_2$  on the DAY zeolite and silicalite were measured at temperatures ranging from 25 C to 100 °C and  $\text{SO}_2$  partial pressures up to about 40 mmHg (with air, at total pressure of 760 mmHg). All the adsorption isotherms could be well correlated by the Freundlich equation. The heats of adsorption for the DAY zeolite is 6.9 kJ/mole, smaller than that of silicate, 16.9 kJ/mole. The DAY zeolite also adsorbs less amount of  $\text{SO}_2$  than silicalite under the same conditions. These results indicate that the DAY zeolite has a weaker affinity with  $\text{SO}_2$  as compared to silicalite, although the former has a larger surface area and pore size. The adsorption rate constants for the DAY zeolite and silicalite are essentially the same, regardless the substantial difference in the intracrystalline diffusivity of these two zeolites. This suggests that adsorption of  $\text{SO}_2$  on the internal surface of the zeolites is the rate-limiting step.

This research project in year four proceeded as anticipated and achieved expected results described in the proposal, although the project was not in place until the end of November, 1993. The work performed in year four was focused on the synthesis and properties of FGD adsorbents with improved properties, not on development of new FGD processes. It is difficult to provide enough and accurate economic information, at this stage, about the FGD process employing the new adsorbents developed in this work. These adsorbents will be used in dry and self-contained sorption process in which  $\text{SO}_2$  is recovered as a useful product and no waste is generated. Based on the developed technology, the operating costs of the sorption process employing the sol-gel derived

adsorbents developed in this work are estimated to be less than \$200/ton of sulfur removed.

The research project will continue in year five with support from OCDO. The anticipated steps following the work performed in year four include (1) synthesis of the CuO/DAY zeolite sorbent and the alumina sorbents in pellet form; (2) measurements of SO<sub>2</sub> sorption and regeneration on the CuO/DAY sorbent, and of the mechanical strength and attrition resistance of the CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite sorbents and (3) experiments on removal of SO<sub>2</sub> from simulated flue gas using the sorbents developed. It is expected that at the end of year five the novel adsorbents with desired properties and in practically applicable form will be available for pilot tests in FGD sorption process.