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**ULTRAFINE CALCIUM AEROSOL:
GENERATION AND USE AS A SORBENT
FOR SULFUR IN COAL COMBUSTION**

Final Report for the Period
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Volume I. Experimental Work

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Contents

PART I

1	Background Study	1
1.1	Introduction	1
1.2	Background and Relevance	4
1.2.1	Wet/Wet system	6
1.2.2	Wet/Dry System	8
1.2.3	Dry/Dry System	9
1.2.4	Limestone Injection Multistage Burner(LIMB)	11
1.2.5	Hydrate Addition at Low Temperature (HALT)	17
1.3	Modeling of SO_2 Removal	17
1.3.1	Random Pore Model	18
1.3.2	NO_x Removal	21
2	Project Overview	24
2.1	Experimental Design	24
3	Experiments with Organometallic Aerosol	28
3.1	Introduction	28

3.2	Experimental System	28
3.2.1	Experimental Procedure	34
3.3	Results and Discussion	36
4	$Ca(OH)_2$ Aerosol Experiments	47
4.1	Introduction	47
4.2	Experimental System	47
4.2.1	Aerosol Generation and Control	49
4.2.2	Gas Supply and Flow Control	52
4.3	Reaction Chamber and Temperature Control	53
4.4	Gas Analysis and Analyzer Calibration	54
4.5	Powder Collection and Analysis	55
4.6	Experiment	55
4.6.1	Steady $Ca(OH)_2$ aerosol generation	56
4.6.2	Performing Desulfurization Study	57
4.7	Results with $Ca(OH)_2$ Aerosol	58
5	Analytical Model	69
6	Conclusions	75
	Bibliography	77
	Appendix A	83
	PART II	
	Economic Feasibility Study	

List of Figures

1.1	Generic Wet/Wet Flue Gas Scrubbing System [Goldstein, 1990]	7
1.2	Generic Wet/Dry Spray Drying System [Appel, 1989].	8
1.3	Effect of residence time on sulfur removal at 1400K wall temperature [Chang <i>et al.</i> , 1985]	10
1.4	LIMB Process Flow Diagram, [Nolan <i>et al.</i> , 1990]	12
1.5	Effect of Humidification of SO_2 removal [Offen <i>et al.</i> , 1985] . .	13
1.6	Dry SO_2 removal Process (Muzio and Offen, 1987)	14
1.7	Comparison of full-scale SO_2 removal to pilot plant experience [Nolan <i>et al.</i> , 1990]	16
1.8	Particle size effects on conversion vs. time of the solid with uniform distribution of pore size (Yu and Sotirchos, 1987) . . .	20
1.9	Reburn Fuel Vs. NO_x emission (Eskinazi <i>et al.</i> , 1989)	22
3.1	Schematic of Experimental Flow Reactor System	29
3.2	Alumina Aerosol Generation	37
3.3	TEM of aluminum aerosol.	38
3.4	SO_2 removal vs. inlet SO_2 concentration at 625, 700, and 725°C	39
3.5	SO_2 removal vs. Addition ratio (3.0 Al : S)	41

3.6	NO_x removal vs. inlet NO_x concentration at 500°C	43
4.1	Schematic of Experimental system.	48
4.2	Schematic of Flame jet gun and reactor system.	51
4.3	TEM of calcium aerosol.	60
4.4	SO_2 removal vs. reactor temperature.	61
4.5	SO_2 removal vs. mass flow rate of Ca aerosol.	64
4.6	SO_2 removal vs. mass flow rate of Ca aerosol.	65
4.7	SO_2 removal vs. addition ratio (Ca/S) at the reactor temperatures 650 and 750°C.	67
4.8	Sorbent utilization vs. addition ratio at reactor temperatures 650 and 750°C.	68
5.1	Comparison of Theoretical and Experimental results of outlet vs. inlet SO_2 concentration.	72
5.2	Comparison of Theoretical and Experimental results of SO_2 removal vs. sorbent addition ratio.	74

List of Tables

1.1	Global Nitrogen Emission estimates form 1930 to 1980 by continent in million ton (MT) of equivalent NO_2 (Digman and Hammed,1989).	5
1.2	Global Sulfur Emission estimates form 1930 to 1980 by continent in MT of equivalent SO_2 [Dignon and Hameed, 1989]. . .	5
3.1	SO_2 Removal by Alumina Aerosol	40
3.2	NO_x Removal by Alumina Aerosol	44
3.3	SO_2 and NO_x removal by Alumina aerosol (at high reactor temperature and inlet gas concentration)	45
3.4	Simultaneous SO_2 and NO_x removal by Aluminum Aerosol . .	46
4.1	SO_2 Removal by $Ca(OH)_2$	62
4.2	SO_2 removal by $Ca(OH)_2$	66
5.1	Compaision of theoretical and experimental values	71

Chapter 1

Background Study

1.1 Introduction

Coal in the United States is an abundant source of fossil fuel energy. However, its utilization poses several problems to both human health and environmental safety. SO_2 and NO_x removal from flue gas emission has become an extremely important issue in air pollution control. Coal-fired utility boilers account for approximately 70% of SO_2 emissions and 20-25% of NO_x emissions in the United States. These emissions are believed to be major sources of acid rain.

Coal is not a pure hydrocarbon fuel. It contains inorganic matter (ash), nitrogen and sulfur. These form particulates (fly ash), nitrogen oxides, and sulfur oxides. The emission of such pollutants to the atmosphere can be avoided by removing the pollutants from the combustion products, preventing their formation, or removing the constituents which form pollutants from

the coal [Case, 1982].

According to government forecasts, the demand for electric power in the United States will grow at an annual rate of 2.4 percent throughout the 1990's. Coal makes up 80 % of the fossil fuels used today. Coal-fired facilities supply 57 percent of electric power. It can be assumed that coal will be used to meet this demand well into the next century. Because of instabilities in the foreign oil market, the United States must achieve energy independence. Coal burning power plants will help meet this goal. To increase coal utilization, more effective processes to eliminate the hazardous emissions are needed.

Ohio coal, high-sulfur coal, contains an average of 3.5% sulfur by weight [OCDO, 1987a]. This corresponds to an emission potential of more than 6.0 pound of sulfur dioxides per million Btu of coal burned. According to EPA, regulations restrict emission limits from new coal-fired utility plants for between 0.9 to 1.2 pounds of sulfur dioxide per million Btu of coal consumed. In 1985, Ohio's coal-fired electric utility plants registered an overall emission rate of about 4 pounds of sulfur dioxide per million Btu of fuel burned [OCDO, 1987b]. To achieve a standard of 1.2 pounds of sulfur dioxide per million Btu of coal the overall emission rate of Ohio utilities must be reduced by about 70%.

A major part of the operating costs of coal fired power plants is associated with the amount and quality of coal located near the plants. In Ohio, a large concentration of power plants can be found by the Ohio river where south eastern Ohio coal can be inexpensively delivered by barges and trucks from local mines. In recent years, however, due to the growing concerns of the environmental impact of using this high sulfur- coal, there has been consid-

erable discussion of changing to higher priced, low- sulfur eastern coal. Since the mid 1960s, in an attempt to reduce the general level of sulfur dioxide emissions, Ohio power utilities have experimented with several desulfurization systems (lime and limestone wet scrubbers.) While these technologies have proven their abilities to effectively control SO_2 emission, they have also established their primary detractor; namely their extraordinary high costs and large waste management problems. Henceforth, it is very important to refine these existing systems and to develop new technologies that are effective and economically feasible.

Calcium compounds such as limestone, dolomite, and hydrated lime have been investigated as sulfur dioxide sorbents for coal combustion processes. When limestone is injected into a flue gas stream, several factors can retard its sulfur-capture ability. Direct limestone injection into the combustion zone tends to reduce efficiency because $CaSO_4$ is unstable at combustion temperatures. The use of pulverized limestone particles as sorbents, either in the combustion zone or post combustion processing, can result in under-utilization of the sorbent due to pore mouth plugging by $CaSO_4$ sintering at high temperatures, and other losses of reactive surface area. Previous studies have shown that sulfur dioxide removal is more effective if limestone sorbent particles are small in size, with high surface areas per unit mass.

Aerosols are defined as small particles (solid or liquid) finely dispersed in gases. The particles are usually less than 10 microns in size. Submicron size aerosols are called ultrafine aerosols. Studies conducted at Ohio University and elsewhere have demonstrated that ultrafine aerosols, which have the highest surface area per unit mass, have enhanced potential to efficiently

remove sulfur dioxide from combustion gases.

The goal of this project is to generate a very fine aerosol containing calcium and alumina sorbent materials. In experimental studies, liquids as well as solids were made into ultrafine aerosols by using a suitable aerosol generator. The following methods were attempted:

- 1) Liquid vaporization using aluminum isopropoxide.
- 2) High temperature flame jet using powdered calcium hydroxide.
- 3) Selective entrainment of calcium hydroxide powder by a fluidized bed.

Studies were carried out to determine the dynamics of SO_2 and NO_x capture by these ultrafine aerosols. Aerosol characteristics such as particle size distribution and specific surface area were also determined.

1.2 Background and Relevance

The problem of emissions from coal combustion have been studied by various researchers. J. Dignon and S. Hameed (1989) developed statistical models to estimate global emissions of SO_2 and NO_x in fossil fuel combustion at ten year intervals from 1860 to 1980. Over this period sulfur emission increased at the rate of 2.9% per year and nitrogen emissions at the rate of 3.4% per year. The ratio of global sulfur emissions to nitrogen emissions has declined steadily; it was nearly 5:1 in the 19th century and became 3:1 by 1980. After the second world war, the most rapid increases in emissions have been registered in Asia, South America, and Africa.

<i>Country</i>	1930	1940	1950	1960	1970	1980
N.America	8.19	6.83	10.0	13.4	22.8	24.2
Europe	6.14	8.20	7.00	10.7	12.8	15.5
Asia	1.42	3.00	4.15	12.3	19.3	27.7
S.America	0.17	0.35	0.38	0.78	1.42	2.34
Oceaniaca	0.15	0.17	0.28	0.44	0.48	0.62
Africa	0.16	0.22	0.40	0.66	1.04	1.86
Total	16.2	18.8	22.2	38.3	57.8	72.9

Table 1.1: Global Nitrogen Emission estimates form 1930 to 1980 by continent in million ton (MT) of equivalent NO_2 (Digman and Hammed,1989).

<i>Country</i>	1930	1940	1950	1960	1970	1980
N.America	21.9	16.5	24.8	24.4	33.7	29.0
Europe	21.4	24.7	20.7	29.5	29.6	30.4
Asia	5.0	8.6	12.0	33.9	43.2	56.5
S.America	0.42	0.48	0.83	1.52	2.52	4.0
Oceaniaca	0.44	0.50	0.80	1.18	1.32	1.51
Africa	0.49	0.66	1.11	1.82	2.72	4.15
Total	49.6	51.4	60.2	92.3	113.1	125.6

Table 1.2: Global Sulfur Emission estimates form 1930 to 1980 by continent in MT of equivalent SO_2 [Dignon and Hameed, 1989].

The first attempts at removal of pollutants from the coal-fired flue gases were taken in England in the late 1930's, but were discontinued due to the fact that the German Luftwaffe used the plumes of vapor given off by the project as a point of orientation during the second blitz of London. After World War II, little interest was shown in the chemical process until the mid to late 60's. Most of the scrubbers in use today are based on concepts worked out during the 1960's. In the United States the first full-scale scrubber begun operating in 1967 at a coal-fired power plant owned by Union Electric of Missouri. Since then, utilities suppliers, architecture and engineering firms, and the federal government have taken part in developing the technology. The 1970's Clean Air Act amendments produced a major impact on the industry, and the utilities began the planning and construction of wet flue gas scrubbers.

Flue gas desulfurization (FGD) systems (mainly throw away systems, generally using limestone or lime based sorbents) can be classified into the following three groups:

1.2.1 Wet/Wet system

The sorbent in solution reacts with the flue gas and the resulting calcium sulfate/sulfite is removed from the scrubber as a slurry. The wet/wet system has been commercialized much more than other systems because the technology is proven and it is cost effective. Although it is an efficient technology (90% SO_2 removal), without proper pH control of the slurry, many problems are associated with the large amount of slurry disposal as well as operational problems such as excessive $CaSO_3/CaSO_4$ scaling, spray nozzle plugging,

Figure 1.1: Generic Wet/Wet Flue Gas Scrubbing System [Goldstein, 1990]

and corrosion [Goldstein, 1990]. An example of wet/wet system is shown in Figure 1.1

The lime or alkaline slurry is supplied to the spray tower. The SO_2 content in the flue gas reacts with the slurry, while the gas-phase is cooled to the slurry temperature. The desulfurized gas then passes through a mist eliminator and is reheated in order to minimize the corrosion of downstream materials [Maurin, 1985]. The disadvantages of this system are: (a) wet scrubbers require expensive corrosion resistant alloy coatings and, (b) pumping costs are extremely high compared to dry scrubbing.

Figure 1.2: Generic Wet/Dry Spray Drying System [Appel, 1989].

1.2.2 Wet/Dry System

Wet/dry systems involve the use of a humidified scrubber with a liquid water phase within the scrubber. The output products of the scrubber are dry. An example of a wet/dry system is shown in Figure 1.2. It is similar to the wet/wet system but in this case the alkaline slurry is finely atomized. Here the water in the finely dispersed particles evaporates upon contact with the hot flue gases allowing the sorbent to absorb the SO_2 before impacting the spray dryer's wall. Only a dry reaction product is left, which does not corrode the walls. The reaction between the dissociated SO_2 and dissolved $Ca(OH)_2$

can be shown as follows:

Babu *et al.* (1986) measured the rate of SO_2 sorption into a $Ca(OH)_2$ solution using a laminar jet apparatus. They concluded that the reaction in the solution was instantaneous.

The advantages of wet/dry scrubbing are: (a) the waste product is dry and, (b) expensive alloys or coatings are not needed in the reaction environment. The disadvantages are the pumping cost and close water loop requirements that are associated with this type of slurry injection method.

1.2.3 Dry/Dry System

In a dry/dry system there is no liquid water phase within the scrubber and the exhaust product that is collected in an electrostatic precipitator or a bag house is dry. This is the simplest and least expensive technology. One of the dry/dry processes involves injecting a Ca-base sorbent $CaCO_3$ or $Ca(OH)_2$ directly into the combustion chamber. When heated, sorbent particle decompose to CaO particles which reacts with SO_2 in the furnace exhaust gas stream to form $CaSO_3/CaSO_4$.

McElroy (1987) classified dry scrubbing techniques into three categories:

- 1) In-furnace and over-furnace zone injection (1800 - 2100°F) 2) convective

Figure 1.3: Effect of residence time on sulfur removal at 1400K wall temperature [Chang *et al.*, 1985]

zone injection (800 - 1100°F), 3) post-furnace humidified in-duct injection (less than 350°F).

There have been studies on dry/dry systems. SO_2 removing action in the dry/dry system was enhanced by particulate collection devices such as ESP and baghouse (Pohl,1985). It has been shown that humidification improved SO_2 removal efficiency as the flue gas approaches adiabatic saturation for the sorbent injection system. In this system about 50 to 70 % SO_2 removal efficiency can be reached for low and medium-sulfur coal.

1.2.4 Limestone Injection Multistage Burner(LIMB)

One of the methods of low cost control of SO_2 and NO_x emissions is the Limestone Injection Multistage Burner (LIMB). It is based on the injection of a dry sorbent into the boiler for direct capture of SO_2 in the flue gas, combined with the use of low- NO_x burners for reduction of NO_x emissions. LIMB technology tests were conducted on the coal-fired, 105 MWe, Unit 4 boiler at Ohio Edison's Edgewater station. During the initial test runs of LIMB in September 1987, SO_2 removal was approximately 55-60% at a Ca/S ratio of 2.0. The NO_x emission goal was 0.5 lb per million Btu. A full-scale humidification system was added to the unit in 1988. The humidification system was designed to condition the flue gas to reduce ash resistivity as well as to increase overall SO_2 removal by promoting downstream sorbent/gas reaction. LIMB operation at a Ca/S ratio of 2.0 has been shown to be capable of achieving approximately 55-72% SO_2 removal depending on the specific sorbent and degree of humidification employed. It was also possible to operate the low- NO_x burners with an average emission of 0.48 lb per million Btu.

The combustion of calcium enriched coal was studied by Chang *et al.* (1985) in a laminar flow reactor. The variables were residence time, oxygen concentration, reactor temperature and amount of calcium additive. Results indicated that sulfur capture increased with the residence time and oxygen concentration, and was proportional to the Ca/S ratio of the coal. Experiments were carried out at 1400K and 1600K reactor wall temperatures. Results showed that lower particle peak temperatures and longer residence

Figure 1.4: LIMB Process Flow Diagram, [Nolan *et al.*, 1990]

times in the region favored CaSO_4 formation and improved sulfur capture. High sulfur removal in the case of 1400K wall temperature could be due to direct formation of CaSO_4 by the reaction $\text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4$.

Several investigators have shown that calcium utilization in the temperature range of interest for LIMB is influenced by the available surface area of the calcine in the sulfation temperature window. Calcium utilization in excess of 30% could be achieved with a Ca/S ratio 2.0 if a calcine with a surface area exceeding $40 \text{ m}^2/\text{gm}$ was used.

The EPA's LIMB program is currently focusing on the injection of limestone materials just above the furnace outlet and ahead of the super heater. To commercialize LIMB technology, a special focus required on effects that are related primarily to the increased quantity of particulate matter that must flow through the boiler, ESP, and handling equipment. Precautions

Figure 1.5: Effect of Humidification of SO_2 removal [Offen *et al.*, 1985]

Figure 1.6: Dry SO_2 removal Process (Muzio and Offen,1987)

must be taken to avoid the potential for deposits at wet/dry interfaces and for high pH conditions associated with ash handling.

Recently, dry sorbent emission control technology is undergoing evaluation at the large pilot plant level (Muzio and Offen,1987). Interest in this technology is due to the recognition that sorbent performance could be improved by avoiding the hot flame use (Chughai,1986), successful implementation of this technology in West Germany, and the need for a lower cost moderate SO_2 control technology in anticipation of acid rain legislation. Figure 6 is an example of a dry SO_2 removal process. Experiments were conducted at furnace injection temperatures of 1100-1250°C using a variety of calcium-based sorbents. Fine powder sorbent is injected into the furnace

and the sorbent undergoes the following two step reaction:

Ca(OH)_2 injection is still in the demonstration phase in the United States. Thermodynamically, CaSO_4 is not stable above 1250°C in an environment typical of high-sulfur coal-fired combustion products. Pilot tests were conducted with an inlet SO_2 concentration of 2000-3000 ppm (corresponding to 2.5-3.5% sulfur coal). Figure 1.7 compares the SO_2 obtained during these demonstration. The comparison can be summarized as follows:

<i>Sorbent</i>	<i>pilot test</i>	<i>Full scale</i>
CaCO_3	30 – 40%	20 – 30%
Ca(OH)_2	50 – 60%	60 – 65%
$\text{Ca(OH)}_2, \text{Mg(OH)}_2$	70 – 80%	55%

EPRI and other agencies are continuing to develop dry sorbent technology as a lower cost option to wet scrubbing when SO_2 reduction up to 60% is acceptable.

Dry scrubbing with fabric filters works in two phases: (i) in the transport line section where fine powders are injected and mixed with the gases, and (ii) across the sorbent cake which develops at the fabric filter (Keener and Biswas).

Figure 1.7: Comparison of full-scale SO_2 removal to pilot plant experience
[Nolan *et.al.*, 1990]

1.2.5 Hydrate Addition at Low Temperature (HALT)

Hydrate Addition at Low Temperature (HALT) process studies have been carried out by Babu (1986), Blythe (1986), Rice and Bond (1990), and many others. In this process, a dry sorbent $Ca(OH)_2$ and a fine spray of water are introduced separately. Absorbed water plays a key role in promoting SO_2 capture. Pilot-and demonstration-scale tests of dry injection have shown 50-70% SO_2 removal with an inlet concentration of 2000-3000 ppm using a Ca/S ratio of 2.0 and an approach of 6-12°C to adiabatic saturation temperature. The efficiency of SO_2 removal is primarily a function of reaction kinetics between the sorbent and flue gas.

1.3 Modeling of SO_2 Removal

High temperature limestone/lime sulfation kinetics are critical elements in SO_2 control technology studies. Many papers on mathematical modeling as well as experimental results in this area of studies have been published (Potter 1969; Borgwardt 1970; Hartman and Coughlin 1976, 81; Bhatia *et al.* 1980, 81; Chirstman and Edgar 1983; Yu and Sotirchos 1987; Garman and Boni 1987; Gullett and Bruce 1987). Development of extensive surface area and concurrent pore structure is necessary for the production of a highly reactive sorbents. Experimental results of SO_2 and O_2 with limestone have shown substantial influence of the geological origin of stone, its porosity and particle size, gas concentration of SO_2 and temperature, pressure, and residence time on the reaction and conversion (Potter, 1969; Borgwardt,

1970). Borgwardt (1970) found that the reaction of SO_2 with limestone was first order and the rate of reaction decreased rapidly as sulfation continued. The diffusional resistance developed in the interior of the particle became the limiting factor after the conversion reached 20 % or higher. Although an extensive pore structure develops during calcination of limestone, the sulfation reaction causes a large decrease in porosity of the reaction products (Hartman and Coughlin 1976). Carbonate rocks and their calcines having large pore values and small grains are best suited as sorbents.

1.3.1 Random Pore Model

For fluid/solid reactions, the random pore model was developed by Bhatia and Perlmutter (1980, 81) which allows for arbitrary pore size distribution in the reacting solid. By considering several idealized pore size distributions it was shown that a solid having a uniform pore size is intrinsically less reactive than the one possessing a pore size distribution. The random model predicts that when temperature is raised, increasing diffusional resistance decreases the surface area developed at any conversion. When there is an increase in the volume of solid phase, and if the initial porosity is not large enough, rapid surface pore closure results in incomplete conversions. The conversion-time behavior and the expected ultimate conversion can be very sensitive to the variation in surface area and porosity accompanied by an increase in the volume of the solid phase. When nucleation is rapid in the regime of kinetic control, the overall rate of reaction was found to be [Bhatia and Perlmutter

(1980, 81)]

$$\frac{dX}{dt} = \frac{k_n C^n S_0 (1 - X) \sqrt{(1 - \psi \ln(1 - X))}}{(1 - \epsilon_0)} \quad (1.1)$$

From the grain model[Bhatia and Perlmutter (1980,81)]

$$\frac{dX}{dt} = \frac{k_s C^n S_0 (1 - X)^m}{(1 - \epsilon_0)} \quad (1.2)$$

where m is identified as a shape factor that depends on the grains: for spheres $m=2/3$, for cylinders $m=1/2$ and for flat plates $m=0$. C is the concentration of the reactant, ϵ is porosity, k_n is the boundary layer mass-transfer coefficient, and ψ is the structural parameter. Eq.(2) incorporates the structural parameter of the solid in terms of porosity and surface area. It predicts a monotonically decreasing reaction rate because the reacting surface is receding.

Experimental results show that the natural procedure persists during the calcination process and that carbonate rocks already porous prior to their calcination are, in general, better suited for sulfation than common dense limestones.

Chirstman and Edger's (1983) model accounts for the resistances for the overall reaction such as mass transfer across a mass transfer boundary layer, (through the porous medium and through the solid product), as well as surface reaction kinetics. The resistance depends on both the initial pore size and the extent of conversion. The reaction rate decreases as the outer layer is plugged. Hartman and Coughlin (1976) overcome this problem with the grain model by noting that a certain amount of residual porosity associated with the largest pores remained after the bulk of the outer shell was plugged.

Figure 1.8 Particle size effects on conversion vs. time of the solid with uniform distribution of pore size (Yu and Sotirchos, 1987)

By using this residual porosity as an adjustable parameter, they obtained a smooth decrease in the reaction rate up to the ultimate conversion.

Random pore models were presented by Sotirchos and Yu (84, 85) and Bhatia (85) for solids with pore size distributions for use under reaction conditions controlled by intrinsic kinetics and diffusion in the product layer. The pore closure behavior depends on the form of pore size distribution, the extent of the intraparticle diffusional limitation, the intrinsic reactivity of the solid, the particle size and the ambient condition.

1.3.2 NO_x Removal

NO_x emissions have a significant role in affecting tropospheric and stratospheric ozone, in contributing to acid rain, in impacting human health, visibility, and in forest dieback. It is receiving considerable attention nationally and internationally.

The 1989 symposium on stationary combustion was attended by over 4,000 individuals representing 40 domestic and ten foreign utility companies, as well as government agencies. It focused primarily on developments in combustion NO_x technology: selective catalytic reduction (SCR), and combined NO_x - SO_2 control process. Key points discussed included the dramatic increase in full scale retrofit demonstrations of low NO_x combustion and the substantial amount of development activity in the United States and abroad to optimize NO_x controls on oil- and gas-fired boilers.

To reduce NO_x emission from stationary sources in the US, primary emphasis has been on retrofit combustion modifications for conventional pulverized coal-fired boilers. These boilers account for 70 percent of all U.S. utility NO_x emissions. Low NO_x burners with overfire air are the preferred approach for tangentially fired and wall fired units. Reburning remains the only widely discussed option for cyclone boilers (Eskinazi *et al.*, 1989). In Figure 9 data indicates that reburning with coal, fuel oil and natural gas can achieve NO_x reduction of between 50 to 75 percent from a baseline of 1,000 ppm to 250 ppm. The most developed and widely applied postcombustion NO_x control technology is selective catalytic reduction. Extensive research is currently underway to determine the effects of NO_x emissions. Selective

Figure 1.9: Reburn Fuel Vs. NO_x emission (Eskinazi *et al.*, 1989)

noncatalytic reduction (SNCR) technologies are receiving increased attention in the United States and Europe. Results with urea injection show the potential for 30 to 50 percent NO_x reduction.

A study of combined SO_2/NO_x removal from flue gas by electron beams has been performed by Helfrich (1987). When a high energy beam of electrons is directed into flue gas, abundant quantities of radicals and free atoms are generated. The radicals and atoms containing oxygen react with SO_2 and NO_x to form acids. These acids can be removed by reaction with an alkali to form solid salts. These reactions are enhanced by a high humidity, low temperature flue gas. The quantity of SO_2 removed by the electron beam is independent of inlet SO_2 concentration as a result of zeroth order reaction kinetics with respect to SO_2 . NO_x removal efficiency is increased as inlet SO_2 concentration increases due to the formation of nitro-sulfuric compounds. 30 to 90 percent SO_2 removal across the electron beam can be achieved at a dose of 1 Mrad. NO_x removal occurs almost entirely in the electron beam and is strongly dependent on radiation dose and SO_2 concentration. For high sulfur levels, 80 to 90 percent removal of NO_x can be achieved at 1.5 to 2.0 Mrad.

Chapter 2

Project Overview

2.1 Experimental Design

As was stated in the last chapter, ultrafine aerosols have the potential of being extremely efficient sorbents for SO_2 and NO_x . The objectives of this project were:

- (1) To demonstrate technical feasibility of producing ultrafine aerosols. A method is to be developed for producing ultrafine aerosols to be used as SO_2/NO_x sorbents.
- (2) To demonstrate the technical feasibility of using ultrafine calcium-rich aerosols for in-furnace and/or post-furnace sulfur capture, both the rate of capture and percent calcium utilization must be determined for real world applications in sulfur dioxide removal from coal combustion flue gases.
- (3) Provide preliminary economic estimates of the cost effectiveness of using ultrafine calcium-containing aerosols as sulfur capture sorbents, i.e. the

information generated in accomplishing the first two objectives will be used as the basis of a comparative analysis of the cost effectiveness of applying ultrafine calcium-containing aerosols to in-furnace injection and spray drying sulfur removal processes.

Studies conducted at Ohio University and elsewhere have demonstrated that ultrafine aerosols, which have the highest surface area per unit mass, have enhanced potential to efficiently remove sulfur dioxide from combustion gases. Therefore it is proposed to generate a very fine aerosol calcium-rich sorbent (or similar aerosols) for gas conditioning. The aerosol will be generated by vaporization of the sorbent compound and subsequent homogeneous nucleation. In experimental studies liquids as well as solids will be converted into ultrafine aerosols by using suitable aerosol generator. The aerosol generator could be a simple bubbler or a flame spray jet using powders of calcium compounds. Studies will then be carried out to determine the dynamics of sulfur dioxide capture by the ultrafine aerosol.

ref?

The primary objective of this research was to generate fine aerosols and to use them for coal combustion SO_2/NO_x gas removal purposes. From the background study on the dry scrubbing system, it can be concluded that the most important experimental parameters are addition ratio, reactor temperature, residence time, total inlet flow rate and inlet SO_2 concentration. Addition ratio is the inlet molar ratio of calcium to sulfur. Before any experimentation, it was necessary to decide and investigate the values of each of the parameters. Each of these parameters were investigated individually and the effects on SO_2 removal were determined. Three different approaches were used to generate aerosols:

(1) An organometallic-based aerosol was generated by the controlled evaporation and subsequent homogeneous nucleation and condensation of aluminum isopropoxide. Gas (SO_2 , NO_x) adsorption/removal then occurred due to the reaction of the acid gases with the aerosol at high temperature. Since the aerosol has a high surface area, the removal rate is enhanced. In addition, there may be reaction of SO_2 and NO_x with aluminum isopropoxide in the vapor phase. In this method, the variable parameters were inlet SO_2/NO_x concentration, reactor temperature and addition ratio (≤ 4). Values of the parameters for the organometallic aerosol experiments were follows:

Reaction temperature: 450 - 800°C

Carrier gas flow rate: 4 lpm.

Inlet SO_2 flow rate: 0.1 to 0.8 lpm .

Inlet NO_x flow rate: 0.1 to 0.8 lpm .

Aluminum Isopropoxide heating temperature range: 190 to 235°C.

Reactor length: 89 cm.

(2) A flame jet gun was used to generate ultra-fine spheroidized particles of calcium oxide, which in turn were to be reacted directly with the simulated flue gas stream.

(3) Finally, a small fluidizer was used to introduce controlled amounts of calcium hydroxide powder aerosol directly into the experimental flue gas stream. Here the variable parameters were also inlet SO_2 concentration, reactor temperature and addition ratio. The total flow rate and residence time were kept constant. For the Ca -aerosol experiment the parameters were:

Length of the reactor: 93 cm.

Inlet concentration of SO_2 : 2000 ppm.

Total gas stream flow rate: 3.13 lpm.

Reactor temperature range: 450 to 1000°C.

Addition ratio: ≤ 2 .

Of the three aerosol generation methods mentioned above, only the flame jet gun failed to yield an acceptable level of experimental and mechanical performance; for the flame jet, the generated particles included large agglomerations of calcium hydroxide. A brief discussion will be presented for this method in chapter 4. Details and results regarding the organometallic aerosol experiment are presented in chapter 3. The fluidized $Ca(OH)_2$ details and results may be found in chapter 4. In chapter 5, an analytical model has been developed, and the results from the model are compared with the experimental results.

Chapter 3

Experiments with Organometallic Aerosol

3.1 Introduction

Two different systems have been used in this investigation. In this chapter, the first of these two systems will be discussed. The experiments described in this chapter involve the use of an organometallic source for the aerosol. This system was investigated because prior experiments had shown that both SO_2 and NO_x can be removed.

3.2 Experimental System

A tubular flow reactor was fabricated for studies on SO_2 and NO_x removal from gases using an aerosol generated from aluminum isopropoxide.

Figure 3.1: Schematic of Experimental Flow Reactor System

Figure 3.1 is a schematic diagram of the experimental system. The experimental system uses an externally-heated tubular flow reactor with a nucleation aerosol generator. Gases containing 1 % SO_2 or NO_x were diluted with N_2 , and then introduced into the reactor. Nitrogen was used so that the nucleation generator would not be clogged by oxidized powders. Aluminum isopropoxide was heated in the nucleation generator. The aluminum isopropoxide vapor was picked up by a carrier gas (N_2) which carried it to the reactor where it was decomposed to form an aerosol. Gases containing SO_2 and NO_x were introduced into this flow reactor. The aluminum-containing aerosol reacted with SO_2/NO_x in the flow reactor. The reacted gases were then analyzed to determine the SO_2/NO_x removal efficiency of the equipment.

For convenience in discussion, the overall system is divided into four subsystems: (a) gas supply; (b) aerosol generator; (c) reactor; and (d) analyzer.

(a) Gas Supply

Gas was supplied from cylinders containing N_2 , SO_2 and NO_x . Both the SO_2 and NO_x gas cylinders contained certified concentration of 2,000 ppm, and 10,000 ppm, respectively nitrogen basis mixture. N_2 was used as a carrier gas. Pressure regulators controlled the outlet pressure of the gas cylinder at 20 psi. Gas flows in the system were controlled by using Matheson (600 series) rotameters. Sample calibration charts were provided with the rotameters by the manufacturer. However, these references applied only to the meter with the control valve at the up stream end. But the experimental system was set with the valve on the down stream end of the meter so the steady volume flow

rate could be maintained even if the downstream pressure was changed. Charts for these meters were developed at Ohio University (Wiseman, 1988). Prior to any experimentation, flow measurements were calibrated using two methods: The first method was based on the formula,

$$Q_n \approx Q_r \left(\frac{\rho_r}{\rho_n} \right)^{\frac{1}{2}},$$

where ρ_r and ρ_n are respectively the densities of the reference and the new gases. Q_n and Q_r are respectively the flow rates of the reference and the new flow at the same rotameter setting. The second method was direct flow measurement using a wet test meter. Once the rotameters were calibrated and metered on the panel, they were connected to the reactor using standard plastic (for N_2) and teflon (for SO_2 and NO_x) tubing for transport of these gases.

(b) Aerosol generation

The nucleation chamber is identified as Furnace 1 in Figure 3.1. It was used for heating the organometallic. It was fabricated with a thin walled metal cylinder, and was mounted inside a second cylinder. The outer wall of the metal cylinder was wrapped with a heating tape. To minimize the heat loss, the outer cylinder was covered with thick fiberglass insulation. To maintain the chamber at a constant temperature, a thermocouple was placed within the metal cylinder and connected to a proportional controller (Love Control Corporation, Model 49). The controller was set at the desired temperature. After an initial heat-up period, the temperature of the furnace was controlled

to $\pm 4^\circ\text{C}$. A quartz tube (22 mm diameter), closed at one end, was partially filled with the organometallic powder and placed in Furnace 1 (inside the metal cylinder) for heating the organometallic. The organometallic powder was heated to produce a vapor, and the vapor condensed into an aerosol. It was originally envisaged that a possible way of desulfurization would be vaporizing calcium organometallic at high temperature. The fine and extra fine CaO aerosol formed by vaporization and subsequent condensation may be an effective SO_2 absorber (Alam, 1986). Unfortunately a suitable chemical compound to produce CaO vapor under laboratory conditions was not found. Therefore, instead of a calcium compound, aluminum isopropoxide was used to produce an aluminum aerosol for desulfurization. The molecular weight of aluminum isopropoxide is 204.25 and the chemical formulae is $((\text{CH}_3)_2\text{CHO})_3\text{Al}$ and melting point $128\text{-}132^\circ\text{C}$. Consequently, the temperature in the Furnace 1 was kept at the range of $190\text{-}235^\circ\text{C}$. Experiments confirmed that aluminum isopropoxide is successful in capturing both SO_2 and NO_x .

(c) Flow Reactor

The flow reactor consisted of a one inch outer diameter and 55 inch long stainless steel tube passing through two tubular electric furnaces. The inlet of the reactor was connected to the Al -vapor supply pipe by an O ring joint. To prevent the condensation of the Al -vapor, the supply pipe was made as short as possible. Two furnaces, called Furnace 2 and Furnace 3, were used to heat the reactor tube. Furnace 2 has a control knob for adjusting the temperature. By manual operation of this known temperature, a constant

temperature could be maintained. The temperature in Furnace 3 was controlled by a proportional controller. In this flow reactor, aluminum aerosol and vapors were heated to decompose and simultaneously react with SO_2 as well as NO_x . The glass fiber insulation formed a good thermal barrier between the inside of the furnace and the outside environment. The outlet of the tube was cooled by room air and provided a good sampling location before venting the reacted gas and powder.

(d) Gas Analyzer System

The gas analyzer system was a critical component of the entire process. Three instruments were used for this purpose. The first instrument used was a COSA 5000 Stack Emission gas analyzer. COSA 5000 is a portable device with electrochemical sensors. An on board microprocessor calculates all measurements to the end point in seconds. A built-in thermal printer produces a hard copy of the results. The inlet flow of COSA is 2 lpm.

The COSA analyzer was used to measure SO_2 and low concentrations of NO_x . By inserting the probe via a filter into the exhaust, the concentration of SO_2/NO_x was measured. The concentration was read from the digital display. It could be used for a maximum concentration of SO_2 / NO_x of 2000 ppm. The COSA instrument was not very suitable for this experimental system. The electro-chemical sensors of the analyzer seemed to get saturated after 30 minute of use, causing the concentration on the display to seem to be less than the expected value. Therefore, the instrument was calibrated with a calibrated gas prior to each experimental run.

A Chemiluminescent NO/NO_x Analyzer (Thermo Electron Corporation

Model 10 AR) was used to measure higher concentration NO_x gas. The Chemiluminescent reaction of nitric oxide and ozone is the basis of Thermo Electron's Model 10 instrument with full-scale ranges from 2.5 to 10,000ppm. It includes an NO_2 to NO converter (thermal conversion of nitrogen dioxide to nitric oxide) for subsequent measurement via the chemiluminescent process. The inlet sample flow is 2 SCFH and it can be used to analyze a gas of concentration up to 2500 ppm.

For experiments with higher concentrations of SO_2 (about 2000 ppm), a Pulsed Fluorescent SO_2 Analyzer (Thermo Environmental Instrument Inc. Model 40) was used (description is given in chapter 4).

A Gelman sciences 2220 filter holder with a microfiber filter, was used to collect the sample powder for analysis.

3.2.1 Experimental Procedure

The experimental procedure was comprised of two parts:

- 1) Aluminum aerosol generation and calibration
- 2) Utilization of aerosol in SO_2/NO_x removal studies.

Aluminum isopropoxide powder was taken in the quartz tube, weighed and placed in the Furnace 1. Furnace 1 was set to the desired temperature (from 190°-235°C). Furnace 2 and Furnace 3 were also set to the desired temperature (from 400°-800°C). When Furnace 1 reached the desired evaporation temperature of the aluminum isopropoxide powder, N_2 was passed through the system as shown in Figure 3.1, and thus the vapors were picked up and carried into the flow reactor. After running the system for 20 to 25 min-

utes, the weight of the quartz tube and the elapsed time was determined. The weight difference divided by the total time was the rate of aerosol generation. The above procedure was repeated by varying the temperature of Furnace 1 in the range from 190° to 235°C.

To remove SO_2 by the aerosol, N_2 and SO_2 gas cylinder connections were opened and the outlet pressure was set at 20 psi in the regulator. Rotameters were adjusted to the desired flow rates ($N_2=4$ lpm, $SO_2=0.1-0.8$ lpm). Both gases were introduced at room temperature into the reactor. The probe of the analyzer was inserted in the exhaust duct and the initial concentration of SO_2 was measured. Aerosol was generated by homogeneous nucleation and condensation as described above, and the SO_2 was introduced into the system. After running the system for about 10 minutes, the final concentration of SO_2 was measured at the exhaust. The whole procedure was repeated with different temperatures and initial concentrations of SO_2 . Some experiments were carried out with NO_x instead of SO_2 , and with both SO_2 and NO_x . At high concentrations of SO_2/NO_x , air (8 lpm) was introduced in the exhaust system after the reactor so that concentration of SO_2 and NO_2 could be measured without saturating the COSA analyzer. Powder samples were collected by using the Gelman filter holder and then analyzed for particle size by Transmission Electron Microscopy (TEM). The system produced very small quantities of powder in a given run, so extensive chemical analysis was not carried out.

3.3 Results and Discussion

The generation rate of ultrafine aluminum aerosol was accomplished by controlling the temperature of Furnace 1. This controls the vapor generation rate which then decomposes into an aerosol. It should be noted here that the SO_2/NO_x gases could also have reacted with some of the organometallic vapor. Figure 3.2 shows the rate of aerosol generation versus the temperature. The maximum aerosol generation rate was 0.1025gm/min, at 235°C as shown in Figure 3.2. The average size of the generated aerosol was 0.3 μm as measured by TEM (shown in Figure 3.3).

In this system aerosol can be generated at a steady rate for about an hour. After this amount of time, the vaporization rate could change drastically because of blockage in the vapor delivery system. SO_2 removal results using this system are shown in Figures 3.4. The SO_2 removal varied from 55 to 95 % with the range of inlet concentrations of 120 to 600 ppm and reactor temperatures in the range of 500 to 725°C while the sorbent feed rate was kept constant. As would be expected, SO_2 removal increased with increasing aerosol generation rate and reactor temperature. Note that, in this particular experiment, the sorbent feed rate is fixed while SO_2 concentration was increased. This is because the sorbent feed rate could not be changed reliably during a run.

Experiments were carried out with higher inlet SO_2 concentration (1522 ppm) and at temperature 725°C varying the addition ratio as shown in Figure 3.5. It shows the SO_2 removal up to 95 % with an addition ratio of 3.2. SO_2 removal increases with increasing addition ratio.

Figure 3.2: Alumina Aerosol Generation

Figure 3.3: TEM of aluminum aerosol.

Figure 3.4: SO_2 removal vs. inlet SO_2 concentration at 625, 700, and 725°C

Run Number	Inlet SO_2 in ppm	Addition Ratio	SO_2 Removal %	Percent Utilization
SO-1 (625°C)	558	0.64	43.01	67.0
	452	0.80	44.47	55.4
	343	1.07	45.19	42.2
	232	1.60	47.41	29.6
	117	3.21	68.38	21.3
SO-2 (625°C)	579	0.62	41.80	67.5
	468	0.77	42.95	55.4
	355	1.03	38.95	37.2
	240	1.55	48.75	31.5
	122	3.08	62.30	20.2
SO-3 (700°C)	589	0.61	46.35	76.2
	477	0.76	47.80	62.9
	362	1.01	51.38	50.7
	244	1.52	59.43	39.0
	123	3.06	74.80	24.5
SO-4 (725°C)	580	0.62	51.90	84.0
	470	0.77	55.53	72.0
	356	1.03	64.89	62.9
	240	1.55	78.33	50.6
	122	3.08	95.08	30.8

Table 3.1: SO_2 Removal by Alumina Aerosol

Figure 3.5: SO_2 removal vs. Addition ratio (3.0 Al : S)

The results of NO_x capture using an organometallic sorbent are shown in Figure 3.6. NO_x removals as high as 92%, using an inlet concentration of 1318 ppm, were observed. All the experiments were carried out with a residence time of approximately 5 seconds. The reacted compound was tested in the chemistry department at Ohio University with infrared spectroscopy (IR). It was observed that sample contained hydroxide, sulfide, and sulfite, which confirmed the previous speculation.

Collectively it is seen that the organometallic system has proven to be an effective method of removing both SO_2 and NO_x . Table 3.3 shows SO_2 removals of up to 93% at an inlet concentration of 2196 ppm and an addition ratio of 3.86. NO_x capture of up to 95% was achieved with inlet concentration 2075 ppm and an addition ratio of 3.40. Simultaneous SO_2 and NO_x capture results and are also shown in Table 3.4. These last results show 99% sorbent utilization. The process is very simple and very effective. There are indications that both high SO_2/NO_x removals and high sorbent utilizations can be achieved through the use of higher addition ratios and higher reaction temperatures.

It was difficult to control and change the sorbent feed rate in this system. To maintain fixed sorbent feed rate, the values of carrier gas flow rate and Furnace 1 temperature must be kept constant. This method is probably not economically attractive for commercial use but these experiments have proven it to be highly promising in the laboratory environment.

Figure 3.6: NO_x removal vs. inlet NO_x concentration at 500°C

Furnace Temp.	Inlet NO_x in ppm	Addition Ratio	NO_x Removal %	Percent Utilization
500°C	1318	0.53	46.28	87.0
	1123	0.64	45.41	71.1
	919	0.80	42.98	53.9
	705	1.06	54.61	51.3
	481	1.60	65.28	40.9
	247	3.18	91.90	28.9

Table 3.2: NO_x Removal by Alumina Aerosol

Furnace Temp. °C	Inlet Conc. of SO_2 (ppm)	Outlet Conc. of SO_2 (ppm)	Addition Ratio %	SO_2 Removal %
625	1506	1218	0.10	19
675	1509	1010	0.25	33
700	1512	653	1.04	56
725	2100	200	3.63	90
800	2196	165	3.86	93

Furnace Temp. °C	Inlet Conc. of NO_x (ppm)	Outlet Conc. of NO_2 (ppm)	Addition Ratio %	NO_x Removal %
800	1790	130	2.17	92
850	2075	95	3.40	95

Table 3.3: SO_2 and NO_x removal by Alumina aerosol (at high reactor temperature and inlet gas concentration)

Furnace Temp.	Inlet SO_2 in ppm	SO_2 Removal %	Inlet NO_x in ppm	NO_x Removal %	Addition Ratio
625°C	1006	14.31	699	47.35	0.23
625°C	1427	14.00	1250	41.00	0.20

Table 3.4: Simultaneous SO_2 and NO_x removal by Aluminum Aerosol

Chapter 4

$Ca(OH)_2$ Aerosol Experiments

4.1 Introduction

The schematic diagram shown in Figure 4.1 is the experimental system in which $Ca(OH)_2$ powder was aerosolized in a special fluidized bed and then introduced into a flow reactor for removing SO_2 from the gas stream. In this set of experiments, the aim was to determine the desulfurization efficiency of a powder sorbent at various rates of powder generation and SO_2 concentrations.

4.2 Experimental System

For convenience in discussion, the overall system is divided into five major subsystem:

- 1) Gas supply and flow control.

Figure 4.1: Schematic of Experimental system.

- 2) Aerosol control and generation.
- 3) Reaction chamber and temperature control.
- 4) Analyzer calibration and gas analysis.
- 5) Sample collection and analysis.

4.2.1 Aerosol Generation and Control

This part of the experiment was accomplished using the modified fluidizer apparatus as shown in the upper right panel (B) of Figure 4.1. The principle of operation of this aerosol generator is that powders will become entrained in a flow and only very fine powders are entrained by low flow velocities. Once the powder is entrained by the flow it becomes an aerosol.

A very fine aerosol was produced by flowing air through an oscillatory cylinder. The bottom of the cylinder was filled with fresh drierite crystals in order to prevent caking of the upper powder bulk. The powder bulk was separated from the drierite using a combination of a steel mesh and paper filter screen. This screen was changed with every batch of new powder. The aerosol flow was controlled by the air flow using a calibrated Matheson 603 low volume rotameter before the fluidizer. After flowing through the fluidizer, the air stream becomes an aerosol stream because it has entrained fine particles of the reagent powder. This stream is then directed to the top of the reaction chamber via $\frac{1}{2}$ inch Tygon tubing. At the top of the reactor this flow is mixed with the dilute SO_2 mixture which is described in the next section.

Since the flow tube was the same diameter of $\frac{1}{2}$ inch, the increased

volume flow increased the velocity of the aerosol stream and yielded good injection into the top of the reactor. Since some particles stuck to the wall of the teflon tubing due to the boundary layer effects, an in-line powder trap was used before the reactor to collect these non-aerosolized powders.

It should be mentioned here that some experiments were carried out with a flame jet gun to determine if fine aerosol could be produced by heating and reaction of powders by flame. The flame jet gun is one of the simplest and most inexpensive methods of generating an aerosol. Flame jets have been used to produce aerosols such as ceramic powders. A common example of a flame aerosol generator is a fuel rich oxy-acetylene flame which produces soot as the aerosol. Other examples of flame aerosol generators are the flame jet used to spray coatings of metals and ceramics on surfaces. Examples include the Mogul Powder Jet (Miller INC.) and Eutectic TERADYN flame jet. For the flame jet to be successful for this project it must be operated at high temperatures (approx. 5400°F) longer dwell time, and under conditions which tend to enhance ultrafine aerosol formation.

A TERADYN flame jet was selected and acquired for the project. This flame jet was installed, and experiments were carried out with limestone particles. Figure 4.2 shows the schematic of the experimental system.

Results from experiments showed that, while fine aerosols were produced in such a flame, a large fraction of the powder did not vaporize. Instead, there was some coagulation of this large fraction, which was highly undesirable. Due to the very poor results of the flame jet gun experiment, the experiment was modified towards a more efficient and repeatable method. This led to the development of the fluidizer described at the beginning of this section.

Figure 4.2: Schematic of Flame jet gun and reactor system.

4.2.2 Gas Supply and Flow Control

As shown in the upper left panel (A) of Figure 4.1, the simulated flue gas composition and volume flow rates were controlled using a mixture of compressed air and bottled SO_2 gas. The compressed air was received directly from the laboratory bench air supply while the SO_2 gas cylinders were received as certified 2,000 ppm and 10,000 ppm air-basis mixtures. Flow control was determined using separate Matheson (600 series) rotameters with the inlet pressures regulated to 40 psi at all times.

Prior to any experimental run, each rotameter was calibrated with the correct gas using a wet test meter at 40 psi inlet and atmospheric outlet pressure. Different rotameters were used for each gas, but as more information was gained the following flow rates proved to be most effective for this system.

Flow	Quantity (lpm)	Rotameter
air into fluidized bed	0-2.48	603
air to dilute SO_2	2.48-0	603
SO_2 (10,000 ppm)	0.65	602
SO_2 (2,000 ppm)	0.80	602

Before mixing the two gas streams, it was necessary to pass the air supply through a drying chamber filled with drierite crystals. This allowed for removal of water and compressor oil vapor from the air supply stream. Once the air was effectively scrubbed, it was turbulently mixed with the SO_2 at a $\frac{1}{2}$ inch T-section just outside of the reactor tube inlet. This mixed stream is

then combined with the powder reagent stream at the top of the furnace as shown in the system schematic. A $\frac{1}{4}$ inch teflon tube was use for SO_2 , and $\frac{1}{4}$ inch plastic tubes were used for air gas transport.

4.3 Reaction Chamber and Temperature Control

Panel (C) of Figure 4.1 shows the flow reactor that was used for this experiment. The reactor consists of a 1 inch outer diameter stainless steel tube passing through the electric furnace. The reactor connects to stainless steel inlet and outlet tubes with *O*-ring fittings. The 93 cm, single zone, Lundberg vertical tube Furnace (model 54453-V) operates at 208 V with a maximum temperature of 1500°C at 6857 W. The furnace is instrumented with platinum/platinum-13% rhodium (type R) thermocouples. It has eight silicon carbide heating elements. It is controlled by a Control Console (LUNDBERG Model 59545-A). Clamps were used to hold the reaction tube vertical at high temperatures. Fiberglass insulation formed a good thermal barrier between the inlet outlet of the furnace and the outside environment. The outlet tube below the furnace was cooled by the outside air to near the room temperature, providing a good side stream sampling location before venting the reacted gases (and powder) to the hood.

4.4 Gas Analysis and Analyzer Calibration

The instrumentation shown in panel (D) of Figure 4.1 performs the most critical and sensitive role in the entire experiment. It consists of a pulsed fluorescent SO_2 analyzer (Thermo Environmental Instrument Inc. Model 40). The principle of operation of the monitor is based upon the measurement of the fluorescence of SO_2 produced by its absorption of ultraviolet radiation.

Once the gas/powder mixture stream emerges from the hot section of the reaction chamber it is necessary to separate the sorbent solids from the reacted gas stream and analyze it to find the gas concentration levels. These goals are simultaneously accomplished by allowing the SO_2 gas analyzer to draw a continuous sample directly from the exhaust stream and pass through a micro porosity filter (Gelman Sciences 2220). The filter separates the sorbent, and, due to its metallic construction, allows the gas sample to be cooled to room temperature. Thus, the delicate SO_2 analyzer can test a temperature conditioned particle gas sample. Once tested, the sample is recombined with the exhaust gases down stream from the inlet sampling particles.

Before discussing the main experimental procedure, the calibration of the SO_2 analyzer needs to be discussed. Prior to doing any experiment the SO_2 analyzer was always calibrated by using a calibration gas of known certified concentration. The calibration was done as follows:

The analyzer was set up to sample (through the filter) directly from a low flow stream of calibrated SO_2 gas. In this experiment this was accomplished by opening and shutting the ball valve located at the T-section before the filter (Figure 4.1). A low flow Matheson rotameter (pre calibrated) is used to

adjust the calibration gas flow to a level that just exceeds the known sampling inlet flow of the SO_2 analyzer. Sampling is done across the filter so that the inlet pressure sensitive calibration may match the stream sampling conditions as closely as possible. For this experiment, calibration was done using a certified 2,000 ppm air basis SO_2 mixture. This procedure was performed before every sampling to ensure the best possible data.

4.5 Powder Collection and Analysis

A Gelman Sciences 2220 filter was used at the exhaust to collect the reactant powder. A vacuum pump was used at the other end of the filter to draw the aerosol through the filter.

4.6 Experiment

The experimental procedure was comprised of two parts:

- 1) Steady $Ca(OH)_2$ aerosol generation.
- 2) Performing desulfurization study.

The start up of the experimental procedure involving the calibration the of apparatus. The apparatus calibrated include the rotameters, powder fluidizer, furnace and the gas analyzer. All apparatus were calibrated prior to each experimental run.

4.6.1 Steady $Ca(OH)_2$ aerosol generation

The height of the $Ca(OH)_2$ powder bed in the fluidizer container and the height at which the cylinder was stationed strongly influenced the generation of aerosol. The best mass flow rate was obtained with the cylinder $\frac{3}{4}$ filled with the $Ca(OH)_2$. The cylinder was placed at the same height as the top of the furnace. The shortest connection length between the fluidizer and reactor tube produced optimum aerosol generation. Once the $Ca(OH)_2$ bed height and the position of the fluidizer were fixed, the mass flow rate was varied by changing the air flow through the rotameter. The air flow rate was varied in the range of 0.44-2.33 lpm and the aerosol generation rate was in the range of 6.53-28.85 mg/min.

The mass flow rate of the aerosol was determined by collecting the sample powder on a 2 inch diameter glass microfiber filter, for a measured period of time. The weight difference of the filter before and after the sample collection divided by the time gives the mass flow rate. An electronic balance made by Sartorius Balance (Balance Sci Inc., minimum reading is 0.0001 gm) was used for weighing the filter. The aerosol generation was determined to be steady for a long periods of time. Therefore, this aerosol generator was much more stable than the nucleation generator discussed in the last chapter. As mentioned earlier, the low flow rates of the air flowing through the fluidizer entrains only the smallest particles and thus produces a stream of ultrafine aerosol going into the reactor.

4.6.2 Performing Desulfurization Study

The operating variables such as inlet SO_2 concentration, addition ratio, the furnace temperature, total gas flow rate, and residence time for SO_2 capture in the high temperature fluidized $Ca(OH)_2$ bed were calculated, or established on the basis of known values, or the dimensions of the reactor. The selected values were: inlet SO_2 concentration [2000 ppm], addition ratio $[(Ca/S)$ preferably less than 4], furnace temperature [in the range of 450 to 900°C], total inlet mixture flow rate [3.13 lpm], and residence time [7.34 sec]. The aim of the experiment was to remove SO_2 flow gases.

Before start up, all the tubes including the reactor, generator and transport line were cleaned. The first step of the experimental procedure was to turn on the room exhaust fan and the SO_2 analyzer. The analyzer takes about 10 minutes to warm up. The calibrated SO_2 gas was opened, the outlet pressure was adjusted to 40 psi on the regulator and the flow rate on the rotameter was set to the desired value. The calibrated SO_2 was passed directly to the analyzer and it was calibrated, and the calibrated SO_2 gas flow was then stopped. The SO_2 (10,000ppm) supply valve, powder fluidizer air, and dilution air supply valves were opened and the outlet pressures were adjusted to 40 psi. The rotameters readings for dilution air, powder fluidizer air, and SO_2 (1 %) were set to the desired value (dilution air = 2.48 to 0.44 lpm; P_{air} = 0.44 to 2.48 lpm and SO_2 =0.65 lpm).

The gas stream was passed through the reactor at room temperature. Then it was drawn into the analyzer from the end of the reactor. The inlet SO_2 concentration was recorded from the analyzer, and then all gas supplies

were shut off. The furnace was set at the desired temperature (30 to 45 min required to reach the set point temperature). When the furnace reached the temperature, the oscillator of the fluidizer was turned on. The powder air, dilute air and SO_2 (1%) supplies were opened and the fluidized powder and SO_2 mixture stream passed through the reactor. The reaction then took place between SO_2 and $Ca(OH)_2$. The reactant stream was drawn to the analyzer through the filter. The gas was analyzed and outlet SO_2 concentration was recorded. The sample powder was collected at the exhaust using a filter for analysis of the particle size, and surface area.

4.7 Results with $Ca(OH)_2$ Aerosol

Determining the efficiency of SO_2 removal by an aerosol of fine $Ca(OH)_2$ was the primary objective of this project. The inherent benefit of using a $Ca(OH)_2$ -based dry sorbent injection system on a commercial power plant is that waste management problems of the existing lime spray slurries is reduced by injecting and disposing of dry powders.

In this method, experimental results were very encouraging: steady aerosol generation was obtained with higher mass flow rates and for long periods of times. Steady aerosol generation was the primary motivation of this experiment. Earlier studies at Ohio University indicated that a major problem of this project is in generating a controlled, steady flow of aerosol. However, it has been possible to overcome this problem and to generate and control the flow of the fine aerosol for SO_2 capture study. It was noted in Chapter 1 that the particle size, surface area, and porosity of the sorbent are very important

for the study of FGD. Sample powders were therefore collected for analysis.

Particle diameters were measured by centrifugal particle size analyzer (Horiba, CAPA-300) and transmission electron microscopy (TEM). The average diameter was determined manually from TEM photographs. Figure 4.3 shows that the particles appear in clusters. The average size of the particles was measured to be $0.4\mu\text{m}$. The BET surface area of the powder was also measured using a Quantector (Quanta Chrome Corporation, Model No. QSJ1-1), and was found to be $41\text{ m}^2/\text{gm}$.

To ensure that the mass flow rate was repeatable, the calibration of mass flow rate was carried out several times with the same air (carrier gas) flow rate. In addition, before every desulfurization experiment, the mass flow rate was determined for each powder air flow rate to get the accurate addition ratio.

In the desulfurization experiment, the focus was on the two effects: addition ratio (addition ratio is defined as the ratio inlet $\text{Ca}(\text{OH})_2$ to inlet SO_2 on molar basis) and furnace temperature. At the beginning, experiments were carried out with a very low mass flow rate (1.0 mg/min) to find out the behavior of the reaction between $\text{Ca}(\text{OH})_2$ and SO_2 and also the power deposition on the wall of the reactor tube. For lower powder flow rates, the amount of powder adhering to the wall was a significant fraction of the flow rate. Therefore, error was introduced in the calculation of percent SO_2 removal. However for large flow rates ($> 10\text{mg/min}$), the amount of the wall deposition was insignificant due to the large amount of powder entered in the stream. While the deposits could react with SO_2 over a long time period, the amount of deposit was insignificant compared to the powder flow

Figure 4.3: TEM of calcium aerosol.

Figure 4.4: SO_2 removal vs. reactor temperature.

rates. Figure 4.4 shows the SO_2 removal rates for different temperatures at

Temp. in ° C	Inlet SO_2 Conc. ppm	Outlet SO_2 Conc. ppm	% Removal of SO_2	Addition Ratio	% Sorbent Utilization
450	1975.0	1275.0	35.00	0.67	52.3
600	1995.0	1092.0	45.12	0.67	67.5
800	1990.0	1015.0	49.00	0.67	73.0

Table 4.1: SO_2 Removal by $Ca(OH)_2$.

constant addition ratio of 0.87. Figures 4.5 and 4.6 show the results of SO_2 removal versus mass flow rate at different reactor temperatures (550, 650, 700 and 750°C). There is a slight variation in the results of Figures 4.5 and 4.6, even though the experiments were run at the same reactor temperature, inlet SO_2 concentration, and mass flow rate. The desulfurization studies show that the SO_2 removal varies with the temperature and addition ratio. The SO_2 removal varies from 47 to 73 % in the range of temperature 550 to 800°C and addition ratio of 0.82 to 1.54.

Figures 4.7 and 4.8 respectively show the variation of SO_2 removal rate and sorbent utilization with addition ratio. SO_2 removal increases with increasing addition ratio and reactor temperature.

However, sorbent utilization seemed to remain unchanged with increasing addition ratio. Utilization ratio is defined as: $\frac{[Ca(OH)_2]_{ideal}}{[SO_2]_{ideal}} / \frac{[SO_2]_{used}}{[Ca(OH)_2]_{in}}$. The

ratio $\frac{[Ca(OH)_2]_{ideal}}{[SO_2]_{ideal}} = 1$. Therefore, utilization ratio = $\frac{[Ca(OH)_2]_{in}}{[SO_2]_{used}}$. The total flow rate (3.13 lpm) and inlet SO_2 concentration (2000) were kept constant throughout the whole experiment. The temperature of the reactor wall and that of the flow stream were measured several times with a thermocouple. The wall temperature was found to be 6% higher than that of the flow stream. The original plan was to vary the reactor temperature up to 1000°C. But about 750°C was found to be a optimum temperature for higher SO_2 removal. After 800°C, the SO_2 removal rate was reduced.

Figure 4.5: SO₂ removal vs. mass flow rate of Ca aerosol.

Figure 4.6: SO_2 removal vs. mass flow rate of Ca aerosol.

Inlet SO_2 Concentration = 1994 ppm Temperature = 550°C				
Mass Flow Rate 10^{-3} gm/min	SO_2 Conc. in ppm	% Removal of SO_2	Addition Ratio	% Sorbent Utilization
6.53	1850.00	7.22	0.35	20.9
10.65	1750.00	12.23	0.57	21.7
13.03	1505.00	24.52	0.69	35.6
16.30	1440.00	27.78	0.87	32.3
25.05	1086.00	45.53	1.33	42.4
Inlet SO_2 Concentration = 1994 ppm Temperature = 650°C				
6.53	1709.00	14.29	0.35	41.3
10.65	1478.50	25.85	0.57	45.9
13.03	1341.50	32.72	0.69	47.4
16.30	1203.50	39.64	0.87	46.1
25.05	1048.50	47.41	1.33	35.8
28.85	850.50	57.34	1.54	37.6
Inlet SO_2 Concentration = 1994 ppm Temperature = 750°C				
6.53	1640.50	17.72	0.35	51.3
10.65	1490.50	28.81	0.57	51.3
13.03	1278.00	35.90	0.69	52.1
16.30	880.00	55.71	0.87	64.5
25.05	646.00	67.60	1.33	51.0
28.85	531.50	73.34	1.54	48.1

Table 4.2: SO_2 removal by $Ca(OH)_2$.

Figure 4.7: SO_2 removal vs. addition ratio (Ca/S) at the reactor temperatures 650 and 750°C.

Figure 4.8: Sorbent utilization vs. addition ratio at reactor temperatures 650 and 750°C.

Chapter 5

Analytical Model

The experimental data show definite trends which are to be expected. The removal rates of SO_2 and NO_x are enhanced by increase in temperature, and by increase in the addition ratio. In order to check the experimental data, a simple mathematical model has been developed in order to attempt to describe the SO_2 capture behavior of the aerosols.

This model makes several simplifying assumptions:

- (a) The flow in the tube reactor is ideal plug flow.
- (b) The system is isothermal. The temperature is everywhere equal to the furnace temperature.
- (c) The rate expression for capture can be described by a simple second order rate expression,

$$-r = k C_A C_B \quad (5.1)$$

where

$$k = k_0 e^{-E/RT}, \quad (5.2)$$

r is the rate of SO_2 removal, k is the rate constant, C_A is the concentration of SO_2 , and C_B is the concentration of aluminum-containing aerosol.

(d) All aerosol sites are considered to be equally accessible to the SO_2 . The aerosol particles can react to extinction. The reaction product layer does not represent a resistance to the SO_2 capture reaction.

Based on these assumptions, two linked, first-order differential equations can be formulated describing the concentration profiles for components A (SO_2) and B (unreacted aerosol) in the reactor. These differential equations are written as:

$$-v \frac{dC_A}{dx} - k C_A C_B = 0 \quad (5.3)$$

and

$$-v \frac{dC_B}{dx} - n k C_A C_B = 0 \quad (5.4)$$

where v is the linear gas velocity in the reactor, x is the linear distance from the entrance of the reactor, and n is a stoichiometric coefficient ($n=0.67$ for Al aerosol and $n=1.0$ for Ca aerosol) that relates the reaction rate of A and B such that:

The two modeling equations are subject to the boundary conditions $C_A = C_{A0}$ and $C_B = C_{B0}$ at $x = 0$. [C_{A0} and C_{B0} are inlet concentrations of the two reactants.]

The modeling equations can be solved using a numerical initial value problem solving method such as Runge-Kutta. The attached Fortran programs in Appendix A does this by using a set of IMSL subroutines.

One set of aluminum aerosol/ SO_2 capture data (Table 5.1) has been modeled using this set of differential equations. One data point in this data set (inlet $SO_2 = 558$ ppm) was used to calculate a value for the reaction rate constant, k . The reaction rate constant is the only adjustable parameter used to fit this data set. The model was then used to give the predicted values for the remaining four data points. The results indicate that the model, even though

Furnace Temp.	Inlet SO_2 in ppm	Addition Ratio	Observed Outlet SO_2	Predicted Outlet SO_2
625°C	558	0.64	318	324
	452	0.80	251	245
	343	1.07	188	171
	232	1.60	122	105
	117	3.21	32	46

Table 5.1: Comparison of theoretical and experimental values

highly simplified, does provide a reasonably good fit to the experimental data as shown in Figure 5.1. The calculations were then repeated by using data

Figure 5.1: Comparison of Theoretical and Experimental results of outlet vs. inlet SO_2 concentration.

from the calcium hydroxide runs in the fluidizer system. For the calcium runs, the activation energy was added as an adjustable parameter enabling the prediction of SO_2 capture efficiencies at different temperatures. The results are plotted in Figure 5.2. While the scatter in the data is considerable, the overall trend is still very similar. These results provide additional validity to the experiments.

Figure 5.2: Comparison of Theoretical and Experimental results of SO₂ removal vs. sorbent addition ratio.

Chapter 6

Conclusions

The goal of this project has been to develop aerosol generators, aerosol flow reactor for removal of SO_2 , and to optimize the use of the sorbent. In addition, a simple model was developed to validate the experimental data. Finally, an economic feasibility was carried out to examine the calcium aerosol system. The feasibility study appears in part II of this report.

The results show that ultrafine aerosol can be generated by a fluidized hydrated lime bed and by nucleation and condensation of organometallic compound. The average size of the aerosols were respectively $0.4 \mu m$ and $0.3 \mu m$. The desulfurization studies with $Ca(OH)_2$ sorbent show that SO_2 removal can achieve up to 73 % with an addition ratio of 1.54. Percent SO_2 removal increases with higher sorbent addition ratio but best sorbent utilization was seen to be at the addition ratio of ≈ 1 .

SO_2 and NO_x removal by organometallic aerosol also shows promising results. About 98 % removal is possible for stoichiometric ratio ≥ 3 and to

the approach reactor temperature and residence time.

The results of flue gas desulfurization by dry scrubbing in the flow reactor using $Ca(OH)_2$ aerosol are very encouraging. Additional experiments are required to provide additional data on these systems, particularly on the chemical analysis of the sorbents. The analysis of the gas composition was particularly difficult and time consuming. Better analytical equipment would be extremely helpful in reducing the time required for experiments.

Further research in particle chemical composition is recommended for the confirmation of these obtained results and to improve results obtained in this project. In particular, the results at temperatures over 800°C was unsatisfactory although improvements were expected until at least 1000°C was reached. The results from the economic feasibility indicate that the powder entrainment system can be economically quite attractive. The system can be technically feasible on a larger scale because the powder injection can be done by using standard systems, and the powder grinding can also be done by using equipment that has been developed for soda lime systems. The reader is referred to part II of this report for details.

The organometallic system developed in this project produced novel results. Both SO_2 and NO_x were removed simultaneously by this reagent. An economic feasibility of this system was not carried out because the reagent is costly. However, this system deserves further research because organometallics may be utilized in addition to other sorbents to remove the NO_x .

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Appendix A

FORTRAN programs

Fortran programs for mathematical models for SO_2 capture are as follows:

<p style="text-align: center;">CAAL FORTRAN A:</p> <p style="text-align: center;">Mathematical Model for SO2 Capture</p> <p style="text-align: center;">Version: 0390a</p>

The Fortran program begins here:

```

      INTEGER      MXPARM, NEQ
      PARAMETER    (MXPARM=50, NEQ=2)
C
      INTEGER      IDO, ISTEP
      REAL         FCN, FLOAT, PARAM(MXPARM), X, XEND, TOL, Y(NEQ)
      REAL         PPMSO2, WTCAL, RKON, TEMP, XTOT, DIA, VOLRAT
      REAL         CSO2, CAL, VEL
      INTRINSIC    FLOAT
      EXTERNAL     FCN, IVPRK, SSET
C
      REAL         KKON, RATIO
      COMMON       /STUFF/ KKON, RATIO
C
C      INPUT VALUES FOR PARAMETERS USED IN THE PROBLEM.
C
C      PPMSO2 IS THE INLET CONCENTRATION OF SO2 IN PPM.
C
C      PPMSO2 = 117.
C
C      WTCAL IS THE INLET RATE OF ALUMINUM ISOPROPOXIDE ADDITION
C      IN GRAMS PER MINUTE.
C
C      WTCAL = 0.0085
C
C      RATIO IS THE STOICHIOMETRIC REACTION RATE RATIO.
C
C      RATIO = 0.6666667
C
C      XTOT IS THE REACTOR TUBE LENGTH IN METERS.
C
C      XTOT = 0.6
C
C      DIA IS THE REACTOR TUBE INSIDE DIAMETER IN METERS.
C
C      DIA = 0.0254
C
C      TEMP IS THE REACTION ZONE TEMPERATURE IN DEGREES CELCIUS.
C
C      TEMP = 625.0

```

RKON IS THE REACTION RATE CONSTANT.

RKON = 200000.

VOLRAT IS THE TOTAL VOLUMETRIC FLOW RATE OF THE GASES TO THE REACTOR (ASSUMED MEASURED AT 25 C) IN LITERS PER MINUTE.

VOLRAT = 4.00

CALCULATE SOME IMPORTANT SYSTEM NUMBERS.

CSO2 IS THE SO2 CONCENTRATION IN MOLES PER LITER EVALUATED AT THE REACTOR TUBE TEMPERATURE (0.040898 GMOLES PER LITER AT 25 C).

CSO2 = (PPMSO2*1.0E-06*0.040898)/((TEMP + 273.0)/298.0)

CAL IS THE ALUMINUM CONCENTRATION IN MOLES PER LITER EVALUATED AT THE REACTOR TUBE TEMPERATURE.

CAL = (WTCAL/204.25)/(VOLRAT * ((TEMP + 273.0)/298.0))

VEL IS THE VELOCITY IN METERS PER SECOND EVALUATED AT THE REACTOR TUBE TEMPERATURE.

VEL = (VOLRAT * ((TEMP + 273.0)/298.0)/((3.14159/4.0) * (DIA**2))) * 0.001/60.0

KKON IS A LUMPED CONSTANT USED IN THE LINKED DIFFERENTIAL EQUATIONS.

KKON = RKON/VEL

THE INITIAL CONDITIONS.

X IS THE LENGTH DOWN THE REACTOR IN METERS.

X = 0.0

Y(1) IS THE CONCENTRATION OF SO2 IN GMOLES PER LITER AT REACTOR CONDITIONS.

Y(2) IS THE CONCENTRATION OF ALUMINUM IN GMOLES PER LITER AT REACTOR CONDITIONS.

Y(1) = CSO2

Y(2) = CAL

SET THE ERROR TOLERANCE.

TOL = 0.0005

```

C
C  SET THE INITIAL PARAM VECTOR TO THE DEFAULT VALUES.
C    (THE PARAM VECTOR IS USED BY THE IVPRK SUBROUTINE.)
C    SSET IS AN IMSL SUBROUTINE.
C
C    CALL SSET (MXPARM, 0.0, PARAM, 1)
C
C  SOLVE THE PROBLEM USING THE IMSL ROUTINE IVPRK.  IVPRK IS A
C  RUNGE-KUTTA INITIAL VALUE PROBLEM SOLVER.
C
C    IDO      = 1
C    DO 10 ISTEP=1, 100
C        XEND = FLOAT(ISTEP)*XTOT*0.01
C        CALL IVPRK (IDO, NEQ, FCN, X, XEND, TOL, PARAM, Y)
C        WRITE (5, '(I6,3F12.9)') ISTEP, XEND, Y
10    CONTINUE
C
C  RELEASE THE WORKSPACE.
C
C    IDO      = 3
C    CALL IVPRK (IDO, NEQ, FCN, X, XEND, TOL, PARAM, Y)
C    STOP
C    END
C
C  FCN IS THE SUBROUTINE THAT INCLUDES THE ORDINARY DIFFERENTIAL
C  EQUATIONS TO BE SOLVED.
C
C    SUBROUTINE FCN (NEQ, X, Y, YPRIME)
C    INTEGER      NEQ
C    REAL         X, Y(NEQ), YPRIME(NEQ)
C
C    COMMON       /STUFF/ KKON, RATIO
C    REAL         KKON, RATIO
C
C    YPRIME(1) = DY(1)/DX.
C    YPRIME(2) = DY(2)/DX.
C
C    YPRIME(1) = -KKON * Y(1) * Y(2)
C    YPRIME(2) = -KKON * RATIO * Y(1) * Y(2)
C    RETURN
C    END
C
C  TTTTHHHHHHAAAATTTT'S ALL FOLKS!!!!!!!
C

```

CAAL2 FORTRAN A:
Mathematical Model for SO2 Capture
Version 0891a

The Fortran program begins here:

```

      INTEGER      MXPARM, NEQ
      PARAMETER    (MXPARM=50, NEQ=2)

```

```

C
      INTEGER      IDO, ISTEP, I
      REAL         FCN, FLOAT, PARAM(MXPARM), X, XEND, TOL, Y(NEQ)
      REAL         PPMSO2, WTCAL(100), RKON, TEMP, XTOT, DIA, VOLRAT
      REAL         CSO2, CAL, VEL, B0, RKON0
      INTRINSIC    FLOAT
      EXTERNAL     FCN, IVPRK, SSET

```

```

C
      REAL         KKON, RATIO
      COMMON       /STUFF/ KKON, RATIO
      WRITE (5,*) '      REACTOR TEMPERATURE = 750 C '
      WRITE (5,*) '      I      WTCAL      ISTEP      XEND      '
&Y1 '      Y2      Y3      Y4'

```

```

C
      DO 20 I=1,100

```

```

C
C      WTCAL IS THE INLET RATE OF CALCIUM HYDROXIDE ADDITION
C      IN GRAMS PER MINUTE.

```

```

C      WTCAL(I) = 0.03*FLOAT(I)/100.0

```

```

C
C      INPUT VALUES FOR PARAMETERS USED IN THE PROBLEM.

```

```

C      PPMSO2 IS THE INLET CONCENTRATION OF SO2 IN PPM.

```

```

C      PPMSO2 = 1994.0

```

```

C      RATIO IS THE STOICHIOMETRIC REACTION RATE RATIO.

```

```

C      RATIO = 1.0

```

```

C      XTOT IS THE REACTOR TUBE LENGTH IN METERS.

```

```

C      XTOT = 0.9144

```

```

C
C
C   DIA IS THE REACTOR TUBE INSIDE DIAMETER IN METERS.
C
C   DIA      = 0.0254
C
C
C   TEMP IS THE REACTION ZONE TEMPERATURE IN DEGREES CELCIUS.
C
C   TEMP      = 750.
C
C
C   RKON IS THE REACTION RATE CONSTANT.  RKON0 AND B0 ARE
C   PARAMETERS IN THE ARRHENIUS EXPRESSION.
C
C   RKON0     = 8629139.5
C   B0        = 6241.72
C   RKON      = RKON0*EXP(-B0/(TEMP+273.0))
C
C
C   VOLRAT IS THE TOTAL VOLUMETRIC FLOW RATE OF THE GASES TO THE
C   REACTOR (ASSUMED MEASURED AT 25 C) IN LITERS PER
C   MINUTE.
C
C   VOLRAT    = 3.13
C
C   CALCULATE SOME IMPORTANT SYSTEM NUMBERS.
C
C   CSO2 IS THE SO2 CONCENTRATION IN MOLES PER LITER EVALUATED AT
C   THE REACTOR TUBE TEMPERATURE (0.040898 GMOLES PER
C   LITER AT 25 C).
C
C   CSO2      = (PPMSO2*1.0E-06*0.040898)/((TEMP + 273.0)/298.0)
C
C
C   CAL IS THE CALCIUM CONCENTRATION IN MOLES PER LITER EVALUATED
C   AT THE REACTOR TUBE TEMPERATURE.
C
C   CAL       = (WTCAL(I)/74.09)/(VOLRAT * ((TEMP + 273.0)/298.0))
C
C
C   VEL IS THE VELOCITY IN METERS PER SECOND EVALUATED AT THE
C   REACTOR TUBE TEMPERATURE.
C
C   VEL       = (VOLRAT * ((TEMP + 273.0)/298.0)/((3.14159/4.0) *
C   & (DIA**2))) * 0.001/60.0
C
C
C   KKON IS A LUMPED CONSTANT USED IN THE LINKED DIFFERENTIAL
C   EQUATIONS.
C
C   KKON      = RKON/VEL
C
C   THE INITIAL CONDITIONS.
C
C   X IS THE LENGTH DOWN THE REACTOR IN METERS.
C
C   X         = 0.0

```



```

C      Y(1) IS THE CONCENTRATION OF SO2 IN GMOLES PER LITER AT
C      REACTOR CONDITIONS.
C      Y(2) IS THE CONCENTRATION OF CALCIUM IN GMOLES PER LITER AT
C      REACTOR CONDITIONS.
C
C      Y(1)  = CSO2
C      Y(2)  = CAL
C
C      SET THE ERROR TOLERANCE.
C
C      TOL    = 0.0005
C
C      SET THE INITIAL PARAM VECTOR TO THE DEFAULT VALUES.
C      (THE PARAM VECTOR IS USED BY THE IVPRK SUBROUTINE.)
C      SSET IS AN IMSL SUBROUTINE.
C
C      CALL SSET (MXPARAM, 0.0, PARAM, 1)
C
C      SOLVE THE PROBLEM USING THE IMSL ROUTINE IVPRK.  IVPRK IS A
C      RUNGE-KUTTA INITIAL VALUE PROBLEM SOLVER.
C
C      IDO    = 1
C      DO 10 ISTEP=1, 100
C        XEND = FLOAT(ISTEP)*XTOT*0.01
C        CALL IVPRK (IDO, NEQ, FCN, X, XEND, TOL, PARAM, Y)
C        IF (ISTEP.EQ.100) THEN
C          Y1 = Y(1)
C          Y2 = Y(2)
C          Y3 = (Y(1)*((TEMP+273.0)/298.0))/(1.0E-06*0.040898)
C          Y4 = ((1994.0-Y3)/1994.0)*100.0
C          WRITE (5, '(I6,F12.5,I6,F10.7,2F12.9,F9.2,F8.2)') I, WTCAL(I),
C            ISTEP, XEND, Y1, Y2, Y3, Y4
C          WRITE (5,*) ' ISTEP ', ISTEP, ' XEND ', XEND, ' Y1 ', Y1, ' Y2 ', Y2, ' Y3 ',
C            Y3, ' Y4 ', Y4
C          WRITE (5, '(I6,4F12.9)') ISTEP, XEND, Y1, Y2, Y3
C        ENDIF
C      CONTINUE
C
C      10
C
C      RELEASE THE WORKSPACE.
C
C      IDO    = 3
C      CALL IVPRK (IDO, NEQ, FCN, X, XEND, TOL, PARAM, Y)
C      CONTINUE
C
C      20
C      STOP
C      END

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89

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C      FCN IS THE SUBROUTINE THAT INCLUDES THE ORDINARY DIFFERENTIAL
C      EQUATIONS TO BE SOLVED.
C
C      SUBROUTINE FCN (NEQ, X, Y, YPRIME)
C      INTEGER      NEQ
C      REAL         X, Y(NEQ), YPRIME(NEQ)
C
C      COMMON       /STUFF/ KKON, RATIO
C      REAL         KKON, RATIO
C
C      YPRIME(1) = DY(1)/DX.
C      YPRIME(2) = DY(2)/DX.
C
C      YPRIME(1) = -KKON * Y(1) * Y(2)
C      YPRIME(2) = -KKON * RATIO * Y(1) * Y(2)
C      RETURN
C      END
C
C      TTTTHHHHHHAAAATTTT'S ALL FOLKS!!!!!!!
C
C

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90

END DATE
9-27-93