**OHIO COAL
RESEARCH CONSORTIUM**

1996

FINAL REPORTS SUMMARY

MASTER

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OHIO COAL RESEARCH CONSORTIUM

FIFTH YEAR

FINAL REPORTS SUMMARY

**for the period
September 1, 1994 through February 29, 1996**

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

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December, 1996

OHIO COAL RESEARCH CONSORTIUM

FIFTH YEAR FINAL REPORTS SUMMARY

**for the period
September 1, 1994 through February 29, 1996**

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 SO₂ 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 eleven studies in these areas.

PREFACE

As a part of its efforts to ameliorate the effects of sulfur in Ohio coal, the OCDO in late 1988 established a consortium of four Ohio universities, called the Ohio Coal Research Consortium, to conduct a multi-year fundamental research program. The consortium research work is to represent an integrated, cooperative program among all of the consortium 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.

OCDO is providing this status, in summary form, of the project work completed in the Consortium's fifth 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_2 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_2 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.

* Please note the reference to the current Consortium-2 program and to the Monograph on dry scrubbing at the end of this report.

- ♦ 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/91-1.1
OCDO Grant No. CDO/R-87-2C/B

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

Final Report for the Period
September 1, 1994 to February 29, 1996

by

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March 1996

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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 the flue gas desulfurization. The goal is to provide fundamental research kinetics and effects of sorbent properties, aimed at improving SO_2 removal and increasing sorbent utilization in a cost effective manner.

The fifth year project work has been carried out in two phases: 1) modified sorbent studies to understand the influence of sorbent modifications (both physical and chemical) on reaction mechanism, and 2) development of a comprehensive sulfation model to interpret and predict short-time simultaneous calcination, sulfation and sintering processes.

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 weight % at 1353 K. The modified hydrate possesses higher surface area (about $45 \text{ m}^2/\text{g}$) as well as internal porosity (32%). Results indicate higher capture ability 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. Work with modified calcium carbonate sorbent (Forsby carbonate) has generated some very interesting results. Forsby carbonate has shown conversions of 50% while the ligno modified and pure linwood hydrate show only about 36% and 30% respectively. Forsby carbonate has thus shown nearly 70% higher capture than the pure hydrate. The extraordinary sulfur capture ability shown by Forsby carbonate makes it a viable sorbent for Furnace Sorbent Injection (FSI) process. It is evident that Forsby carbonate's initial high surface area and associated pore structure translate into optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. It has been observed in prior studies that not all the limestone samples with initial high surface area exhibit very high sulfation conversion. The pore size distribution of their calcines show a preferential dominance of very small pores, and much like Linwood carbonate sample, such high concentration of small pores leads to premature pore plugging. Therefore, there must

exist an optimum pore structure affiliated with the uncalcined carbonate, which on calcination, makes the nascent pore size distribution of CaO favorable for the sulfation reaction. Identifying the optimum pore distribution of original carbonate powder has not been attempted in this study and presents an area for future work.

The results of this investigation bring up an interesting comparison between limestone and hydrated lime sorbents. Some of the earlier studies employed very low surface area (non-porous) carbonates and also of average size larger than the hydrates. So, the higher conversion shown by the hydrate sorbents most probably has been a result of smaller particle size. When particle size is equally small for both these powders, the advantage of hydroxides may have resulted from a more favorable pore size distribution of its calcine. This can be explained if we consider the initial structure of the hydroxide sorbents, which is more porous with an inherent distribution of pore sizes. As a result, the size distribution of its nascent calcine is shifted to the larger sizes, preventing rapid reaction termination caused by pore-mouth-plugging. In case of carbonates, the small CaO pores experience severe pore-mouth-plugging which restricts its final utilization. However, when the parent carbonate powder is porous and possesses a favorable pore size distribution, the calcine pore structure can make the carbonate powder a more attractive furnace-injection sorbent than typical $\text{Ca}(\text{OH})_2$ powders.

The comprehensive modeling work represents an initial effort to develop a comprehensive framework for predicting the total sulfation process. The model incorporates the pore model (for sulfation) into the framework of the grain model (used for calcination and sintering) and therefore represents a unique approach. However, it involves some simplifying assumptions and some inherent limitations. Neglect of intraparticle diffusion resistance and consideration of SO_2 and H_2O (from calcination) diffusivities, use of the limiting product layer control to model the initial rate data could be the two important drawbacks. The model parameter values as well as the activation energies for reaction and product layer diffusion match very well with the literature. The high activation energy obtained for product layer diffusion serves to corroborate the solid-state diffusion mechanism proposed earlier.

OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC/94-1.2

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

Fifth year final report

by

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February 1996

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

EXECUTIVE SUMMARY

The focus of this project is on sorbent injection technologies using dry, calcium-based sorbents for high-sulfur coal flue gas desulfurization. The goal is to provide research findings on handling, transport and dispersion of sorbent powder, aimed at improving SO_2 (to at least 90%) removal and increasing sorbent utilization in a cost-effective fashion. With this goal, the purpose of this project is to investigate the fundamental aspects of powder technology relevant to the fine sorbent powders, and to provide means of improving sorbent performance through superior dispersion and reduced dispersed particle size.

The fifth year's project contains three phases, Phase I "Characterization of Electrostatic Properties", Phase II "Cohesive Strength of Modified Sorbents", and Phase III "Modeling of Powder Dispersion". Work under Phase I involves characterization of the sorbents in terms of their electrostatic properties. Phase II investigates the flow properties of several calcium-based sorbents under different handling and transporting conditions. In Phase III, experimental studies are performed to measure the sorbent powder size distribution in different apparatuses and under different conditions. The population balance model proposed in previous studies can reasonably simulate these experimental results.

In phase I, the effects of antistatic agents on the electrostatic properties of $\text{Ca}(\text{OH})_2$ have been examined. Aluminum oxide (a free-flow agent) has been found to have little influence on the charge generation. The addition of carbon black to $\text{Ca}(\text{OH})_2$ seems to result in a less charge accumulation. It is found that the alumina and silicon oxide tend to be charged positively and negatively, respectively. The results on the bulk density show that the addition of alumina to $\text{Ca}(\text{OH})_2$ results in an increase in both loosely packed bulk density and the tapped density at small percentages of alumina followed by a decrease in both densities as more alumina is added. The effects of CTAB on the charging ability of $\text{Ca}(\text{OH})_2$ was determined. Aluminum oxide was found to improve the flowability of $\text{Ca}(\text{OH})_2$ better than silicon dioxide. The presence of CTAB did not seem to affect the size distribution of $\text{Ca}(\text{OH})_2$ during transport.

In Phase II, the effect of lignosulfonate concentration on the cohesive strength of the modified lignosulfonated hydrates have been examined. The results show that the modified hydrates become less cohesive as the concentration of the lignosulfonate surfactant increases in the sorbent. Also, in

coordination with project 1.1, a new sorbent has been prepared for mechanical testing to evaluate its flow properties. This sorbent, Forsby limestone, was observed to have a very high capability of sulfur capture. A particle size distribution analysis has been performed on three sorbents using the sedigraph to study the effect of the surfactant used. The tested sorbents are: modified sugar hydrate with a sugar weight concentration of 1.5 %, modified CMA hydrate with 1.5 % weight concentration of calcium-magnesium acetate added to the water of hydration, and an unmodified pure hydrate. The sedigraph analysis shows finer particles in the modified hydrates. Mechanical testing of the sorbents shows that the surfactant used have improved the flow properties of the modified hydrate.

In Phase III, the agglomerate size distributions have been measured using a cascade impactor at both the entrance and the exit of a powder flow system. The experimental results show that the agglomerate size at the entrance is larger than that at the exit of the system, which verifies the agglomerate breakup mechanism proposed in the powder dispersion model in the last year. Experiments are conducted to measure the agglomerate size distribution in the powder transport apparatus of Project 1.1 under high temperature conditions. The population balance model proposed last year can reasonably simulate the experimental results. Efforts are also taken to simulate the experimental results of the agglomerate size distribution in the powder dispersion nozzle which were reported in the previous final reports. It is found the value of the breakup parameter in the model almost remains constant at about 4.9×10^{-9} under all conditions.

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

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FINAL REPORT

OCRC-94-1.8

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

February 28, 1996

EXECUTIVE SUMMARY

Aim

A search is being carried out for new calcium-based 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 current year objectives include the study of sorbents made by hydrating ordinary or Type I portland cement or portland cement clinker (a cement intermediate) under carefully selected conditions.

Current Year Results

During the current year, the hydration of portland cement in a stirred pressure vessel at temperatures up to 180°C , and in a high speed, stirred ball mill at stirring rates of 3000 rpm has been studied. In addition, the hydration of clinker (a cement intermediate that is ground with a small amount of gypsum to make cement) has been studied. The apparatus that has been used in this work is a stirred glass flask apparatus. The grinding medium that has been used in these experiments is MgO -stabilized ZrO_2 beads or Y_2O_3 -stabilized ZrO_2 beads. The variables studied have included hydration time, hydration temperature, stirring rate, slurry concentration and

SiO₂ addition. The sorbents have been characterized by infrared spectroscopy, X-ray powder diffractometry, BET surface area measurement, and SO₂ uptake measurement (as determined with a bench scale sand-bed sorber).

The results obtained show that an excellent portland cement sorbent can be prepared by milling cement at 120°C at 600 rpm for 15 minutes with MgO-stabilized ZrO₂ beads. They also show that clinker, which is cheaper than cement (since it is an intermediate in the preparation of it) can be used interchangeably with cement as a starting material. Further, it is clear that while a high surface area may be a desirable property of a good sorbent, it is not a requisite property. Among the hydration reaction variables, milling time is highly important, reaction temperature is important and stirring rate and silicate-to-H₂O ratio are moderately important. The components of hydrated cement sorbent are various combinations of C-S-H, calcium silicate hydrate: Ca(OH)₂; AFm, a phase in hydrated cement which can be approximated as [Ca₂(Al,Fe)(OH)₆]₂(SO₄,CO₃,2OH)·6H₂O; α-Ca₂(SiO₃OH)(OH); Ca₃Al₂(SiO₄)(O₄H₄)₂; alite, ~ Ca₃SiO₅; and belite, ~ β-Ca₂SiO₄; with C-S-H. Ca(OH)₂ and AFm being the desirable components. The addition of active SiO₂ to the reaction mixture can increase the amount of C-S-H and reduce the amount of Ca(OH)₂ in the sorbent. Overly vigorous conditions can reduce the amount of C-S-H and increase the amount of α-Ca₂(SiO₃OH)(OH) in it.

The hydration times have been decreased from a previously reported minimum of 3 hours to the above stated 15 minutes. This results in a much lower projected process costs since stirring is energy intensive.

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

Collaborations

Analytical work was done on samples of hydrated cement sorbent for Prof. Keener of the University of Cincinnati. Also help on the preparation of hydrated cement sorbent was obtained from personnel of Union Process Corporation (Akron) in the grinding laboratories of Union Process.

OHIO COAL RESEARCH CONSORTIUM

Subcontract Agreement No.OCRC/92-2.1

INVESTIGATION OF TRANSPORT PROCESS
INVOLVED IN FGD

Final Technical Report
For the Fifth Year
Report Period: Sept, 1994 to February, 1996

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March, 1996

EXECUTIVE SUMMARY

This report describes the work done in the fifth year of the project " Investigation of Transport Processes Involved in FGD".The objectives of this five year plan of study were 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 .In the fourth year the spray cocurrent flow interaction was investigated and a criterion was developed for predicting the flow reversal. Reversal results in deposition of water droplets on the duct wall and occurs when the spray has entrained all the cocurrent flowing stream . Tests on the swirl nozzles in air were conducted and the results indicated that

the mixing is enhanced and the turbulence intensities in the radial direction show an increase of 10 to 30 %.

The following was accomplished in the fifth year. The sorbent injection facility was modified by adding a heater so as to obtain cocurrent flowing air at temperatures (upto 160°F) to simulate the higher flue gas temperatures. Spray cocurrent flow interaction tests were conducted at the higher temperatures . Larger size droplets survived the higher temperature cocurrent flow resulting in larger size droplets downstream of the spray nozzle in the test section. The flow reversal criterion, developed in the fourth year report, successfully predicted the flow reversal for these test conditions also. Tests were conducted with particle laden jet to understand the cocurrent flow particle interactions and flow reversals. A new correlation for potential core length for the particle laden jet was developed from the test data. The criterion for spray reversal was used with the new potential core relation. The criterion successfully predicted the flow reversal for particle laden flows. These criteria will allow the designer to avoid the flow conditions which will result in flow reversal and deposition of droplet and sorbent particles on the duct wall and floor which can lead to poor sorbent utilization. Tests were conducted on two new swirl nozzles and the simple nozzle. The test data indicated better mixing characteristics for the swirl nozzles. A set up for conducting tests with the swirl and simple nozzles in simulated flue gas containing sulfur dioxide in University of Cincinnati's Sprayer Dryer facility was designed and constructed.

Tests were then conducted with simulated flue gas at University of Cincinnati. The help and cooperation of Dr.T.Keener and his graduate students in conducting the tests and in the analysis of the lime sorbent used is very much appreciated. The test results are very encouraging and indicate substantial improvement, upto 140 % ,in sulfur capture by lime when swirl nozzle 1 is used over the results obtained for the simple nozzle. The swirl nozzle has 4 blades mounted on its outer diameter which swirl the flow. No additional energy is required . The improved mixing resulting from the swirl nozzle has enhanced the sorbent utilization during these tests. Further optimization and improvement in nozzle design is recommended which may be very useful in enhancing sorbent utilization in dry FGD methods.

The chapter on " Transport Processes involved in FGD " for the OCDO manuscript was completed and sent to Dr. Sampson. All the fifth year tasks were addressed and completed .

Two participants Ms.A.Plantner (B.S. Mechanical Engineering) and Mr.M.Assar (Ph.D, Mechanical Engineering) graduated in 1995. Following articles were written and presented in 1995.

1. "Particle Laden Jet and Spray Interaction and Reversal in Cocurrent flow", C.Yurteri, J.R.Kadambi and V.Kadaba, accepted for the 9th International Symposium on Transport Phenomena(ISTP-9) in Thermal-Fluids Engineering ,Singapore 1996/ International Journal of Transport Phenomena, December, 1995.

2. "Spray Reversal in Cocurrent Air Flow in a Horizontal Duct", V.P. Kadaba, C.Yurteri and J.R. Kadambi ,Gas Liquid Flows-1995-FED- Vol.225 , American Society of Mechanical Engineers, New York,NY , 1995 , and also presented at the Summer Annual Fluids

Engineering Conference at Hilton Head, S.C. August 1995.

3. Submitted a chapter on "Transport Processes in FGD" in Dry Sorbent Injection Technology for Sulfur dioxide emission control being published by OCRC for OCDO . December, 1995.

OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC-4.1

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

Final Report for the Period
September 1, 1994 to February 29, 1996

by

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Ohio State University, Columbus. ~

March 1996

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 and economizer sections of a coal-fired boiler. Selenium was chosen as the candidate heavy metal to be studied because of its high volatility and associated difficulties in removal. Mercury being the most volatile of all the trace elements present in coal, has already being singled out for extensive studies by different research programs, funded by EPA, DOE, and EPRI. However the results of the proposed study can be suitably extended to tackle emission problems related to other trace heavy elements.

A thorough mechanistic investigation of the Se-Ca(OH)₂ interaction at both medium and high temperatures has been conducted in this project and is published as a paper entitled, "Selenium Capture using Sorbent Powders: Mechanism of Sorption with Hydrated Lime," to the *Environmental Science & Technology* journal. Experiments were performed in the two temperature ranges in the presence and absence of O₂; desorption studies were conducted to characterize the nature of interaction; and XRD/XPS and Ion Chromatography studies were performed for species identification. It was inferred from these findings that the selenium capture was significantly more in the medium temperature range (450-650°C) than in high temperature range (800-1000°C) and the captured selenium species in the medium temperature range is in the form of calcium selenite (CaSeO₃) and a reaction scheme was proposed for the CaO/SeO₂ interaction:

This reaction process does not require the participation of oxygen, as was confirmed by various analytical techniques and supported by the experimental evidence.

Results of the high-temperature studies indicate much reduced capture at these temperatures with negligible selenium sorption above 900°C. In contrast to the medium-temperature runs, results at these temperatures show a decreasing selenium capture by the sorbent as temperature increases. This behavior was attributed to the decomposition of calcium selenite at higher temperatures.

An Entrained Flow Reactor (EFR) system was designed and constructed in order to study the short time Se-Ca(OH)₂ interaction under entrained flow conditions. the EFR system was designed to conduct experiments with residence time in the range of 1-5 seconds and at temperatures upto 1000°C. Experiments were conducted in the EFR to test the capturability of selenium species by Ca(OH)₂. Results from these experiments indicate that Ca(OH)₂ captured as much as 1100 ppm of selenium species for a residence time of 3.0 seconds under entrained conditions. Thus suggesting the feasibility of Dry Sorbent Injection technique in removing selenium species from flue gas by using calcium based sorbents.

In actual flue gas atmosphere Ca-based sorbents are exposed to various gaseous species including SO₂. The presence of SO₂ along with SeO₂, in the gas phase, could lead to various interactions. Experiments were conducted to determine the selenium capture by the Ca(OH)₂ sorbent, under differential conditions, in an atmosphere with containing SO₂. Results from these experiments indicate that Ca(OH)₂ interacts independently with SO₂ and SeO₂ (no significant gas phase interaction between SeO₂ and SO₂ in the temperature window of interest) in medium temperature range forming CaSO₄ and CaSeO₃ respectively.

OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC-4.2

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

Final Report for the Period
September 1, 1994 to February 29, 1996

by

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Suhas Mahuli
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Liang-Shih Fan

Ohio State University, Columbus, OH

March 1996
(Revised October 1996)

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

EXECUTIVE SUMMARY

The work is mainly focused towards investigating the sorption phenomena of a representative chalcophile, arsenic (As) species, 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. Based on the preliminary thermodynamic analyses it was determined that under the temperature ranges of interest (400-600°C and 800-1000°C) arsenic trioxide (As_2O_3) is the main arsenic species in the flue gas environment and thus is considered as the source of arsenic species for further experimental studies. 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.

Experimental studies were carried out in a differential bed reactor to study the arsenic sorption behavior of three fly ash samples, viz., NIST, Zimmer, and Pickway fly ash. Zimmer fly ash seems to show not only the highest capture among the three, it also showed the highest water non-leachable arsenic capture. Hence, it was proposed to conduct more mechanistic studies with Zimmer fly ash. Desorption studies with the post sorption sample has shown significant reduction in captured arsenic species content following exposure to high temperatures in an arsenic-free environment. These results strongly suggest that interaction between fly ash particles and arsenic species is physical in nature involving reversible physical adsorption.

Studies were also conducted with calcium hydroxide as the chosen representative dry sorbent. This served as comparative studies between fly ash and dry sorbents. This will enable us to predict the behavior of arsenic when exposed to both fly ash and sorbent which is the case under actual boiler conditions. Experimental results show that $\text{Ca}(\text{OH})_2$ captures significant amounts of arsenic species. To gain further insight into the capturing mechanism of calcium hydroxide experiments were performed at various temperatures and exposure times. Studies with $\text{Ca}(\text{OH})_2$ in the medium and high temperature ranges have yielded

interesting results. Amount of arsenic captured by the sorbent in both the temperature windows was found to be nearly identical. The effect of exposure time on amount of capture and the sorption capacity of the sorbent were also investigated. Experiments were conducted in the differential reactor for sorption times as low as 15 min. and as high as 24 hours. Sorbent showed high initial capturability but with increasing exposure time the amount of arsenic captured was found to asymptotically approach a saturation level.

An Entrained Flow Reactor (EFR) system was designed and constructed in order to study the short time As-Ca(OH)₂ interaction under entrained flow conditions. The EFR system was designed to conduct experiments with residence time in the range of 1-5 seconds and at temperatures upto 1000°C. Experiments were conducted in the EFR to test the capturability of arsenic species by Ca(OH)₂. Results from these experiments indicate that Ca(OH)₂ captured as much as 2250 ppm (0.252 wt % CaO utilization) of arsenic species for a residence time of 3 seconds under entrained conditions. Further more entrained flow reactor studies showed nearly identical arsenic capture by the sorbent at 600°C and 900°C reaction temperatures thereby corroborating the results obtained from differential bed reactor experiments.

Project Number: OCRC/4.8

Project Title: Evaluation of Type I Cement Sorbent Slurries in the U.C. Pilot Spray Dryer Facility

Name of Grantee:
Address Civil & Environmental Engineering Department
University of Cincinnati
Cincinnati, Ohio 45221
(513) 556-2518

Project Manager: Tim C. Keener

Period of Performance: November 1, 1994 - February 28, 1996

FINAL REPORT

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

Date: July 31, 1996

Other Investigators: S.J. Khang, CO-PI
G. Robert Meyers, Graduate Student

EXECUTIVE SUMMARY

Objectives

This research was focused on evaluating hydrated cement sorbents in the U. C. pilot spray dryer. The main goal of this work was to determine the hydration conditions resulting in reactive hydrated cement sorbents. Hydration of cement was achieved by stirring or by grinding in a ball mill at either room temperature or elevated temperatures. Also, the effects of several additives were studied. Additives investigated include calcium chloride, natural diatomite, calcined diatomaceous earth, and fumed silica. The performance of these sorbents was compared with conventional slaked lime. Further, the specific surface area and pore volume of the dried SDA sorbents were measured and compared to reactivity. Bench-scale tests were performed to obtain a more detailed picture of the development of the aforementioned physical properties as a function of hydration time.

Conclusions

Over 95% SO_2 removal of a simulated high sulfur flue gas was achieved for hydrated cement sorbents produced under certain conditions and used in the pilot spray dryer at approach to saturation temperatures of $\sim 11^\circ \text{C}$. Typically, hydrated cement sorbents more reactive than slaked lime were produced, but their reactivity was found to be a function of their preparation method. Grinding the material in a ball mill at room temperature with no additives resulted in the most reactive sorbents for the entire study.

Only the tests in which the cement sorbent was hydrated in a ball mill at a temperature of 70°C and with calcium chloride additive at room temperature resulted in cement sorbents that exhibited an increase in uptake over cement sorbents hydrated for the same amount of time at room temperature without additives. Although none of the elevated temperature or additive tests served to improve the reactivity of the enhanced cement sorbents beyond the maximum reactivity achieved by ball milling at room temperature without additives, all of them were at least as reactive as slaked lime. These results indicate that hydrated cement has the potential to be a very efficient and cost effective flue gas desulfurization sorbent in spray drying applications.

The baseline calcium hydroxide and cement results were used to estimate sorbent cost effectiveness based on the cost of the reagent. Calculations indicated a cost of about \$80/ton of SO₂ removed for quicklime, and a cost of \$70/ton SO₂ for the cement sorbents. This corresponds to a savings of \$10/ton of SO₂ removed, or 12.5 percent. As a further example, actual coal fired boiler operating data was used to calculate an annual savings in reagent cost of over \$600,000. Clearly, there is potential for significant cost savings in operating a spray drying system using hydrated cement in place of the conventional slaked lime.

Project Number: OCRC/93-4.9
Name of Grantee: University of Cincinnati
Address: Chemical Engineering Department
University of Cincinnati
Cincinnati, Ohio 45221
Phone number: (513)556-2789
Project Manager: Soon-Jai Khang

FINAL REPORT

Kinetic Studies of Dry Sorbent for Medium Temperature Applications

This Project was funded in part
by the Ohio Coal Development Office
Department of Development
State of Ohio

Date: July 12, 1996 (Revised)

Other Project Investigators:

T. C. Keener, Co-PI

Z. Wang, Graduate Assistant

EXECUTIVE SUMMARY

The purpose of this project is to investigate the fundamental nature of sorbent reactivity and reaction kinetics in the medium temperature range from 600°F (315°C) to 1200°F (649°C) available in the convective pass of a boiler upstream of the economizer, where dry sorbents are injected to remove SO₂ from the flue gas. Research focuses on the mechanisms of sorbent-flue gas interaction under economizer and hot baghouse conditions utilizing the experimental setup and the results of the first four years of research.

During the first year study, it was shown 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 well explored in the literature and yet, thought to be one of the important factors that limit the eventual utilization of calcium-based sorbents. During the second year study, it was shown that the majority of gas-solid reactions with small sorbent particles practically reached its final conversions within the first one 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 one second of reaction time, the sulfation reaction of dolomitic hydrate continues beyond one second of reaction time. Based on the preliminary test results, it was shown that the temperature range of 900°F (482°C) to 1000°F (538°C) appeared to be a favorable zone for the injection of dolomitic sorbent while the range of 1000 to 1200°F (538 to 649°C) was favorable for lime

sorbent under the tested flue gas conditions in the duct work. During the fourth year, the interference of carbonation reaction to sulfation reaction was investigated as well as the concentration dependency of the sulfation reaction. The data showed that the carbonation did not interfere the sulfation reaction rate for reactions taking place less than one second, although the long-term sulfation conversion would be lower with carbonation. However, there was significant decrease in carbonation conversion when the sulfation reaction took place simultaneously.

During the fifth year, research work has been focused on studying the reaction mechanisms and kinetics of medium temperature sorbent injection FGD process in terms of the n-th order deactivation kinetic model. The first-order deactivation model has been successfully applied for carbonation, sulfation and simultaneous reaction. For carbonation reaction, a constant concentration model is applied. For sulfation reaction, since the concentration of SO_2 changes significantly after reaction, it is considered a variable in the model development. For the simultaneous reaction, based on the observations from experimental data on conversion changes for both carbonation and sulfation reactions, it is concluded that the nascent form of CaCO_3 produced from carbonation reaction can further react with SO_2 to form CaSO_3 . Kinetic studies have shown that the proposed models fit the experimental data well. This model is particularly useful for the dry sorbent reactions, since the apparent rate constants rapidly decrease during the first one second of exposure to various gaseous reactants.

Project Number: OCRC/4.10

Project Title: The Effect of Additives on Lime Dissolution Rates

Name of Grantee:

Address: Civil & Environmental Engineering Department
University of Cincinnati
Cincinnati, Ohio 45221
(513) 556-2518

Project Manager: Tim C. Keener

Period of Performance: November 1, 1994 - February 28, 1996

FINAL REPORT

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

Date: July 31, 1996

Other Investigators: S.J. Khang, CO-PI
J. Wang, Graduate Student

EXECUTIVE SUMMARY

Spray drying processes have different physical and chemical features compared with wet scrubbing operations. The dissolution rates of lime and limestone could become a critical limiting step for desulfurization. Spray drying processes contain two phenomena that are totally different from wet scrubbing. One is the short residence time of the liquid phase in droplets, and the second are the highly concentrated ions in droplets and the ion interactions accompanying the water evaporation. According to the literature, the second phenomenon has a relationship to the lime dissolution rate, and because of these phenomena, the lime dissolution rate needs special considerations and studies. Since the dissolution rate can become the limiting step for the overall SO_2 removal in spray dryers (as seen from using different sorbents such as NaOH , Ca(OH)_2 , and CaCO_3), higher dissolution rate could mean higher sorbent utilization. Based on the above reasons, the objectives of this study were;

1. Conduct experiments to measure the dissolution rate of lime. Study the mechanisms of the sorbent (Ca(OH)_2) dissolution rates and the factors that have the greatest effects on the dissolution rate.
2. Study the influence of additives on lime dissolution rates. These additives may exist as trace compounds in the sorbents, the products of the SO_2 , or other gaseous pollutants reacted with the sorbents or added as artificial additives.
3. Incorporate these results into a predictive model which could be used to anticipate changes to performance from baseline conditions.

Six organic additives were tested for their effect on lime dissolution rate. These were phenol, sucrose, glycerin, ammonium acetate, urea, and ethyl-alcohol. For the three additives phenol, sucrose, and glycerin in the additive concentration range of less than 10% by weight, phenol has the greatest effect on lime dissolution rate. When phenol concentrations reach 20%, the lime dissolution rate declines because not all the phenol in water is dissolved. Sugar

enhances the dissolution rate of lime steadily. Adding glycerin to the solution seems to result in little improvement on lime dissolution over pure water, and an increase in glycerin concentration leads to no further improvement in the lime dissolution rate. For all the organic additives, ammonium acetate has the greatest effect in enhancing lime dissolution rate. Urea increase lime dissolution slightly. Alcohol decreased the lime dissolution rate.

Six inorganic additives were also tested for their effects on lime dissolution rate. They were NH_4Cl , NH_4NO_3 , NH_4I , $(\text{NH}_4)_2\text{SO}_4$, CaCl_2 , and NaCl . It was found that most ammonium inorganic compounds have the ability to increase lime dissolution rate. This phenomenon was first considered a chemical reaction, but the activation energy calculated from further tests on NH_4Cl dissolution rate versus temperature indicated that NH_4Cl accelerated the mass transfer process. With a 2% NH_4Cl weight concentration, the lime dissolution rate increased by almost 40 times. The experiment results also showed that ammonium sulfate does not give similar results on lime dissolution enhancement. Further studies found that the insignificant effect by ammonium sulfate is due to the lower solubility of calcium sulfate which could be deposited back onto the calcium hydroxide and prevent further dissolution into the solution.

In pilot plant tests, ammonium chloride as an additive to increase dissolution rate was found to increase SO_2 uptake significantly. Tests with 0.5% concentration addition of NH_4Cl to the slaked lime solution showed a 50% increase in SO_2 removal for a simulated high sulfur coal flue gas. The 0.5% concentration increase was estimated to increase the lime dissolution rate by a factor of two, indicating the sensitivity to SO_2 uptake to the lime dissolution rate.

The results of the bench scale and pilot scale tests on additives have been incorporated into a numerical predictive model called SPRAYMOD-M. This model is a comprehensive coupled heat and mass transfer description of the reaction mechanisms responsible for removal of SO_2 in spray dryers. The model has been modified to incorporate the results from these studies concerning the improvements in removal efficiency and dissolution rate via the use of additives. These effects include increased hygroscopicity and enhanced dissolution of the parent calcium hydroxide particles into the slurry water.

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

FINAL REPORT

Project Duration: September 1994 to March 1996
(Second Year Report)

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March 29, 1996

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.

In the second year, the work was extended to examine three different aspects:

- (I) understanding the mechanisms of capture of metals by vapor phase sorbents,
- (ii) role of chlorine in speciation of metals and its importance in metals capture, and
- (iii) capture of mercury by aerosol transformation.

It was established that aerosol formation rates for Hg species is rather slow under typical combustion conditions, and hence would not be an effective way of capture of mercury. However, the use of titania based sorbents have provided exciting results. This is being developed further for effective capture of Hg species in combustion environments.

Several theoretical investigations were also carried out to better understand and predict trace metal behavior in combustion environments. Publications and conference presentations resulting from work this year is 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 contacted us for further development and commercialization of this approach for metal control.

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.

Final Report
OCDO Agreement Grant No.: OCRC/94-4.14
Reporting Period: 9/1/94~2/29/96

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

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

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March 20, 1996
(Revised, Aug.5, 1996)

Submitted to:

Ohio Coal Development Office, Department of Development, State of Ohio

Executive Summary

In the past year (1994-1995), our research supported by OCDO was focused on (1) synthesis of sol-gel derived alumina supported CuO sorbents in the practical granule form; (2) study of mechanical, sulfation and regeneration properties of the alumina supported CuO sorbents; and (3) preparation of DAY zeolite supported CuO sorbents. The research was aimed at developing novel sorbents possessing better sulfation properties and improved attrition resistance for use in the dry-regenerative flue gas desulfurization (FGD) process for efficient removal of SO_2 .

A sol-gel granulation method was developed to prepare spherical γ -alumina granular supports and supported CuO granular sorbents for flue gas desulfurization. The size of the granules ranges from 1 mm to 5 mm. The prepared spherical γ -alumina granular supports were found to have: (1) desirable pore texture including large surface area ($380 \text{ m}^2/\text{g}$), large pore volume ($0.5 \text{ cm}^3/\text{g}$), narrow pore size distribution (20-60 Å) and controllable average pore size (35 Å) and (2) excellent mechanical properties including high crushing strength ($> 100 \text{ N}$ per granule) and attrition resistance ($0.033 \text{ wt.}\%/\text{h}$). These mechanical properties are far better than the commercially available alumina granules or zeolite pellets.

In comparison with the sol-gel derived sorbents in powder form or other similar sorbents reported in literature, the spherical γ -alumina supported CuO granular sorbents prepared in this work have: (1) higher loading (30-40 wt.%) of CuO dispersed in the monolayer or sub-monolayer form and (2) larger SO_2 sorption capacity ($>20 \text{ wt.}\%$) and faster sorption rate. It also shows that CO_2 has negligible effects on the desulfurization properties of these sorbents. These favorable desulfurization results and the desirable pore texture and mechanical properties make the γ -alumina supported CuO granular sorbents prepared in this work very attractive for use as sorbents for flue gas desulfurization.

Research efforts were also made to prepare DAY zeolite supported sorbents with various CuO contents by the microwave and conventional thermal dispersion methods at different conditions. Monolayer or sub-monolayer coating of $\text{Cu}(\text{NO}_3)_2$ or CuO was achieved on several DAY supported sorbents by the microwave heating method but not by the conventional thermal dispersion method. The DAY zeolite supported CuO sorbents prepared by the microwave heating method can adsorb up to 15 wt.% of SO_2 . The results obtained have demonstrated the feasibility of effective preparation of zeolite supported sorbents by the microwave heating method.

The sulfation kinetic study shows that for sorbents with more than 20 wt. % CuO the sulfation process can be described by a reaction kinetics of second order with respect to the concentration of CuO coated on the support. For sorbents containing 20 wt% or less CuO the interaction of support $\gamma\text{-Al}_2\text{O}_3$ with SO_2 plays an important role in influencing the sulfation process. The kinetic study suggests that increasing the monolayer coating amount of CuO on the support not only increases the sorption capacity but also improves the sulfation rate. Modeling of the regeneration process shows that the regeneration kinetics for the sol-gel derived γ -alumina supported CuO sorbents with methane or hydrogen as the reducing gas can be partly described by the zero or first order reaction model.

POSTSCRIPT

With this Fifth Year Final Summary Report, the initial Five-Year program has been brought to a contractual close. The main part of the program, the dry scrubbing studies, are summarized in a detailed Monograph entitled "Dry Scrubbing Technologies for Flue Gas Desulfurization." This Monograph will be available in 1997. Contained in this monograph are chapters on the following:

Chapter 1, "Flue Gas Desulfurization (FGD) for Acid Rain Control", a literature review that defined the scope of the Consortium.

Chapter 2, "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 SO₂ removal. The lowering of water vapor pressure may be the primary cause for enhancement.

Chapter 3, "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-SiO₂-H₂O) sorbents were developed and evaluated for SO₂ uptake.

Chapter 4, "Transport Process Involved in FGD," which, along with Chapter 5, 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 velocimetry are used to develop non-intrusive procedures for examination of flow reversal zones in ducts.

Chapter 5, "Sorbent Transport and Dispersion." This study examines the cohesive nature of powders and its influence on powder dispersion due to sheer stress in nozzles to simulate flow structure in a nozzle is presented. A model that simulates flow structure in a nozzle is also developed.

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 $\text{Ca}(\text{OH})_2$ Sorbent Injection FGD Process". Medium temperature ($600^\circ - 1100^\circ \text{F}$) 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", which, 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", which, along with Chapters 8 and 9, all advance 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.

Following a one-year hiatus OCDO initiated in September, 1996 a second Consortium program, Consortium-2. Consortium-2 has similar but broader purposes than Consortium-1.