AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

OCDO--94012363

Project Number: OCRC/90-1.3
Project Title: Kinetics Studies, Thermal Decomposition and Carbonation
Name of Grantee: University of Cincinnati
Address: Chemical Engineering Department
University of Cincinnati
Cincinnati, Ohio 45221
(513) 556-2789
Project Manager: Soon-Jai Khang

FINAL REPORT

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

Date: September, 1993

RECEIVED

FEB 22 1994

DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

Other Project Investigators:

T. C. Keener, Co-PI
Y. K. Kao, Co-PI
A. Wang, Graduate Assistant

MASTER

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

EXECUTIVE SUMMARY	i
I. INTRODUCTION	1
A. PROBLEM STATEMENT	1
B. PROJECT OBJECTIVES	1
II. TECHNICAL DISCUSSION	2
A. LITERATURE REVIEW	2
B. MODIFIED DROP TUBE REACTOR DESIGN/CONSTRUCTION	10
C. DROP TUBE TEST RESULTS	13
D. SLOW - REACTION STUDIES	42
III. FUTURE WORK	53
IV. CONCLUSION	53
REFERENCES	56

LIST OF FIGURES

Figure 1. General FGD Process	3
Figure 2. Utilization of Genstar PHDL over a Wide Range of Injection Temperature, with Coal Firing.	5
Figure 3. Configuration of Bench Scale Reactor for Low Temperature Sulfation Studies.	7
Figure 4. Pilot Plant Facility	7
Figure 5. Decomposition Temperature of Mg and Ca Compounds	9
Figure 6. The Modified Drop Tube Reactor System.	12
Figure 7. Schematic Diagram of the Sorbent Feeder.	13
Figure 8. Dehydration Reaction Under the Medium Temperature Range	18
Figure 9. Dehydration Reaction in the Residence Time from 35ms to 75 ms	19
Figure 10 Carbonation Reaction within Residence Time from 50ms to 100ms	23
Figure 11. Carbonation Reaction under Medium Temperature Range	24
Figure 12 BET Surface Area Change with Reaction Temperature in Carbonation Reaction	25
Figure 13. BET Surface Area Change with Residence Time in Carbonation Reaction ...	26
Figure 14. C%, H% and S% in the Product of Sulfation/Carbonation Reaction	28
Figure 15. Conversions of the Sulfation/Carbonation Reaction	31
Figure 16. S% in the Products from the Sulfation Reactions of Ca(OH)_2 and CaO	36
Figure 17. Conversion of Sulfation Reactions of Ca(OH)_2 and CaO	36
Figure 18. Sulfation Reaction of Ca(OH)_2 in TGA	37
Figure 19. Sulfation Reaction of CaO in TGA	37
Figure 20. Reactivity of fresh CaO in Air	38
Figure 21. Thermal Decomposition of Original Ca(OH)_2	40
Figure 22. Decomposition of Sorbent Products	40
Figure 23. Decomposition of Sorbent Product.	41
Figure 24 The Reaction of Fresh CaO in Air	41
Figure 25. Decomposition of Sorbent Product	42
Figure 26. Sulfur Contents in the Reacted Sorbent	49
Figure 27 Carbonate Content in the Reacted Sorbent	50
Figure 28. Available lime contents in the reacted sorbent	51
Figure 29. BET Surface Area in the Reacted Sorbent	52

LIST OF TABLES

Table I. Experimental Condition for Bortz's Tests	6
Table II. Dehydration Reaction of Ca(OH)_2	14
Table III. Dehydration Reaction of Ca(OH)_2	15
Table IV. Dehydration Reaction of Ca(OH)_2	16
Table V. Carbonation reaction of Ca(OH)_2 at 900°	20
Table VI. Carbonation reaction of Ca(OH)_2 within 50 ms	21
Table VII. BET Surface Area from the Carbonation Reaction.	22
Table VIII. Simultaneous Carbonation-sulfation Reaction of Ca(OH)_2	27
Table VIII. The Conversions from the Simultaneous Carbonation/ Sulfation Reaction	30
Table X. Sulfation Reactions of Ca(OH)_2 and CaO	32

EXECUTIVE SUMMARY

The purpose of this project is to study the fundamental nature of the sorbent reactivity and reaction kinetics in the medium temperature range from 600 to 1200°F available in the convective pass of a boiler upstream of the economizer, where dry sorbents and anhydrous ammonia are injected to reduce SO_2 and NO_x from the flue gas.

During the first year, it was found that a significant portion of unused sorbent was reacted with carbon dioxide in a simulated flue gas (~14%) and produced calcium carbonate. This behavior had not been actively reported in the literature, and thought to be one of the important factors that limit the eventual utilization of calcium based sorbents. During the second year, it was found that the majority of gas-solid reactions with small sorbent particles are practically reached its final conversions within 0.5 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, the experimental techniques were refined to measure the sorbent kinetics within the first 50 milliseconds. Although the sulfation reaction of hydrated lime levels off below 0.5 second of reaction time, the sulfation reaction of dolomitic hydrate continues beyond 1 second of reaction time. The following conclusions are drawn from the results of the third year of study.

- The dehydration conversion increased with reaction temperature from 3% at 600°F to 36% at 1100°F. The dehydration conversion increased dramatically over 900°F. The dehydration conversion increased with residence time continuously from 5% at 35ms to 16% at 75ms.
- The fresh CaO from the dehydration reaction of $\text{Ca}(\text{OH})_2$ is very active in air. As soon as the fresh CaO is exposed to air, it rapidly rehydrated due to the moisture in air and reaction with CO_2 to form CaCO_3 .
- The carbonation conversion increases slightly with residence time from 50ms to 75ms. It appeared that the carbonation conversion reached its upper limit after 75 ms.

Carbonation conversion increases with reaction temperature and the conversion increases rapidly over 900°F .

- In the simultaneous carbonation/sulfation reaction the carbonation conversion increased continuously with the reaction temperature from 600°F to 1100°F. Contrary to the carbonation reaction where the carbonation conversion increased with reaction temperature even in the higher temperature range, the sulfation conversion reached its maximum value at the temperature around 1000°F. The existence of this optimum sulfation reaction temperature may be due to the competing carbonation reaction which consumes the active sorbent($\text{Ca}(\text{OH})_2$) and impedes the sulfation at higher temperature. The conversion to CaO increased with reaction temperature first and then reached its upper limits at about 1000°F .
- By comparing the sulfation conversion of $\text{Ca}(\text{OH})_2$ and CaO at 900°F and residence times from 50 to 75 ms, it is found that the sulfation conversion of CaO at this temperature range was significant and could not be ignored. The TGA results also indicated the importance of the reaction between CaO and SO_2 in medium temperature range.
- The carbonation reaction took place simultaneously with sulfation reaction under the fixed bed and drop-tube reactor conditions. The carbonation reaction rate increased continually with temperature, while the sulfation reaction rate increased with temperature in the range from 600°F to 700°F, then decreased under the fixed bed condition which was the typical condition for a hot baghouse. The existence of an optimum desulfurization temperature, which was found to be approximately 700°F for the fixed bed condition, appeared to be due to the competing reaction of CO_2 and the diffusion resistance of SO_2 through the particle layer in the fixed bed.

I. INTRODUCTION

A. PROBLEM STATEMENT

Coal fired power plant is the major source of SO_2 emission. The 1990 Clean air Act Amendment requires to cut SO_2 emission by 50%. The Phase I, takes effective in January 1995, will affect over one hundred existing power plants in the nation and 41 sources in Ohio whose sulfur dioxide emission exceeds the 2.5 lbs sulfur dioxide per million Btu standard.⁽¹⁾⁽²⁾ The combined capacity of about 6,000 MW, which is currently on high sulfur Ohio coal, is affected and more than 863,000 tons/year of sulfur dioxide should be reduced in Ohio alone.

Since the New Clean Air amendment requires a moderate sulfur dioxide emission cut for the existing plant⁽³⁾, also since the service lives of the impacted existing power plants are generally less than twenty years, the use of the expensive wet scrubber or spray drier (costing over \$ 1,000 per ton of sulfur dioxide removal) is not an economic approach. Additionally, the limited space for the existing power plant makes it difficult to add the space needed for a wet scrubber or spray drier system.

The over all objective of this project is to improve and develop cost effective retrofit utilizing dry calcium-based FGD Processes for removing SO_2 from combustion gases. A series of experimental tests was conducted in the second year to study the interaction between the calcium-base sorbent and flue gas. The test results showed that the majority reactions between the flue gas and the sorbent were not progressing rapidly after 500 ms, which imply the importance of the mechanism of the reactions within the first 500ms. This year's research is focused on studying all aspects of the sorbent-flue gas reaction kinetics within the first 500ms in the medium temperature range.

B. PROJECT OBJECTIVES

The long term objective is to study the fundamental nature of the sorbent reactivity

and reaction kinetics by systematically conducting kinetics experiments on the flue gas-calcium based sorbent reaction and analyzing the experimental data which would enable us to develop a realistic model. This experimental and modeling work should provide practical guides for dry FGD process development.

The objective of the third year's research is to experimentally and theoretically study the kinetics of the dehydration, carbonation and sulfation reactions between the flue gas and the hydrated sorbent within the first 100ms. The experimental conditions were in the medium temperature range with a special emphases on the temperature of 900°F region, representing the majority conditions of the economizer injection process.

II. TECHNICAL DISCUSSION

A. LITERATURE REVIEW

In this section, general background of sorbent injection FGD processes are briefly described. A literature review on the related previous work is also given to identify the research status and the practical needs.

In dry sorbent injection FGD process, sorbent powder is injected into the upper furnace or the duct to react with SO_2 . The desulfurization product is removed from the flue gas stream in the particulate collector. As shown in Figure 1, three types of sorbent injection processes are available or under development for removing SO_2 .^{[(4)][5][6]}

1. Furnace injection at the temperature around 2000°F using calcium-based compounds (CaCO_3 , CaO and Ca(OH)_2). This kind of process is relatively well understood.
2. Economizer injection at the temperature between 800°F and 1000°F using calcium-based hydrates.

Figure 1. General FGD Process

3. Post furnace injection of slurry into low temperature duct, or injection of the solid powder with water slurry or steam humidification to achieve a high relative humidity. The sorbents are calcium- or sodium-based hydrates.

This project is focused on the research of economizer injection process.

In the sorbent economizer zone injection FGD process, hydrated sorbents are injected into a temperature envelope centered around 1000°F which is generally found prior to the economizer section to react with SO₂. The desulfurization product is removed from the flue gas stream in a particulate collector (As shown in Figure 1.)^{[7][8][9]}. The majority of Ca(OH)₂ injected in the economizer react directly with the SO₂ as following:

In contrast to furnace injection process where reaction temperature is around 2000°F, Ca(OH)₂ reacts directly with SO₂ since the temperature is too low for complete dehydration reaction. In this temperature range the main product is CaSO₃ instead of CaSO₄^[10]. The reaction rate in this range is comparable or even higher than that at 2000°F.

The ability of hydroxides to react rapidly with SO₂ at temperatures below 1200°F was first noted in an earlier phase of a EPRI-sponsored Dry Sorbent Emission Control program. These tests showed that SO₂ capture levels with Genstar pressure hydrated dolomite decreased as the injection temperature was gradually reduced from 1800°F to approximately 1200°F but again increased with further reductions in injection temperature. This prompted a short study at the Southern Research Institute^[11] where Genstar pressure hydrated dolomite was injected at temperatures range from 200°F to 2400°F. As shown in Figure 2^[12], a double hump behavior was observed, confirming that a second sulfation window existed between 800°F and 1200°F.

Figure 2. Utilization of Genstar PHDL over a Wide Range of Injection Temperature, with Coal Firing.

These initial encouraging results proposed a new sorbent injection process in which sorbent was injected at the duct section between the outlet of the low temperature superheater and the inlet of the economizer. In terms of engineering consideration, there are three advantages of the new process over the furnace injection process:

1. The sorbent injection location at 1000°F is typically just above or in the economizer section, eliminating any possible negative impact of sorbent injection on the radiant heat exchanger.
2. The relatively low injection temperature should allow the insertion of simple sorbent injectors into the flow stream and good mixing should be more easily achieved.

3. Because surface area and porosity decay due to thermal sintering can probably be neglected at these low sorbent temperatures, increasing sorbent reactivity through generating high reactivity hydroxides looks very promising.

A series of medium temperature sorbent injection studies were conducted by S.J.Bortz and G.R.Offen^{[12] [13]} with a bench scale drop-tube reactor and a pilot-scale facility (as shown in Figure 3 and Figure 4). The experimental conditions of these reactors are shown in Table I.

Table I. Experimental Condition for Bortz's Tests

	Drop Tube Reactor	Pilot Scale Test
Reaction Temperature °F	500°F - 1200°F	900°F - 1200°F
Calcium Sorbents	Longview, Genstar Calcium.	Commercial
Particle Size	1 - 6 μ m	1 - 6 μ m
Ca/S Ratio	1 - 2.7	1 - 2.2
Flue Gas Composition	SO ₂ 3000ppm, CO ₂ 10%, H ₂ O 15%, O ₂ 4%, N ₂ Balance	SO ₂ 2500ppm, CO ₂ 14%, H ₂ O 7%, O ₂ 5%, N ₂ Balance

The tests results showed that:

- The reaction rate of calcium hydroxide with SO₂ and CO₂ at around 1000°F was significantly faster than the reaction rate of CaO with SO₂ and CO₂.
- The sulfation reaction was strongly temperature dependent in the medium temperature range. With the calcium hydroxide sorbents used thus far,

Figure 3. Configuration of Bench Scale Reactor for Low Temperature Sulfation Studies.

Figure 4. Pilot Plant Facility

maximum utilizations ranging from 25-45% have been achieved at a temperature near 1000°F in a resident time of 250ms or less. Above 1000°F, a large percentage of the hydroxide was converted to both CaCO_3 and CaO , while below 1000°F, the utilization was limited by the initial porosity of the hydroxide which reacted without dehydration.

- The sulfation rate in this temperature range was very high, at the temperature around 1000°F, sorbents achieved nearly their final utilization level in only about 500 ms.
- Because the chemical reaction rate was so fast, even though particles were small, diffusion of SO_2 (but not CO_2 , which has a concentration 30 times greater than that of SO_2) through the particle can be a controlling factor. Consequently, the rate of reaction with SO_2 can be diffusion limited, while the reaction rate with CO_2 is still chemically limited. Therefore decreasing the particle size and keeping the surface area constant will shift the ratio of $\text{CaSO}_3/\text{CaCO}_3$ formed to higher values, and increasing surface area without decreasing the particle size will decrease the ratio of $\text{CaSO}_3/\text{CaCO}_3$ by increasing the reaction rate with CO_2 .
- The smaller size and larger surface area led to higher sorbent utilization. The tests showed that 70%-80% SO_2 removals were achieved for hydrate with a mean diameter of 2-3 μm , surface area of 20-40 m^2/g at $\text{Ca/S} = 2$.

The optimum injection temperature is currently explained by the difference in the decomposition temperatures (Figure 5). When temperature is above the decomposition temperature of CaSO_3 , a significant amount of SO_2 is re-released, which causes a decrease in sorbent utilization.

Figure 5. Decomposition Temperature of Mg and Ca Compounds^[13]

Besides, a series of experimental studies was conducted in the drop tube reactor in the second-year's research of this project. following results were obtained:

- The carbonation conversion significantly increases with reaction temperature. But the increase due to the reaction time change is very small. All carbonation reactions seem to be completed well below 0.5 second. Higher temperature and longer reaction time appear to be preferable to the carbonation of dolomitic lime.
- Similar to the case for carbonation, high temperature and long residence time will increase the sulfation of dolomitic lime.
- Sulfation processes in the simultaneous carbonation/sulfation reaction were suppressed as compared to the individual sulfation reaction due to the competing carbonation reaction of sorbent. In the reaction condition of the drop tube reactor the carbonation conversion is almost 2 times greater than the sulfation conversion in a simultaneous carbonation/sulfation process.

In conclusion, the fundamental and experimental study of the economizer injection FGD process has just begun. Although some primary experimental results have been obtained, the mechanism of the medium temperature reactions is still a mystery. The experimental data, especially kinetic data, is of crucial importance in order to understanding the complicated reaction mechanisms, which are fundamental to process development and process optimization.

B. MODIFIED DROP TUBE REACTOR DESIGN/CONSTRUCTION:

A series of experimental tests were conducted during the second year of the project to study the dehydration, carbonation, sulfation and the simultaneous carbonation/sulfation reactions of calcium-based sorbent. The test results showed that the majority reactions between the flue gas and the sorbent were not progressing rapidly after 500 ms, which indicated the importance of the mechanism of the reactions within the first 500 ms..

Since the diameter of the reaction chamber of the drop tube reactor used for the preliminary study was not small enough, the tests for the reactions within 500 ms require a large amount of reactant gas that became too expensive to run the tests. To rectify this situation, a modified design has been made this year. In the modified drop tube reactor system, the diameter of the reaction chamber was reduced from 1.5 inches to 0.5 inches, requiring only 1/9 of the reactant gas. The preheater and sorbent feeder were also improved.

The modified drop tube reactor system is shown schematically in Figure 6. The reactor system consisted of a furnace, a preheating and reaction tubes, a heat exchanger, a sorbent feeder, an N₂ gas quenching and diluting system, and a sorbent collection system. The reactor consisted of two concentric stainless steel tubes (0.5 inch and 1.5 inch O.D. respectively) which were housed within a tube furnace. The furnace was a 3-feet-long, 3-inch-I.D. Lindberg model 55347-4, with three independently controlled heating zones, capable of maintaining a temperature up to 1200°C. Reactant gas was preheated in the annular volume between the outer (1.5 inch O.D.) shell and the inner (0.5 inch O.D.) reactor tube. The

reactant gas entered the bottom of the reactor and passed upward through the preheating zone to the top of the reactor and then made a 120° turn to enter the inner tube forming two hot jets. At the top of the reactor, sorbent particles were injected into the reactor just above the incoming hot jets by means of a feed system described below. Thus, the sorbent stream was impacted by the hot reactant gas jets within a very short period of time. The jet impaction caused substantial loss of momentum that created severe turbulence and in turn caused rapid heating of the sorbents. Heat transfer calculation^[14] indicated that sorbent particles of less than 10µm size would be heated within a few milliseconds after injection into the reactor, providing a well mixed isothermal mixture of the gas and solid particles. The gas and the entrained particles passed downward through the isothermal reactor tube and as soon as sorbent particles left the reaction chamber, they were quickly quenched and diluted by large amount of nitrogen gas supplied from N₂ cylinder. The particles were collected with a paper filter. The maximum temperature of the exhausted gas through the paper filter was around 45°C. To provide a realistic humidity of a flue gas, water was injected by a syringe pump at the top of the preheater where the gas temperature was kept above the boiling point of the water. To monitor temperature profile inside the reactor, five type-K thermocouples were inserted into the reactor chamber through the stainless steel thermocouple ports. The output signals from the thermocouples were sent to a computer data acquisition system.

The sorbent particles used in the study, due to their small particle size (less than 10µm) and adhesive nature, are very difficult to transport stably. A modified sorbent feeder was designed to provide a reliable feeding condition. The schematic diagram of the sorbent feeding system was shown in Figure 7. The sorbent particles were entrained by the carrier gas, which flowed over the surface of a sorbent bed and discharged out of a side-branch tube. The sorbent feeding rate was controlled by changing the carrier gas flow rate and the position of the carrier gas tube. A series preliminary tests indicated that a stable flow of the sorbent particles could be obtained with this type of sorbent feeder for small sorbent particle. During the drop tube tests the particle feeder was capable of injecting sorbent as small as 2µm at a rate of 250mg/min. The gas flow through the reactor was variable from 15 to 50 L/min to control particle residence time from 50 to 100 ms, respectively, at temperatures of

Figure 6. The Modified Drop Tube Reactor System.

600 to 1100 °F.

The CaCO_3 , Ca(OH)_2 and CaO contents in the product sorbent were measured by a LECO Element Analyzer and the TGA system. The CaSO_3 contents in the product sorbent were measured by a LECO Total Sulfur Analyzer. The pore structure of the sorbent, especially the surface area has a significant impact on sulfur capture efficiency of the sorbent. Surface areas was estimated using the BET method from the nitrogen adsorption/desorption isotherms. Thus parallel to the kinetics, variations in the surface area of the sorbent during the course of the reaction was measured during the third year's study.

Figure 7. Schematic Diagram of the Sorbent Feeder.

The residence time of the sorbent particles inside the reaction chamber was calculated by the fluid dynamics model. For the particle size of the sample of our experiment (2 - 10 μm), the calculation results from the fluid dynamics model indicated the slippage between the gas and the particle can be safely ignored. Therefore, we can assume in this very dilute particle system, particle residence time is practically equal to gas residence time.

The principle of the above experimental setup was for short residence time of sorbent particles and quick quenching and diluting by the use of large amount of N_2 gas to stop the reactions at any stage.

C. DROP TUBE TEST RESULTS:

The experimental studies for the dehydration, carbonation and simultaneous

carbonation/sulfation reactions of $\text{Ca}(\text{OH})_2$ were conducted in the drop tube reactor. The reactivity of CaO was also studied in conjunction with the above tests to verify the importance of the reactions of CaO in the medium temperature range.

$\text{Ca}(\text{OH})_2$ technical powder was used as the solid sorbent. The sorbent properties were listed below:

Technical Grade Powder (MMD - 5 μm)

Available Lime: 96.6%

BET Surface Area: 10.1 m^2/g

I. Dehydration Reactions:

The dehydration tests were conducted in the drop tube system under the following experimental condition :

temperature: 600°F - 1100°F

reaction time: 35, 40, 50, 75, 100 ms

reactant gas: pure N_2

sorbent: $\text{Ca}(\text{OH})_2$ technical powder

gas flow rate: 15 L/Min - 50 L/Min

The results are listed in Table II. and Table III.

Table II. Dehydration Reaction of $\text{Ca}(\text{OH})_2$
(Resident time = 50 ms)

	C% (wt%)	H% (wt%)
$\text{Ca}(\text{OH})_2$ Reactant	0.937	2.583
600 °F	1.920	2.604
750 °F	2.300	2.434

900 °F	2.423	2.306
1000 °F	2.294	2.376
1100 °F	2.537	2.328

Table III. Dehydration Reaction of $\text{Ca}(\text{OH})_2$
(Reaction Temperature 900°F)

	C% (wt%)	H% (wt%)
$\text{Ca}(\text{OH})_2$ Reactant	0.937	2.583
40 ms	2.188	2.432
50 ms	2.462	2.377
75 ms	2.283	2.388
100 ms	1.829	2.490

As shown in Table II and Table III, for all the dehydration tests, the carbon contents in the products were significantly higher than that in the initial $\text{Ca}(\text{OH})_2$. Since in all of the dehydration tests, pure N_2 cylinder (99.99% of N_2) was used as the reactant gas source, this high carbon content in the products became a mystery.

Several efforts were made to try to find out the reason for this high carbon content in product. First, the system was re-sealed to eliminate any possible leakage. Then reaction chamber, sorbent feeder and collecting chamber were cleaned carefully to remove any sorbent which might have deposited on reactor tube wall before. Even after these precautions, the carbon content in products of the dehydration was still high. Therefore, the only possible way that product can gain its carbon content was during the collection of product from the drop tube system and subsequent sample weighing step prior to element analysis.

To eliminate any further carbonation and re-hydration reactions of product during sorbent collection procedures, a polyethylene glove bag was introduced to cover the sample collecting window. The glove bag was purged with pure N_2 to remove any residual air from the glove bag. While purging, the sample bottle was inserted into the glove bag. Then, the glove bag's sleeve was closed, the sample collecting window was opened and the product sorbent was loaded into the sample bottle while it is in the glove bag. To avoid the exposure of product sample to air during sample weighing process, the microbalance was put into another glove bag which was purged with pure N_2 .

After the above improvements the dehydration tests were conducted again in drop tube reactor. The carbon content in product was reduced to the normal level which is in a range of initial carbon content of $Ca(OH)_2$. The results of the dehydration data are listed in Table IV.

The experimental data were analyzed and converted to the conversions of the reactions. For the dehydration reaction, the conversion in terms of $Ca(OH)_2$ is defined as:

$$X_{Ca(OH)_2} = \frac{F_{Ca(OH)_2} - F_{oCa(OH)_2}}{F_{oCa(OH)_2}} \quad (1)$$

Where, $F_{oCa(OH)_2} = 94.1\%$, is the initial mole fraction of $Ca(OH)_2$ in $Ca(OH)_2$ technical powder.

F_{CaCO_3} = the mole fraction of $CaCO_3$ in the product.

The calculated conversions in terms of $Ca(OH)_2$ are also shown in Table IV and Figure 8 and Figure 9.

Table IV. Dehydration Reaction of $\text{Ca}(\text{OH})_2$

	Rx time	600 °F	750 °F	900 °F	1000°F	1100°F
H wt%	35 ms	-----	-----	2.3530	-----	-----
	50 ms	2.4300	2.3480	2.2835	1.8735	1.7440
	75 ms	-----	-----	2.1830	-----	-----
Conv %	35 ms	-----	-----	4.909	-----	-----
	50 ms	3.152	6.395	10.087	29.804	35.698
	75 ms	-----	-----	15.704	-----	-----

As shown in Figure 8, the dehydration conversion increased with reaction temperature from 3% at 600°F to 36% at 1100°F. The dehydration conversion increased rapidly over 900°F. Figure 9, shows the dehydration conversion vs. sorbent residence time. The dehydration conversion increased with residence time continuously from 5% at 35ms to 16% at 75ms.

Figure 8. Dehydration Reaction of Ca(OH)_2 Under the Medium Temperature Range (Resident Time 50ms)

Figure 9. Dehydration Reaction of Ca(OH)_2 in the Residence Time from 35ms to 75 ms (Reaction Temperature 900° F)

II. Carbonation Reactions:

As far as the effect of CO₂ on the desulfurization process was concerned, the carbonation tests were performed in the drop tube reactor. The test condition is listed as following:

Temperature: 600°F - 1100°F
Reaction time: 50, 75, 100 ms
Reactant gas: C_{CO2} = 14%, balance with N₂
Sorbent: Ca(OH)₂ Technical Powder.
Gas flow rate: 15 L/Min - 50 L/Min

The experimental data were analyzed and converted to the conversions of the reactions. For the carbonation reaction of Ca(OH)₂, the conversion in terms of CaCO₃ is defined as:

$$X_{CaCO_3} = \frac{F_{CaCO_3} - F_{oCaCO_3}}{F_{oCa(OH)_2}} \quad (2)$$

Where, $F_{oCa(OH)_2} = 94.1\%$, is the initial mole fraction of Ca(OH)₂ in Ca(OH)₂ technical powder.

$F_{oCaCO_3} = 5.9 \%$, is the initial mole fraction of CaCO₃ in Ca(OH)₂ technical powder.

F_{CaCO_3} = the mole fraction of CaCO₃ in the product.

The calculated conversions in terms of CaCO₃ are also listed in Table V and Table VI.

Table V. Carbonation reaction of $\text{Ca}(\text{OH})_2$ at 900°F and 1100°F

	Rxn Temperature	50 ms	75 ms	100 ms
H wt%	900 °F	2.194	2.097	2.170
		2.23	2.208	2.161
	1100 °F	1.743	1.693	1.713
		1.739	1.648	1.645
C wt%	900 °F	2.426	2.666	2.690
		2.401	2.670	2.656
	1100 °F	4.617	4.952	5.004
		4.742	5.010	4.944
Conv. %	900 °F	10.52	12.28	12.45
		10.33	12.30	12.20
	1100 °F	27.35	30.09	30.51
		28.37	30.56	30.02

Table VI. Carbonation reaction of $\text{Ca}(\text{OH})_2$ within 50 ms

	600 °F	900 °F	1000 °F	1100 °F
C %	1.454	2.426	4.479	4.617
	1.495	2.401		4.742
H %	2.556	2.194	1.935	1.743
	2.567	2.230		1.739

Conv. %	3.572	10.52	26.24	27.36
	3.859	10.33		28.37

Carbonation conversion of $\text{Ca}(\text{OH})_2$ vs. residence time under the reaction temperature of 900°F and 1100°F are shown in Figure 10. The carbonation conversion increases slightly with residence time from 50ms to 75ms. It appears that the carbonation conversion reaches its upper limit after 75 ms. Figure 11 shows the carbonation conversion under different reaction temperature. Carbonation conversion increases with reaction temperature and the conversion increases rapidly over 900°F .

The surface area of original $\text{Ca}(\text{OH})_2$ and products were measured with the BET method. The results are shown in Table VII , Figure 12. and Figure 13.

Table VII. BET Surface Area from the Carbonation Reaction.

	Rxn Temperature	50 ms	75 ms	100 ms
Area (m ² /g) Original: 10.1(m ² /g)	600°F	5.774	-----	-----
		5.782	-----	-----
	900 °F	5.168	3.900	4.056
		4.380	3.815	-----
	1100 °F	2.370	2.616	2.303
		2.294	2.281	2.997

Figure 10 Carbonation Reaction within Residence Time from 50ms to 100ms

Figure 11. Carbonation Reaction under Medium Temperature Range
(Resident Time 50ms)

Figure 12. BET Surface Area Change with Reaction Temperature
in Carbonation Reaction (Resident Time 50ms)

Figure 13. BET Surface Area Change With Resident Time in Carbonation Reaction

III. Sulfation/Carbonation Reaction:

A group of simultaneous carbonation-sulfation tests were carried out at the reaction temperature from 600°F to 1100°F. The experimental conditions were:

Temperature: 600°F - 1100°F
Reaction Time: 50 ms
Reactant Gas: $C_{SO_2} = 3000$ ppm, $C_{O_2} = 3\%$, $C_{H_2O} = 8\%$,
 $C_{CO_2} = 14\%$, balance with N_2 .
Sorbent: $Ca(OH)_2$ technical powder.
Gas Velocity: 15 L/Min - 50 L/Min

The results are listed in Table VIII. and Figure 14.

Table VIII. Simultaneous Carbonation-sulfation Reaction of $Ca(OH)_2$
(Resident time = 50 ms)

	C% (wt%)	S% (wt%)	H% (wt%)
$Ca(OH)_2$ Reactant	0.937	0.000	2.583
600 °F	1.457	2.179	2.209
750 °F	1.700	2.589	2.144
900 °F	2.220	4.018	1.660
1000 °F	2.580	3.951	1.567
1100 °F	2.990	-----	1.543

Figure 14. C%, H% and S% in the Product of Sulfation/Carbonation Reaction
(Resident Time 50ms)

The experimental data were analyzed and converted to the conversions of the reactions. The conversions in terms of CaCO_3 , CaO and CaSO_3 in the sulfation/carbonation reaction of Ca(OH)_2 are defined as:

$$X_{\text{CaCO}_3} = \frac{F_{\text{CaCO}_3} - F_{o\text{CaCO}_3}}{F_{o\text{Ca(OH)}_2}} \quad (3)$$

$$X_{\text{CaO}} = \frac{F_{\text{CaO}} - F_{o\text{CaO}}}{F_{o\text{Ca(OH)}_2}} \quad (4)$$

$$X_{\text{CaSO}_3} = \frac{F_{\text{CaSO}_3} - F_{o\text{CaSO}_3}}{F_{o\text{Ca(OH)}_2}} \quad (5)$$

$$X_{\text{Ca(OH)}_2} = \frac{F_{\text{Ca(OH)}_2} - F_{o\text{Ca(OH)}_2}}{F_{o\text{Ca(OH)}_2}} \quad (6)$$

Where $F_{o\text{Ca(OH)}_2} = 94.1\%$, is the initial mole fraction of Ca(OH)_2 in Ca(OH)_2 technical powder.

$F_{o\text{CaCO}_3} = 5.9 \%$, is the initial mole fraction of CaCO_3 in Ca(OH)_2 technical powder.

F_{CaCO_3} = the mole fraction of $CaCO_3$ in the product.

F_{oCaO} = 0.0%, is the initial mole fraction of CaO in $Ca(OH)_2$ technical powder.

F_{CaO} = the mole fraction of CaO in the product.

F_{oCaSO_3} = 0.0%, is the initial mole fraction of $CaSO_3$ in $Ca(OH)_2$ technical powder.

F_{CaSO_3} = the mole fraction of $CaSO_3$ in the product.

The calculated conversions are shown in Table VIII and Figure 15.

Table VIII. The Conversions from the Simultaneous Carbonation/ Sulfation Reaction

	Xcao	Xcaco3	Xcaso3	Xcaoh2
600 °F	0	0.039212	0.057141	0.096353
750 °F	0	0.057637	0.068711	0.126349
900 °F	0.077328	0.097148	0.108475	0.282952
1000 °F	0.088456	0.124012	0.10721	0.319677

The carbon, sulfur and hydrogen contents in the products are shown as a function of the reaction temperature in Figure 14. The hydrogen percentage decreases with the reaction temperature due to the simultaneous carbonation, sulfation and dehydration reactions. The carbon content in the products increases continuously with the reaction temperature from 600°F to 1100°F. Contrary to the carbonation reaction where the carbon content increases with reaction temperature even in the higher temperature range, the sulfur content reaches its maximum value at the temperature around 1000°F. The existence of this optimum sulfation reaction temperature may due to the competing carbonation reaction which consumes the active sorbent($Ca(OH)_2$) and impedes the sulfation reaction at higher temperature. The conversions of $Ca(OH)_2$ to CaO , $CaCO_3$ and $CaSO_3$ during the sulfation/carbonation reactions are shown in Figure 15. The conversion to $CaCO_3$ increased continuously with reaction temperature from 600°F to 1000°F. The conversions to CaO and $CaSO_3$ increased with reaction temperature and then reached their upper limits at 1000°F and 900°F respectively.

Figure 15. Conversions of the Sulfation/Carbonation Reaction
(Resident Time 50 ms)

IV. The Reactivity of CaO

To verify the importance of the reactions of CaO and SO₂ in the medium temperature range, a series of sulfation tests of CaO and Ca(OH)₂ were conducted with the drop tube reactor and the TGA respectively.

The experimental conditions for the Drop Tube tests were:

Temperature: 900°F
Reaction Time: 0.05 second, 0.075 second.
Reactant Gas: C_{SO2} = 2743 ppm, C_{O2} = 2.93%, C_{H2O} = 8%,
balance with N₂.
Sorbent: Ca(OH)₂ technical powder, CaO technical powder.
Gas Velocity: 12.2 m/s, 8.13 m/s.

The experimental conditions for the TGA tests were:

Temperature: 700°F
Reaction Time: 20 minutes
Reactant Gas: C_{SO2} = 2982 ppm, C_{O2} = 3.18%, balance with N₂.
Sorbent: Ca(OH)₂ technical powder, CaO powder formed from
the thermal decomposition of Ca(OH)₂ technical powder.

The results are listed in Table X.

Table X. Sulfation Reactions of Ca(OH)₂ and CaO
in a Drop Tube Reactor
(Temperature = 900°F)

	S% (wt%)	C% (wt%)	H% (wt%)	Conv %
--	----------	----------	----------	--------

Ca(OH) ₂ 50 ms	4.558	1.248	1.939	11.71
Ca(OH) ₂ 75 ms	4.852	1.117	1.954	12.41
CaO 50 ms	3.467	-----	-----	6.519
CaO 75 ms	3.888	-----	-----	7.378

The experimental data were also analyzed and converted to the conversions of the reactions as following:

For the sulfation reaction of Ca(OH)₂, the conversion in terms of CaSO₃ is defined as:

$$X_{CaSO_3} = \frac{F_{CaSO_3} - F_{oCaSO_3}}{F_{oCa(OH)_2}} \quad (7)$$

Where, $F_{oCa(OH)_2} = 94.1\%$, is the initial mole fraction of Ca(OH)₂ in Ca(OH)₂ technical powder.

$F_{oCaSO_3} = 0\%$, is the initial mole fraction of CaSO₃ in Ca(OH)₂ technical powder.

F_{CaSO_3} = the mole fraction of CaSO₃ in the product.

And,

$$F_{CaSO_3} = \frac{\frac{S\%}{32}}{\frac{S\%}{32} + \frac{C\%}{12} + \frac{H\%}{2} + \frac{100 - S\% * \frac{120}{32} - C\% * \frac{100}{12} - H\% * \frac{74}{2}}{56}$$

For the sulfation reaction of CaO, the conversion in terms of CaSO₃ is defined as:

$$X_{CaSO_3} = \frac{F_{CaSO_3} - F_{oCaSO_3}}{F_{oCaO}} \quad (9)$$

Where, $F_{oCaO} = 100\%$, is the initial mole fraction of CaO in CaO technical powder.

$F_{oCaSO_3} = 0\%$, is the initial mole fraction of CaSO₃ in CaO technical powder.

F_{CaSO_3} = the mole fraction of CaSO₃ in the product.

And,

$$F_{CaSO_3} = \frac{\frac{S\%}{32}}{\frac{S\%}{32} + \frac{100 - S\% * \frac{120}{32}}{56}}$$

The calculated conversions in terms of CaSO₃ for both CaO and Ca(OH)₂ are also listed in Table X.

The sulfur contents in the products of sulfation reactions of both Ca(OH)_2 and CaO are shown as a function of the resident time in Figure 16. The sulfation conversion of Ca(OH)_2 and CaO are also shown in Figure 17. By comparing the sulfation conversion of Ca(OH)_2 and CaO at 900°F and residence times from 50 to 75 ms, it is found that the sulfation rate of CaO at this temperature is not low enough to be ignored. The TGA results as shown in Figure 18 and Figure 19 also indicate that the sulfation reaction of CaO at this temperature range cannot be ignored.

Figure 16. S% in the Products from the Sulfation Reactions of Ca(OH)_2 and CaO (Reaction Temperature 900°F)

Figure 17. Conversion of Sulfation Reactions of Ca(OH)_2 and CaO (Reaction Temperature 900°F)

Figure 18. Sulfation Reaction of Ca(OH)_2 in TGA

Figure 19. Sulfation Reaction of CaO in TGA

Figure 20. Reactivity of fresh CaO in Air

As described above in the section of Dehydration Reaction, the newly produced CaO from the dehydration of Ca(OH)_2 is very active in air. A series of TGA tests were performed to investigate these rehydration and carbonation processes.

First the Ca(OH)_2 is dehydrated in N_2 with TGA as shown in Figure 21. The produced CaO was taken out of TGA and set in air for 3 minutes, 8 minutes and 15 minutes respectively. Then the products were analyzed with the element analyzer. The result is shown in Figure 20. The result indicated that both the hydrogen and carbon contents increase dramatically with the resident time in air. After ten minutes the product was put back to TGA to be decomposed again. The result is shown in Figure 22. The first step at about 305°C is the decomposition of Ca(OH)_2 and the second step at about 517°C is the decomposition of CaCO_3 . Since CaO is not so active with CO_2 according to previous study it is believed that after the CaO is exposed in air it would react with H_2O vapor first to form Ca(OH)_2 quickly, and then the formed Ca(OH)_2 would react with CO_2 to form CaCO_3 . To verify this assumption, the original Ca(OH)_2 was left in air for 24 hours, and then the sample was analyzed with element analyzer. The result showed the carbon content increased from the original 0.937% to 2.584%.

To investigate if the cooled CaO forms Ca(OH)_2 and CaCO_3 , the original Ca(OH)_2 was decomposed in TGA and cooled down to 60°C in N_2 , and then exposure to air for one hour and put back in TGA to be decomposed again as shown in Figure 23. The result showed there were still significant amounts of Ca(OH)_2 and CaCO_3 formed.

To investigate the reaction rate of fresh CaO in air, the following TGA test was conducted. First the original Ca(OH)_2 was decomposed in TGA and cooled down to room temperature in N_2 , and then air was introduced into TGA which was set to a isothermal condition of 30°C . The fast weight increase of CaO during these rehydration and carbonation processes was shown in Figure 24. To find out how much Ca(OH)_2 and CaCO_3 were formed during this short period, the product was decomposed again in TGA. The results is shown in Figure 25.

Sample: CA (OH) 2
Size: 9.1880 mg
Method: DECOMPOSITION
Comment: DECOMPOSITION

TGA

File: C:\DEHYCACH.01
Operator: ANSO NANG
Run Date: 8-Jun-93 14:01

Figure 21. Thermal Decomposition of Orininal Ca(OH)₂

Sample: CAO DECOMPOSITED FROM CA(OH)2
Size: 10.1670 mg
Method: DECOMPOSITION
Comment: CAO DECOMPOSITED FROM CA(OH)2. PUT IN AIR FOR 10 MIN

TGA

File: C:\CAO.01
Operator: ANSO NANG
Run Date: 8-Jun-93 16:42

Figure 22. Decomposition of Sorbent Products

Sample: CAO FROM CAOHE
 Size: 20.3880 mg
 Method: DECOMPOSITION
 Comment: DECOMPOSITION OF CAO FROM CAOHE COOL IN N2 80 C. STAY IN AIR 1 H

TGA

File: C:\CAOHE.10
 Operator: ANBO WANG
 Run Date: 7-Jun-93 17:18

Figure 23. Decomposition of Sorbent Product.

Sample: FRESH CAO FROM CA(OH)2
 Size: 5.6240 mg
 Method: ISOTHERMAL AT 30 C
 Comment: CAO REACTS IN AIR

TGA

File: C:\CAOHEHY.08
 Operator: ANBO WANG
 Run Date: 1-Sep-93 17:00

Figure 24 The Reaction of Fresh CaO in Air

Sample: PRODUCT DECOMPOSITION
 Size: 6.1210 mg
 Method: DECOMPOSITION
 Comment: THERMAL DECOMPOSITION

TGA

File: C:\CAO\CHY.07
 Operator: AMO WANG
 Run Date: 1-Sep-93 17:21

Figure 25. Decomposition of Sorbent Product

D. SLOW - REACTION STUDIES

In order to explore the mechanism of the $\text{Ca}(\text{OH})_2$ - Flue gas reactions for a longer reaction time, a series of fixed bed tests were performed during the the first-year project⁽¹⁵⁾. The test data from the drop tube experiment were compared with the test results from the fixed bed experimental studies.

The fixed bed reactor system, as shown in Figure 1, consisted of a reaction chamber, a main heater and preheater, pressure and temperature measurement units, flow rate measurement and control units, and gas sources. The reaction chamber had two similar sections, the upper and lower covers. Each part was 6.5 inches in height with 2.0 inches inside diameter. The temperature inside the chamber was monitored by two type K thermocouples, which were placed $\frac{1}{2}$ inch above the fixed bed, and $\frac{1}{2}$ inch beneath the fixed bed respectively. The fixed bed was supported by a sintered porous metal filter that was 2.0 inches in diameter and 0.2mm in thickness. The main heater surrounded the reaction chamber.

Three gas sources were used: pure CO₂ gas, 2.5% SO₂ (balanced by N₂), and compressed air. The compressed air was filtered to remove the oil and particulate matter. The gases were mixed before entering the preheater. To simulate flue gas, water was injected in the middle section of the preheater where the gas temperature was above the boiling point of water. The amount of water to be injected was calculated by the required H₂O content, the measured water content in the compressed air and the total gas flow rate. Water injection was controlled by a controllable syringe pump.

In the reaction chamber, the simulated flue gas was heated to the required reaction temperature. Driven by the pressure difference across the fixed bed, the reactant gas passed through the fixed bed and reacted with the sorbent. Sorbent particle loading was a difficult problem because the kinetic study required a quick loading of the sorbent into the hot reactor. The solution was first to create a vacuum(-20 psig) in the reactor chamber by fully opening the vacuum valve and closing the main gas valve, and then open the injection valve suddenly so that the sorbent particles would be quickly sucked into the reaction chamber through the injection line and deposited on the filter. During the reaction, the vacuum in the reaction chamber was maintained at -1.0 psig.

Sulfur content was analyzed with a LECO-517 sulfur analyzer. The method is based on the ASTM method E30-47. Brief steps of the method are first to heat the sample at a high temperature (2600°F - 2700°F, 1400°C - 1500°C) in an oxygen environment to drive the sulfur out and convert it into SO₂, and then determine the amount of SO₂ by titration. Surface area was measured with a Quantachrom Monosorb Surface Area Analyzer MS-12 by the BET method. Available lime (The total original Ca(OH)₂ and the Ca(OH)₂ converted from CaO by hydrated are called "available lime") was measured by a wet chemistry method. First, the sample was slaked to form Ca(OH)₂ and then cooled. Then, a sugar solution was added to convert the Ca(OH)₂ into calcium sucate. Finally, the quantity of calcium sucate was determined by titration with a HCl solution to the phenolphthalein endpoint. CaCO₃ content was estimated from the difference between the total alkalinity (calculated as carbonate) and the available lime(calculated as carbonate). The total alkalinity was measure by the following

method: first, use a known excess of standard hydrochloric acid to dissolve and then, neutralize the solid phase carbonate and/or hydroxide. The excess HCl concentration was determined by titration with standard sodium hydroxide to phenolphthalein endpoint. The amount of HCl neutralized was determined from the difference between the quantity of HCl originally added and that back-titrated with NaOH solution.

The experimental conditions for the fixed bed and the drop tube reactor were:

Fix Bed Reactor:

Temperature: 600°F, 700°F, 800°F, 1000°F.
(316°C, 371°C, 427°C, 538°C)

Reaction Time: 10, 20, 40, 60 minutes

Gas Composition: $C_{SO_2} = 3000\text{ppm}$
 $C_{H_2O} = 8\%$
 $C_{CO_2} = 14\%$
 $C_{O_2} = 0\%$
Balanced with Dry Air

Solid Sample: 2.5 g of commercial marble $Ca(OH)_2$ for each run.

Gas Velocity: 3 ft/min. (0.015 meter/second).

Drop Tube Reactor:

Temperature: 600°F - 1200°F
(316°C - 650°C)

Reaction time: 0.5 second

Gas composition: $C_{SO_2} = 3000\text{ppm}$, $C_{O_2} = 3\%$, $C_{CO_2} = 14\%$, $C_{H_2O} = 8\%$, balanced with N_2 .

Sorbent: $Ca(OH)_2$ technical powder, Type-N dolomitic hydrate

Gas velocity: 1.22 m/s

Table IX The Sorbent Properties

	Avai.Lime%	S%	CaCO ₃ %	BET (m ² /g)	MgO %
Commercial Marble Ca(OH) ₂ (used in fixed bed)	93.7	0.0	6.3	16.8	0.0
Ca(OH) ₂ Technical Powder (used in drop-tube)	88.5	0.0	11.5	11.2	0.0
Type N Dolomite (used in drop-tube)	63.2	0.0	2.28	9.0	33.8

The experimental results are shown in Figure 26 to Figure 29. From the experimental results, the following observations were made:

- 1) As shown in Figure 26, in the fixed bed tests, an optimum sulfation reaction temperature of 700°F(371°C) was observed under the residence times from 10 to 60 minutes. The sulfation rate increases with temperature from 600°F to 700°F(316-371°C), then decreases as temperature increases above 700°F(371°C). However the maximum sulfation rate at 700°F(371°C) is not significant when the resident time is over 40 minutes. On the other hand in the drop-tube reactor, the sulfation rate increases continuously with temperature within a range of 600°F - 1200°F(316-650°C). No maximum sulfation rate was observed in the drop-tube tests.
- 2) The reaction rates of CO₂ with calcium-based sorbent are shown in Figure 27. Contrary to the sulfation reactions, the reaction rates of CO₂ in both the fixed bed and the drop-tube reactor increase continually with temperature.
- 3) As shown in Figure 28, the amount of available lime decreases continually with

temperature. The available lime decreases more rapidly at higher temperature.

- 4) The BET surface area (as shown in Figure 29) decreases continually as the temperature increases. The BET surface area decreases more dramatically at higher temperature.

To explain the above phenomena, the chemical and physical processes of the overall process need to be discussed. The major chemical reactions in the medium temperature range are:³

- a. $\text{Ca(OH)}_2(\text{solid}) + \text{SO}_2(\text{gas}) = \text{CaSO}_3(\text{solid}) + \text{H}_2\text{O}(\text{gas})$
- b. $\text{Ca(OH)}_2(\text{solid}) + \text{CO}_2(\text{gas}) = \text{CaCO}_3(\text{solid}) + \text{H}_2\text{O}(\text{gas})$
- c. $\text{Ca(OH)}_2(\text{solid}) + \text{heat} = \text{CaO}(\text{solid}) + \text{H}_2\text{O}(\text{gas})$
- d. $\text{CaSO}_3(\text{solid}) + 1/2 \text{O}_2(\text{gas}) = \text{CaSO}_4(\text{solid})$
- e. $\text{CaO}(\text{solid}) + \text{SO}_2(\text{gas}) = \text{CaSO}_3(\text{solid})$
- f. $\text{CaO}(\text{solid}) + \text{CO}_2(\text{gas}) = \text{CaCO}_3(\text{solid})$

As soon as the hydrated lime is injected into the flue gas, the Ca(OH)_2 immediately reacts with SO_2 and begins to dehydrate simultaneously. The CaO formed from the dehydration reaction may react further with SO_2 . Because there is extra O_2 in the flue gas, the sulfation product, CaSO_3 , may oxidize further to form CaSO_4 . In addition, The Ca(OH)_2 and CaO may also react with CO_2 in the flue gas to form CaCO_3 . These reactions with CO_2 are undesirable for the desulfurization process.

The general physical process^{[16],[17],[18]} includes the following steps:

- a. Bulk diffusion of SO_2 and CO_2 to the particle surface.
- b. Bulk diffusion of SO_2 and CO_2 through the particle layer (exists in the fixed bed only).
- c. Diffusion of SO_2 and CO_2 in the porous particle through the pores.
- d. Diffusion of SO_2 and CO_2 through the products layer of CaSO_3 and CaCO_3 .

The competing reaction with CO_2 and the diffusion resistance of SO_2 through the particle layer appeared to be the major reasons for the existence of an optimum sulfation reaction temperature in the fixed bed condition. At lower temperature, the sulfation process could be controlled by both the reaction kinetics and the diffusion resistance of SO_2 through the product layer. At this stage the sulfation rate would increase with temperature. At $700^\circ\text{F}(371^\circ\text{C})$ the diffusion resistance of SO_2 became dominant so that a further increase in the temperature might not raise the sulfation rate. On the other hand, there was an abundant amount of CO_2 in the flue gas, which reacted with the sorbent and consumed the active sorbent($\text{Ca}(\text{OH})_2$). Since the CO_2 concentration was almost 50 times greater than that of SO_2 in the flue gas, it was possible that the sulfation process was diffusion limited, while the carbonation process was still chemically limited when temperature was over $700^\circ\text{F}(371^\circ\text{C})$. Consequently, a further increase of temperature over $700^\circ\text{F}(371^\circ\text{C})$ would increase the reaction of CO_2 which consumed the available lime and lead to the decrease in the sulfation rate. At longer resident times over 40 minutes, the diffusion of the SO_2 through the particle layer became sufficient enough that the sulfation rate hump was not significant. The experimental observation of a hard sorbent cake formed in the fixed bed especially under the higher temperature was another evidence which emphasizes the importance of the SO_2 diffusion resistance through the particle layer. Besides consuming the $\text{Ca}(\text{OH})_2$, the reaction of CO_2 would form an outside product layer that might hinder further reaction between SO_2 and $\text{Ca}(\text{OH})_2/\text{CaO}$ in the interior of the sorbent particle.

In the drop-tube reactor where particles were suspended in the reactant gas, there was no diffusion resistance of SO_2 through the particle layer. In this case both the carbonation and the sulfation processes could be controlled by chemical kinetics. Increase in the reaction temperature would lead to the increases in the sulfation rate as well as the carbonation rate.

The decrease of the available lime was due to the sulfation and carbonation reactions. At higher temperatures, more calcium carbonate would be produced causing a sharp decrease in available lime. The decrease of the BET surface area was mainly due to the formation of CaSO_3 and CaCO_3 which have larger molar volumes than that of $\text{Ca}(\text{OH})_2$ and would plug

some of the initial pores.

The carbonation reaction takes place simultaneously with sulfation reaction under the fixed bed and drop-tube reactor conditions. The results also indicated that the carbonation reaction rate increased continually with temperature, while the sulfation reaction rate increased with temperature in the range from 600°F to 700°F(316°C-371°C), then decreased under the fixed bed condition which is a typical condition for a hot baghouse. The existence of an optimum desulfurization temperature, which was found to be approximately 700°F(371°C) for the fixed bed condition, appeared to be due to the competing reaction of CO_2 and the diffusion resistance of SO_2 through the particle layer in the fixed bed.

Figure 26. Sulfur Contents in the Reacted Sorbent
(Drop Tube Resident Time 500ms)

Figure 27 Carbonate Content in the Reacted Sorbent
(Drop Tube Resident Time 500 ms)

Figure 28. Available lime contents in the reacted sorbent

Figure 29. BET Surface Area in the Reacted Sorbent

III. FUTURE WORK

- Continue the experimental work investigating the dehydration, sulfation, carbonation and simultaneous dehydration/carbonation/sulfation reactions of Ca(OH)_2 and dolomite within 100ms. In addition, the effects of reactant gas concentration on the sorbent conversions will be studied also.
- The carbonation and sulfation of CaO will be studied further in conjunction with the above investigation to verify the importance of the reactions of CaO in the medium temperature range.
- The influence of sorbent size, sorbent surface area and sorbent pore structure on the medium temperature range reactions will be studied.
- The above experimental findings will be verified by realistic simulation and math modeling work. Dehydration, sulfation and carbonation models of the hydrated lime will be studied in conjunction with the simultaneous dehydration, sulfation and carbonation models. This simulation work will lead to an optimum operating condition for the economizer injection process.

IV. CONCLUSION

The drop tube reactor has been successfully modified and operated. The carbonation, dehydration and sulfation reactions of Ca(OH)_2 within the residence time of 100ms have been studied in the drop tube reactor system. The reactivity of CaO with SO_2 and the reactivity of fresh CaO in air have been investigated also. Besides, The test data from the drop tube experiment were compared with the test results from the fixed bed experimental studies of the first year research of the project. Following results have been obtained during the third year research:

- The dehydration conversion increased with reaction temperature from 3% at 600°F to 36% at 1100°F. The dehydration conversion increased dramatically over 900°F. The dehydration conversion increased with residence time continuously from 5% at 35ms to 16% at 75ms.
- The fresh CaO from the dehydration reaction of Ca(OH)_2 is very active in air. As soon as the fresh CaO exposure to air, it rapidly rehydrated due to the moisture in air and react further with CO_2 to form CaCO_3 .
- The carbonation conversion increases slightly with residence time from 50ms to 75ms. It is appear that the carbonation conversion reach its upper limit after 75 ms. Carbonation conversion increases with reaction temperature and the conversion increases rapidly over 900°F .
- In the simultaneous carbonation/sulfation reaction the carbonation conversion increased continuously with the reaction temperature from 600°F to 1100°F. Contrary to the carbonation reaction where the carbonation conversion increased with reaction temperature even at higher temperature range, the sulfation conversion reaches its maximum value at the temperature around 1000°F. The existence of this optimum sulfation reaction temperature may due to the competing carbonation reaction which consumes the active sorbent(Ca(OH)_2) and impeded the sulfation at higher temperature. The conversion to CaO increased with reaction temperature first and then reach its upper limits at about 1000°F .
- By comparing the sulfation conversion of Ca(OH)_2 and CaO at 900°F and residence times from 50 to 75 ms, it is found that the sulfation conversion of CaO at this temperature range was significant and could not be ignored. The TGA results also indicated the importance of the reaction between CaO and SO_2 in medium temperature range.

- The carbonation reaction taken place simultaneously with sulfation reaction under the fixed bed and drop-tube reactor conditions. The carbonation reaction rate increased continually with temperature, while the sulfation reaction rate increased with temperature in the range from 600°F to 700°F, then decreased under the fixed bed condition which was the typical condition for a hot baghouse. The existence of an optimum desulfurization temperature, which was found to be approximately 700°F for the fixed bed condition, appeared to be due to the competing reaction of CO_2 and the diffusion resistance of SO_2 through the particle layer in the fixed bed.

REFERENCES

1. Ronald Wolk, The Future for Coal-Based Generation, EPRI Journal, December, 1990.
2. J. Makansi, Acid-Rain Control Systems, Power, February, 1990.
3. Bryan Lee, Highlight of the Clean Air Act Amendments of 1990, Journal A & WMA, Vol. 41, No. 1, 1991.
4. Muzio I.J, et al, Assessment of Dry Sorbent Emission Control Technologies, Part I Fundamental Processes, JAPCA(JA&WMA), Vol. 37, No. 5, 1987.
5. Offen G.R., et al, Assessment of Dry Sorbent Emission Control Technologies, Part II Applications, JAPCA(JA&WMA), Vol. 37, No. 5, 1987.
6. Khang, S.J., Keener, T.C., Flue Gas Desulfurization for Acid Rain Control Utilizing Dry Injection Process, Technical Review for OCDO, 1990.
7. Muzio I. J., "Assessment of Dry Sorbent Emission Control Technologies, Part I Fundamental Processes, JAPCA, Vol.37, No.5, 1987.
8. Offen G. R., "Assessment of Dry Sorbent Emission Control Technologies, Part II Applications, JAPCA, vol. 37, No.8,1987.
9. Khang, S.J., Keener, T.C., "Flue Gas Desulfurization for Acid Rain Control Utilizing Dry Injection Process, Technical Review for OCDO, 1990.
10. Blythe, G.M., "EPRI Pilot testing of SO₂ Removal by Calcium Injection Upstream of a Particulate Control Device", paper 35, Proceedings: 1986 Joint symposium on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies, 2, EPRI CS-4966, December 1986.
11. Southern Research Institute Monthly Report No. 18, October 1985, Contract No. 195-83-003 (Dry Sorbent Emission Control).
12. Bortz, s.j., "Dry hydroxide injection at economizer temperatures for improved SO₂ Control." Paper presented at 1986 Joint Symposium on Dry SO₂ and Simultaneous SO₂/NO_x control Technologies, Raleigh, North Carolina, June, 1986.
13. S.j. Bortz, "Hydrate and Process Parameters Controlling SO₂ Removal During Hydroxide Injection Near 1000°F", Presented at first combined FGD and dry SO₂ control symposium, ST. LOUIS, MISSOURI, OCTOBER, 1988.
14. Fan, Liang-Shih, The Ohio State University, OCDO Final Report, Project OCRC/91-1.1, July 1, 1991 to May 31, 1992.

15. Khang, S.J., University of Cincinnati, OCDO Final Report, Project OCRC/90-1.3, September 1, 1990 to June 30, 1991.
16. G.H. Newton, S.L. Chen, J.C. Kramlich, " Role of Porosity Loss on Limiting SO_2 Capture by Calcium Based Sorbent ", AIChE J., Vol. 35, No. 6, 1989.
17. S. Zarkanitis, S. Sortirchos, " Pore Structure and Particle Size Effect on Limestone Capacity for SO_2 Removal ", AIChE J. Vol. 35, No. 5, 1989.
18. B.K. Gullet, K.R. Bruce, " Pore Distribution Change of Calcium-based Sorbent Reacting with Sulfur Dioxide ", AIChE J., Vol. 33, No. 10, 1987.

DATE

FILMED

6/27/94

END