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

Final Report for the Period
September 1, 1992 to August 31, 1993

by

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EXECUTIVE SUMMARY

The focus of this project is on furnace sorbent injection technology using dry, calcium-based sorbents for flue gas desulfurization. The goal is to provide fundamental research kinetics and the effects of sorbent properties, aimed at improving SO₂ removal and increasing sorbent utilization in a cost-effective fashion.

The main focus of the third year work has been to obtain fundamental kinetic data for calcination, sintering and sulfation of calcium hydroxide sorbent. The results, their interpretation, and discussions are the primary focus of this report. Other major portions of this year's work covered in the report include the additions and modifications made to the experimental system, and preliminary results of the studies with modified Ca(OH)₂.

Most of the reactor system and the analytical and measurement techniques were developed in the second year and formed the necessary framework for realizing the project goal. A few design and experimental constraints necessitated modifications and additions which were made in the beginning of this year. A continuous micro-feeder was built in order to feed very small quantities of sorbent, which is essential to maintain differential conditions with respect to SO₂ during sulfation experiments. The particle collection probe was modified with a insulating ceramic cover and cap, in order to reduce its cooling effect and achieve better isothermality within the reactor. A cascade cyclone sampler was added to replace the impactor because the particle loading capacity of the impactor was not sufficient to hold enough powder required for post-reaction analyses.

The sorbent-SO₂ reaction is a extremely fast and complex phenomena with calcination, sintering and sulfation all occurring simultaneously. This work can be divided into three parts; the simultaneous calcination and sintering of Ca(OH)₂, the

isolated sulfation of pre-calcined, pre-sintered CaO, and the simultaneous calcination, sintering and sulfation of Ca(OH)_2 .

Calcination of Ca(OH)_2 has been thoroughly studied for the effect of temperature and particle size on decomposition, and the evolution of surface area and porosity. Temperature effect studies show that there is a drastic decrease in the calcination rate after about 30 ms, at all temperatures. In the initial 30 ms, the reaction proceeds very fast and shows a pronounced influence of temperature and no effect of particle size. After 30 ms however, the reaction proceeds much slower and the influence of temperature is diminished. A shifting controlling regime hypothesis is proposed to explain the above observations, with chemical reaction being the rate limiting step in the initial 30 ms and internal pore diffusion being the slowest at higher residence times. Activation energy calculations were performed for both the regimes and the values of activation energies obtained support the two regime theory.

Particle size was found to have no effect on Ca(OH)_2 conversion below a certain size of $3.6 \mu\text{m}$ (mean aerodynamic diameter). This is true even at higher residence times when pore diffusion is the slowest step. Lack of such effect probably indicates a very high Thiele modulus and the size effect though existing, will not be prominent in terms of solid conversion.

The surface area evolution with calcination represents the net effect of two opposing factors; calcination causes the development of high porosity and high surface area, while sintering causes the agglomeration of grains and leads to decreased surface area. The surface areas for various temperatures were found to be much lower than the earlier reported data in the literature. Sintering is highly influenced by temperature and is fast enough to cause the overall surface area to decrease from the very onset for

temperatures of 1050° C and above. Probably, most earlier studies had poor sorbent/gas mixing and heat transfer resistances across the particle lead to lower sintering rate.

Sulfation with pre-calcined and pre-sintered CaO give valuable insights into independent sulfation reaction alone without any other interfering phenomena. Effect of temperature and particle size on isolated sulfation were studied. Temperature effect studies reveal that there is a drastic drop in the sulfation rate after the initial 30-35 ms at all temperatures. In the initial 35 ms, sulfation proceeds at a very fast rate and shows a strong influence of temperature. At higher residence times, the sulfation reaction rate is much slower but there is still substantial influence of temperature. As in calcination, a shifting regime hypothesis is proposed to explain the observations. Chemical reaction controls the overall reaction initially, but as more product CaSO_4 is formed and covers the CaO surface area, the diffusion through the product layer becomes the slowest step. Surface area effect studies show that the reaction rate is strongly influenced by surface area at higher residence times. High activation energy and high surface area dependence together support the past theory that the product layer transport occurs via ionic diffusion rather than gaseous diffusion.

Sulfation of Ca(OH)_2 shows the combined effect of calcination, sintering and sulfation, all occurring simultaneously. Effect of temperature and particle size on Ca(OH)_2 have been studied. Particle size seems to have no effect on the sulfation rate below a certain particle size of about 5 μm .

Preliminary results of studies with lignosulfonate-modified Ca(OH)_2 have been presented and more work is currently underway. Most of the long term objectives of this research project have been accomplished. Additive enhancement studies and a mechanistic explanation of its working will be the next task. Effect of gas phase

conditions such as SO_2 concentration and other representative process conditions will be studied. Modeling work to account for all the different phenomena and development of a complete structural and mechanistic model that describes the gas-sorbent kinetic interaction will continue into the fourth year.

I. OVERVIEW

A. Background and Scope

The focus of this project is on in-furnace (above the flame) sorbent injection technology using dry, calcium-based sorbents for high-sulfur coal flue gas desulfurization. The goal is to provide research findings on fundamental research kinetics and the effects of sorbent properties, aimed at improving SO_2 removal and increasing sorbent utilization in a cost-effective fashion. With this goal, the purpose of this project is to investigate the fundamentals of sorbent-gas interactions at high temperatures and short residence times.

For furnace injection, the optimum temperature is in the range of 850-1200° C. Below this temperature range, sulfation reaction is too slow; above 1200° C is unfavorable because the product CaSO_4 becomes unstable. Under these conditions, the reaction is extremely fast, in the order of milliseconds.

Sorbents generally used are calcium carbonate or hydroxide. Additives can be mixed with the sorbent to enhance sulfur removal. The particle size is small, typically less than 50 microns.

When the sorbent is injected into the furnace, it undergoes calcination to produce highly porous and reactive CaO which has much higher surface area than the parent solid. The CaO reacts with SO_2 forming a solid product CaSO_4 which has a higher molar volume and thereby causes loss in surface area and porosity. Sintering is the mechanism which causes the solid grains to coalesce when exposed to temperatures below their melting point, and the changes are irreversible.

The mechanistic steps during the sulfation reaction involve diffusion of the bulk gas to the particle exterior, diffusion through the pores to the particle interior, diffusion

through the solid sulfate product layer and then surface reaction at the CaO interface.

It is well documented that CaO derived from hydrated lime (h-CaO) is more reactive than the CaO from limestone (c-CaO) and this project has focused primarily on h-CaO. Use of additives is important for improving sulfur capture, and at present, knowledge of the mechanisms of additives is inadequate.

B. Long term objectives

The long term objectives of this research project is to deliver the following:

1. gas-sorbent interaction kinetics at high temperatures and for the short residence times, with particular emphasis on the < 100 ms range,
2. interrelationship between the kinetics and sorbent properties such as size, structure and chemical content, and the structural properties such as surface area, porosity, pore size distribution, etc.,
3. mechanisms of calcination, sintering, and sulfation reactions occurring independently as well as simultaneously,
4. role of additives in the reaction mechanisms,
5. effect of gas-phase variability and representative process conditions,
6. microscopic model to account for the above, and,
7. a comprehensive set of guidelines based on this study for achieving the project goal.

II. EXPERIMENTAL SYSTEM: ADDITIONS & MODIFICATIONS

In furnace sorbent injection (FSI) technology, calcium based sorbents are introduced directly into the furnace to capture sulfur from the flue gas. The reaction is very fast and substantial sorbent conversion takes place within 200 milliseconds. Although there is no dearth of literature dealing with gas-solid reactions, techniques for accurate kinetic measurement in such a short time scale are virtually non-existent. In this work, a high-temperature entrained flow reactor system has been developed, which along with its probe systems is capable of performing accurate kinetic measurement for short contact time sorbent-gas reactions, with particular emphasis in the less than 100 millisecond time scale.

A. Introduction

Entrained flow reactor systems are commonly used for studying gas-solid reaction kinetics, because external transport resistances are minimal. However, conventional flow systems can not be readily used for the small time scale of interest associated with sorbent-gas reactions. Because of the high temperature dependence of the reaction, it is crucial to maintain the sorbents at low temperatures until injected into the reactor. Once injected, it becomes equally important to heat up the sorbent particles to the reaction temperature as rapidly as possible. Similarly, particle collection in the sampling probe has to be done with immediate quenching of the gas-solid stream to prevent any further reaction from taking place. Any lapse in fulfilling the above three conditions will result in erroneous data. Since the particle residence time of major interest ranges within 0 to 100 milliseconds, it must be estimated to an accuracy of a millisecond or better.

In the past, few attempts have been made to obtain time-resolved measurements for SO₂ removal in the 0 to 200 millisecond range. Milne et al. (1990) employed a phase discrimination probe for sampling solids from the reactor. It appears that the separation of solids, achieved within their probe, may not be complete and some of the fines may be excluded from the subsequent analysis. Gullett et al. (1988) used an axial sampling probe and obtained measurements down to 35 msec. In both the above studies, particle residence time was estimated indirectly from a knowledge of the gas velocity profile, thus requiring an accurate characterization of the fluid motion. This method also required isokinetic sampling since any difference between reactor and probe flow would lead to particle collection, preferential to larger or smaller sizes. With these systems, measurements at low residence time may not be accurate, because at such short time scales, description of the flow pattern suffers from large uncertainties. Moreover, the presence of the sampling probe is likely to alter the velocity profile inside the reactor.

The high-temperature reactor developed for studying sorbent/SO₂ reaction has been designed to eliminate most of the above mentioned problems associated with such experimental systems. The injection and collection probes are equipped with a microcomputer-interfaced data acquisition system, and perform particle injection/sampling, reaction quenching, and optical solids monitoring. The most unique feature of the reactor system is its ability, using the probe combination, to directly measure residence times as low as 10 ms for the solid samples from the high-temperature environment. Details of the high temperature reactor system, its design features and operational characteristics have already been discussed extensively in the second year final report of this project. The complete reactor system is shown schematically in Figure 1. In essence, the reactor set up consists of a furnace, the reactor tubes, a

Figure 1: Schematic of complete reactor system assembly.

particle feeder, a injection probe, a collection probe and a particle separation/classification system. Only the major modifications performed in the beginning of the third year, the need for these changes and their usefulness will be discussed here.

B. Continuous powder feed system

The pulse powder feeder developed in the second year was capable of transporting and injecting sufficient amount of powder into the reactor, however, it had serious drawbacks in terms of accurate estimation of the feeding parameters such as the amount of powder injected in each pulse and also the amount of extra gas put into the reactor with each opening of the solenoid valve. These became relatively more important in case of sulfation studies when the SO_2 concentration in the reactor had to be known accurately. Moreover, the injected amount of powder should be small enough to maintain differential condition with respect to SO_2 concentration in the entire reaction zone. Calculations showed that the amount of powder injected during pulse feeding varied between pulses and ranged from 0.1 to 0.5 mg, which may result in producing a non-differential condition with respect to SO_2 . However, during calcination, that amount of powder, when well dispersed in the reaction zone, was well within acceptable limit to avoid any effect of evolved CO_2 or H_2O on the calcination rate. In view of the process requirements for sulfation studies, a feeder capable of feeding low amount of particles was developed in the first quarter of this year. A schematic of this feeder assembly is shown in Figure 2. The feeder system consists of a 2.54 cm OD and 1.90 cm ID pyrex vessel which is 10.2 cm long. The vessel contains a shallow powder bed at its base, which rests on a filter disc. Fluidizing nitrogen gas enters from the bottom

Figure 2: Schematic of the continuous powder feeder system.

and fluidizes the powder. An off-take tube of 0.8 mm ID carries the particles to the reactor. A vibrator attached to the vessel prevents any channelling of gas through the powder bed. During an experimental run, powder is fed continuously by the feeder to the reactor for about one hour to collect enough powder for kinetic analysis. However, during residence time estimation, the fluidizing gas bypasses the feeding vessel and a high amount (0.5 mg) of powder is injected into the transport line manually by a syringe to produce detectable pulses in the optical systems of the injection and collection probes. During this procedure, the collection line also bypasses the particle collector, but all the pressures and flows are maintained at the conditions of the experimental run.

The new feeder assembly was found to feed powder at a rate of 200 to 600 mg/hr., which is quite satisfactory for sulfation studies. It was also tested whether the little amount of extra gas (0.5 cc over 40-50 msec, about 2-3% of the total flow rate in the reactor) injected with the powder during syringe injection affects the resulting residence time measurements. To test this, different amount of air ranging from 0.5 cc to 2.0 cc was injected with each injection. Resulting residence time measurements did not show any appreciable difference between runs.

C. Modified Collection Probe

The old collection probe developed in the second year had two major concerns. Firstly, it was necessary to reduce the cooling effect of the collection probe on the reactor temperature profile in order to obtain a better isothermality within the reactor. Secondly, it was observed that there is considerable amount of powder deposition on the surface of the funnel-like receiving end of the collection probe. Any deposited powder in the funnel can slip during an experimental run, resulting in contamination of samples

or an error in residence time estimation. In view of these, the collection probe design was modified to eliminate the problems associated with the old design. The schematic of the new collection probe is shown in Figure 3. In the new design, the diameter of the powder-receiving funnel is substantially shortened (9.5 mm), and the funnel also has a much steeper angle (60°). This new arrangement was found to reduce the powder deposition to a large extent. On the other hand, reducing the cooling effect of the collection probe involved more complicated design changes. The diameter of the top 45.72 cm of the probe (stainless steel sheath) was reduced to 1.90 cm from 2.54 cm, and a ceramic cover of the same length and 2.54 cm OD was cemented to that part. In addition, a ceramic cap was fitted to the top of the collection probe, surrounding the funnel. Reducing the diameter of the stainless steel sheath also demanded additional design adjustments in the collection probe head due to shrinkage of the inner space. Unlike the old probe, only one quench/purge gas line entered at the bottom of the new probe. This purge gas is carried to the probe head and then bifurcates into two holes, each ending in the hole containing optical guide. Upon testing, the new probe showed a cooling effect significantly less than that with the old collection probe. With the modified device, the isothermality of the reactor can be controlled within $\pm 20^{\circ}\text{C}$ as opposed to $\pm 50^{\circ}\text{C}$ with the old probe. Figure 4 shows the temperature profile of the reactor at a nominal reactor temperature of 930°C , with the new and the old collection probes, positioned at 15.2 cm from the entrance region.

D. Particle Collection/Classification System

A cascade cyclone sampler made by Graseby Andersen was purchased in the second quarter of this year. Both the cascade impactor or the cascade cyclone sampler

Figure 3: Schematic of the modified collection probe assembly.

Figure 4: Temperature profile of the reactor with the old and new collection probe.

(cyclade) are capable of classifying the particles in various size fractions. For studies investigating sorbent agglomeration during transport, the cascade impactor was used, since it was capable of classifying the powder in more size fractions. Moreover, using a cascade impactor makes it possible to measure the amount of the individual size fraction more accurately. However, for kinetic studies, cascade impactor has limitations due to its low powder loading capacity at each stage. As high amount of reacted solid is required for subsequent analytical procedures, the cascade cyclone sampler is employed for its higher capacity. Figure 5 shows the schematic of the cascade cyclone sampler used in this study. The particle size distribution data is useful for investigating the particle size effect on reactivity. During sulfation experiments, the collection system is kept heated to about 350°C to avoid any H₂SO₄ acid mist condensation on the solid sample. A high temperature ball valve, placed in between the collection probe outlet and the particle collection device helps in collecting the sample without a need to close off reactant gas flow into the reactor. Instead, all the gas stream is diverted towards the bulk outlet of the reactor, where it again passes through a cyclone and a filter assembly to separate particles before being vented out through a master exhaust system. An Edwards 2-stage vacuum pump, at the end of the sampling system facilitates particle collection in the collection probe. Moreover, monitoring the collection probe outlet is essential in order to determine the average size at each stage of the cascade sampler.

E. Post-reaction Analyses

The bulk gas is introduced into the annular region of the high-temperature reactor shown in Figure 1 where it is preheated to the reaction temperature. During calcination experiments, bulk gas constitutes only nitrogen, whereas, during sulfation runs, an

Figure 5: Schematic of the typical individual cyclone in the Anderson cyclade.

air/SO₂ mixture is introduced as reactant gas. This air/SO₂ mixture can be diluted with dry N₂ to change SO₂ conc. in the reactant gas. Due to jet impaction at the reactor entrance block, the injected particle stream from the top rapidly mixes with the gas stream and is instantaneously heated to reaction temperature. After a desired residence time, the partially reacted mixture is sampled by the collection probe, immediately quenched and passed through the particle separation system. The residence time of the particles in the reactor is estimated on-line from the fiber optics system located at the tip of the injection and the collection probes. The residence times can be varied by varying the gas flow rate and/or by moving the collection probe axially.

The particle collection system has already been discussed in detail in the last section. Conducting the experiments at a specific particle residence time, enough sample is collected for subsequent kinetic analysis. For calcination studies, the collected sample is calcined to 100% conversion in a TGA, and the back calculation gives us the degree of calcination achieved within the entrained flow reactor. For sulfation runs, the sampled sorbents are tested for sulfate ion content (Ion Chromatography). The extent of conversion and amount of sulfur capture for a particular reaction temperature can be estimated from this. Using the cascade cyclone sampler for each experimental condition gives us the in-situ particle size distribution, and hence the effect of particle size on reaction kinetics is studied.

III. CALCINATION & SINTERING

Simultaneous calcination and sintering studies were conducted with calcium hydroxide as the calcium-based sorbent. The sorbent was supplied by Linwood Mining and Minerals Corporation. For the calcination runs, as-received sorbent powder was used for kinetic studies. The hydroxide sorbent powder contains 94 % $\text{Ca}(\text{OH})_2$.

A. Experimental

Calcination runs were performed at three different temperatures of 950 (1223 K), 1,050 (1323 K), and 1,115°C (1388 K), and for a variety of residence times, ranging from as low as 10 ms to 500 ms. Effort was made to obtain kinetic data for at least three residence times below 100 ms for each of the temperature. Partially reacted samples were collected in various size fractions in the cascade cyclone sampler. For a particular residence time, the run was terminated only after enough sample was collected for subsequent analytical tests. Extent of calcination in the reactor was measured by allowing complete calcination of the sample in a TGA (Thermogravimetric Analyzer), and noting the amount of further weight loss. Surface area and porosity measurements were carried out by low-temperature nitrogen adsorption in a BET apparatus. Conversion measurements were performed for all the size fractions of the reacted samples.

The high-temperature reactor was kept under nitrogen environment during calcination runs. All the gas flows were monitored with calibrated rotameters. The flowrates (at STP) for the various gas streams were set as follows: bulk N_2 at 10 lpm, injection probe purge at 0.9 lpm, collection probe purge at 2.4 lpm, and feeder flow at

1.6 lpm. A higher value of purge flow was chosen for the collection probe in order to rapidly quench the decomposition reaction.

B. Results & Discussions

B.1 Effect of temperature on Ca(OH)_2 decomposition:

Figure 6 shows the plot of percent decomposition of hydroxide powder against particle residence time for three different temperatures of 950 (1223 K), 1050 (1323 K), and 1115°C (1388 K). Average aerodynamic diameter of the hydroxide powder is 3.6 μm , which is measured in-situ in the solid sampling line. For all the three temperatures, a similar pattern in the calcination curves is observed. In the first 25 to 30 milliseconds of the reaction time, the decomposition curves rise very sharply and exhibit a strong influence of temperature. However, after about 30 milliseconds, the reaction rates slow down considerably. The near-parallel nature of the curves at these longer times clearly show a diminished effect of temperature.

The drastic change observed in the decomposition rate after about 30 milliseconds probably indicates a shift in the reaction controlling regime. During the initial stage of the reaction, instantaneous surface reaction may be the rate limiting step. Such view can be supported by the fact that the conversion exhibits a strong temperature dependence in the early stages of calcination. In this initial time period, most of the hydroxide on the particle surface and close to the particle surface is consumed. As the CaO-Ca(OH)_2 interface moves further inside the particle, diffusion of H_2O from the particle interior through the CaO pores becomes more and more prominent in limiting the reaction rate. As a result, the reaction switches to pore diffusion control regime at the later reaction times. Near-parallel nature of the conversion curves for various temperatures clearly

Figure 6: Effect of temperature on the calcination of $3.6 \mu\text{m Ca(OH)}_2$.

show a low activation energy for the rate determining mechanism, which is typical of a gas diffusional process.

The decomposition rates of Ca(OH)_2 observed in these calcination studies are somewhat slower than the calcination rates observed by Bortz and Flament [1985], who reported a 70 to 75% conversion in the first 50 milliseconds for a temperature range of 700-1100°C. However, like all of the previous researchers, they estimated the particle residence time from an assumed velocity flow profile. Such an assumption ignores the entrance effect at the reactor inlet, i.e., the sorbent/gas mixing zone, and most likely underestimates the residence time to a great extent. Substantial conversion observed within the first 10 milliseconds in this study suggests no limitation of the reaction by external heat transfer resistances, indicating an adequate and rapid mixing at the solid injection point. Further comparison between these results and that of Bortz and Flament [1985] shows that in the initial chemical reaction controlling regime which lasts for only 25 to 30 milliseconds, a higher conversion is obtained in the latter study. For example, at comparable temperatures of 1100-1115°C (1373-1388 K), about 58% decomposition is achieved in this work before the initiation of the second regime; on contrary, Bortz and Flament [1985] observed a 70% decomposition in about the same time period before the intraparticle gaseous diffusion becomes rate controlling. The calcination rates obtained by Mai and Edgar [1989] are lower than the rates reported here. However, those researchers observed a heat-up time lag in their calcination experiments, which is most likely responsible for such low decomposition rates. Calcination data of Roman et al. [1985] agree quite well with the results of this study. Although, no data below 200 ms was reported by Roman et al. [1985], conversion obtained in their study beyond 200 ms is consistently within 5% of the results shown in Figure 6.

B.2 Effect of particle size on conversion:

Figure 7 shows the effect of particle size on Ca(OH)_2 calcination at 1050°C (1323 K). For two different particle sizes of 3.6 and 2 μm (mean aerodynamic diameter), no effect of particle size is noticed. These results probably suggest two primary aspects of the calcination phenomenon. Firstly, for very small particles, no diffusional resistance is significant in the initial stages of the reaction. In this initial period, surface reaction is very rapid and is the main contributing factor to the overall particle conversion. However, if intraparticle gaseous diffusion is significant in the later stages of the reaction, then an influence of particle size is expected. Lack of such effect probably indicates a very high thiele modulus for both the particles, when thiele modulus, ϕ , can be expressed as:

$$\phi = r/3\sqrt{K_v/D_e} \dots\dots(12)$$

where, r = particle radius

K_v = reaction rate constant

D_e = effective diffusivity

If the ratio of K_v to D_e is very high, then ϕ for both the particles will be quite large. For such a high value of ϕ , the effect of particle size, even though existing, will not be very prominent in terms of solid conversion.

Effect of particle size on hydrate calcination at a temperature of 1115°C is shown in Figure 8. Particle sizes are 0.7 μm , 3.6 μm , and greater than 7.2 μm . As observed in the case of 1050°C (1323 K), there seems to be no size effect for the smallest particles. However, for the largest size group, the effect of particle size is quite

Figure 7: Effect of particle size on calcination of $\text{Ca}(\text{OH})_2$ at 1050°C .

Figure 8: Effect of particle size on calcination of $\text{Ca}(\text{OH})_2$ at 1115°C .

pronounced from the very onset of the reaction. This can be explained by the fact that even though substantial hydroxide conversion takes place on and near the particle surface in the initial stage of the reaction, this accounts for a relatively smaller fraction of the whole particle, compared to the particles of smaller sizes. In the latter stages of the reaction, when the intraparticle mass transfer becomes more important, the size effect of the largest size group becomes more visible. In other words, for the largest size group, intraparticle gas diffusion becomes a significant resistance from the very beginning, and as a result, the conversion curve rises somewhat monotonously clouding the phenomenon of shifting controlling regime. In addition, this size group may contain very big particles, which are large enough to experience internal heat transfer resistance.

B.3 Surface area evolution:

Surface area evolution of the sorbent during decomposition reaction depends on the two opposing phenomena of calcination and sintering. Calcination causes the development of a highly porous sorbent possessing a high surface area, whereas, the latter induces the agglomeration of individual grains, thus reducing the surface area. Figure 9 shows the evolution of surface area during calcination of $\text{Ca}(\text{OH})_2$ at three different calcination temperatures. For only one temperature, i.e., at 950°C (1223 K), the surface area of the partially decomposed sorbent exceeds the initial surface area of the hydroxide powder at some point of the calcination reaction. However, this higher surface area rapidly decreases due to sintering and the surface area eventually levels off to an asymptotic value of about $15 \text{ m}^2/\text{gm}$. Contrary to 950°C (1223 K), for the higher temperatures, effect of sintering is extremely pronounced from the very beginning of the decomposition process and the surface area at no point of time exceeds the initial surface

Figure 9: Evolution of BET surface area during calcination of Ca(OH)_2 .

area of 16.9 m²/gm. For 1050°C, the surface area attains the asymptotic value of about 10 m²/gm, where as, for 1115°C, an asymptotic value of 8 m²/gm is obtained. Figure 10 shows the calcination and surface area curves for 1115°C in the same plot for comparison. The surface areas for various temperatures reported here are significantly lower than most of the data available in the literature [Borgwardt et al., 1989; Mai and Edgar 1989]. Results of Mai and Edgar [1989] show that after 1 sec. of calcination at 1000°C, when Ca(OH)₂ decomposition is 90% completed, the evolved surface area reaches a value as high as 32 m²/gm. Borgwardt's [1989] data also showed much higher surface area of resulting CaO than what is observed in this study. However, the results of Roman et al. [1985] agree quite closely with these results. For calcination experiments at 1100°C, they observed a final surface area of 10 m²/gm, which compares well with 8 m²/gm for 1115°C, observed in this study.

The discrepancy between these results and the available data in literature clearly demonstrates a greater effect of sintering encountered in this study. A possible explanation can be that probably in the earlier studies, external heat transfer resistance was significant due to poor sorbent/gas mixing. Moreover, for particles of larger sizes, there was considerable heat transfer resistance across the particle. As a result, sintering slowed down considerably, but calcination progressed at reasonably high rate. The above argument gains further credibility if the surface area evolution curves for smaller and larger particles are compared. Figure 11 shows the surface area evolution of 2 μm and greater than 7.2 μm particles. The larger size group possibly contains some very big particles, with high internal heat transfer resistance. It is probable that the inner core of these particles never experiences the high temperature at which the calcination is being studied. As a result, this size group sinters less and always shows a higher surface area.

Figure 10: Comparison between calcination and surface area for $\text{Ca}(\text{OH})_2$ at 1115° C.

Figure 11: Surface area evolution as a function of particle size for calcination of $\text{Ca}(\text{OH})_2$ at 1115°C .

IV. SULFATION

A. Experimental

Sulfation experiments were conducted with both pre- calcined CaO and raw Ca(OH)₂ powder. The hydroxide powder was provided by the Linwood Mining & Minerals Corporation. The first sample of CaO was prepared by calcining hydroxide powder in batches at a temperature of 1150°C (1423 K), and then sintering for 45 minutes at the same temperature under N₂ flow. The second calcined sample was made by calcining at 1050°C (1323 K), and sintering for 1 hour. The calcination was performed in several batches by putting about 5-10 g of sample in each batch in a 2.54 cm OD stainless steel tube as a fixed bed, supported on glass wool. The calcination tube was inserted into the high-temperature reactor from the bottom in place of the collection probe. Figure 12 shows a schematic diagram of the batch calcination process. A continuous flow of dry N₂ is heated to the calcination temperature by passing it through the annular space between the outer and the inner ceramic tubes, which in turn passes through the powder bed during calcination process. A thermocouple inserted through the injection probe monitors the temperature of the bed during calcination. After calcining and sintering for a specified time period, the 2.54 cm tube is withdrawn from the reactor, and the powder is immediately transferred to a glass bottle. The glass bottle is stored in a desiccator to avoid any moisture uptake by the highly hygroscopic CaO. Sufficient calcined sample was obtained by repeating the calcination process several times.

The calcined sample was tested in the thermogravimetric analyzer (TGA) to check whether complete decomposition of the hydrate powder was achieved by batch calcination. For both the samples, the sorbent exhibited no further calcination in the TGA, indicating 100% calcination in the batch process. However, the calcined powder

Figure 12: Schematic of the batch calcination set-up.

was seen to be highly agglomerated upon its withdrawal from the batch reactor. These agglomerates were first crushed and then screened through a 38 μm sieve to produce finer calcines. Surface areas of both the calcined samples were measured in the BET apparatus. The first sample was found to have a surface area of 3.9 m^2/gm , compared to the 8.5 m^2/gm for the second sample.

Sulfation runs with the first type of CaO powder (surface area = 3.9 m^2/gm) were performed at three different temperatures, namely 950 (1223 K), 1,035 (1323 K), and 1,115°C (1388 K), to investigate the effect of temperature on sulfation rate. Sulfation of the second batch of CaO, possessing high surface area, was also carried out at 1035°C (1308 K). A comparison of the sulfation rates between two different types of CaO indicates the effect of surface area on CaO/SO₂ reaction. Sulfation experiments with the pre-calcined and pre-sintered sorbents make it possible to isolate the sulfation phenomenon from calcination and sintering, and allow us to study the reaction independently. On the other hand, sulfation of raw calcium hydroxide represents all the simultaneously occurring mechanisms, which is typical for furnace sorbent injection process. Sulfation experiments with Ca(OH)₂ were conducted at two different temperatures (1,035, and 1,115°C) to investigate the temperature effect on the overall sorbent/SO₂ interaction phenomena. Role of particle size on sorbent conversion was also examined by measuring the conversion of various size fractions. Similar to calcination studies, emphasis was put on acquiring kinetic data for at least three residence times less than 100 ms. The overall time scale of residence time ranged from less than 10 ms to 300 ms. The cascade cyclone sampler was kept at a temperature of about 330°C during sulfation experiments. This was done as a precaution against acid mist condensation.

For all the sulfation runs, the reactant gas consisted of 5.5 % O₂, 3900 ppm SO₂,

and balance N_2 . The flowrates (at STP) for the various gas streams were set as follows: bulk N_2 at 6.7 lpm, air/ SO_2 mixture (1.5% SO_2) at 3.3 lpm, injection probe purge at 0.9 lpm, collection probe purge at 2.4 lpm, and feeder flow at 1.9 lpm.

The extent of sulfation reaction was determined by measuring concentration of SO_4^{2-} ion in a known amount of sample by ion chromatography technique. An Alltech 320 conductivity detector was used for this purpose. For partially reacted $Ca(OH)_2$ particles, which contain $Ca(OH)_2$, CaO , and $CaSO_4$ compounds, a TGA test was performed to determine the unreacted hydroxide fraction of the sample. The extent of sulfation was then obtained from a combination of both TGA and ion chromatography results.

B. Operational sequence for the experimental runs

Figure 13 shows the schematic of all the gas flows during calcination or sulfation runs. For the calcination runs, SO_2 /air or air flows are not required. Once the reactor is heated to the reaction temperature and the collection probe is positioned at a particular location, the probe purge flows, feeder flow through the bypass, and the N_2 flow for the bulk inlet are adjusted to the required values. The vacuum pump at the end of the sampling line is then started and the bulk outlet line is closed. With all the flows now maintained at reaction conditions, minor adjustments in the furnace temperatures are carried out to achieve an uniform temperature throughout the reaction zone. Once a satisfactory temperature profile is attained, the feeder flow is slowly switched from bypass to the feeder, and the actual experimental run begins. After sufficient sample is collected in the cascade cyclone sampler, the experimental run is terminated by switching the feeder flow back to the bypass line. The cyclone assembly is put back after

Figure 13: Schematic of the flows in and out of the reactor system.

collecting the sample and residence time measurements are performed. During residence time measurements, the feeder N_2 continuously flows through the bypass. Elaborate discussion on residence time measurements are given in the second year final report of this project.

The operational sequence for the sulfation experiments is somewhat different from the calcination runs. In case of sulfation, a stream of SO_2 /air mixture (1.5% SO_2) is blended with bulk N_2 to achieve a specific SO_2 concentration in the reactor. The SO_2 line, which can be switched between the air/ SO_2 cylinder and a pure air cylinder, is put to the pure air line during flow and temperature adjustments. Once the reactor set up is ready for initiating the experimental run, the SO_2 valve is switched to air/ SO_2 cylinder. After some time, when the gas concentration equilibrates inside the reactor, the feeder flow is switched from the bypass to the feeder, and the experimental run begins. Total time required for a typical sulfation run varies between 30 to 45 minutes.

An added concern during sulfation run is the condensation of H_2SO_4 acid mist in the collection system and on the reacted sorbent sample. Though the formation of acid, if any, is in trace quantities, necessary precaution should be taken to prevent any contamination of the sample by acid condensation. In view of this, the cascade cyclone sampler is kept heated by a heating mantle to about $330^\circ C$. The power input to the heating mantle is controlled by a variac, and thus the cyclone temperature is controlled.

C. Results & Discussions

C.1 Effect of temperature on the sulfation of CaO :

This effect is shown in Figure 14. Average aerodynamic particle size of the sorbent is $3.9 \mu m$ with an initial surface area of $3.9 m^2/gm$. As the sorbent applied in

Figure 14: Effect of temperature on the sulfation of precalcined and presintered h-CaO, $3.9 \mu\text{m}$ mean aerodynamic size and $3.9 \text{ m}^2/\text{g}$ surface area.

this sulfation study is pre-calcined and pre-sintered, the results show the effect of independent sulfation reaction without any other simultaneously occurring processes. For all the temperatures, the conversion curves follow a similar pattern. The sulfation progresses very rapidly in the first 30 to 35 milliseconds of the reaction. After this initial period, the sulfation rate experiences a dramatic drop. However, a strong temperature dependence of the reaction can be noticed for both the initial and later stages of the sulfation process.

The drastic drop in sulfation rate after the initial period can be best explained by a shifting controlling regime theory. At the beginning of the sulfation process, the reaction is probably controlled by a surface reaction mechanism. As the reaction product CaSO_4 rapidly covers the available CaO surface, product layer diffusion eventually becomes the rate determining step. A strong temperature dependence observed at these later reaction times supports the past theory that an ionic diffusion through the product layer is the rate controlling mechanism rather than a gaseous diffusion process [Borgwardt et al., 1987; Milne et al., 1990]. If the gaseous diffusion were rate limiting, then the dependence on temperature would be less pronounced than what is observed in the reported data. Typical activation energy for a gaseous diffusion controlling reaction is around 5 kcal/mole; but calculations with these results show an activation energy as high as 32 kcal/mole, which is typical of an ionic diffusion mechanism.

Availability of the low residence time sulfation data for the first time in this field of research helps gain a further insight into the sulfation mechanism. Most of the earlier researchers [Borgwardt and Bruce, 1986; Borgwardt et al., 1987; Milne and Pershing, 1987] suggested that ionic diffusion through the product layer becomes rate controlling from the very onset of the sulfation process. Such a mechanism was accepted for the

modeling purpose even though at the early stages of the reaction, product layer is either non-existent or not thick enough to offer substantial diffusional resistance. The reason for ignoring initial surface reaction was most probably due to the lack of experimental data below 30 milliseconds. On the contrary, this study shows multiple data points below 30 milliseconds, which clearly indicate the existence of a much faster rate controlling regime in the initial times. Moreover, the experimental data obtained in the time scale greater than 50 ms distinctly show the takeover of another controlling mechanism at later times.

C.2 Effect of initial surface area on CaO sulfation:

Figure 15 shows the effect of initial CaO surface area on the sulfation reaction at a temperature of 1035°C (1308 K). The CaO samples have been sintered long enough prior to the reaction study to eliminate the possibility of any further sintering in the reactor. It can be seen from the conversion plot that the sample with higher surface area (8.5 m²/gm) reacts faster than the low surface area (3.9 m²/gm) CaO over the entire time period studied. Moreover, the difference in conversion between the two samples is enhanced with the increasing reaction times. In other words, the effect of initial surface area is more pronounced in the later reaction times when product-layer-diffusion is expected to be the controlling mechanism. Such a phenomenon can be explained by either a simple grain model [Borgwardt and Bruce, 1986] or by a random pore model [Bhatia and Perlmutter, 1981, 1983]. For both the models, the reaction rate is proportional to the sorbent BET surface area when the surface reaction is rate controlling, whereas, for product-layer-diffusion control the rate becomes proportional to the square of the initial surface area. The widening gap between the two conversion

Figure 15: Effect of the initial surface area on the sulfation of h-CaO at 1035° C.

curves clearly exhibits a higher sensitivity on surface area, thus supporting the theory of product-layer-controlling regime.

C.3 Effect of temperature on $\text{Ca}(\text{OH})_2$ sulfation:

The results of temperature effect on sulfation of $\text{Ca}(\text{OH})_2$ are shown in Figure 16. The conversion curves here show a combined effect of all the three simultaneously occurring processes, calcination, sintering, and sulfation. Such a situation closely resembles the furnace sorbent injection conditions. The results clearly show a distinct influence of temperature on sorbent conversion from the very outset of the sulfation reaction. Experimental data for reaction time as low as 6-10 ms show a 16% sorbent conversion at 1035°C (1308 K), whereas, for 1115°C (1388 K), the conversion reaches to about 18%. Over the entire reaction time period (to about 250 ms) studied, sorbent utilization at the higher temperature is always greater than that for the lower temperature. In 0.25 s, a sorbent conversion of 23% is achieved for 1035°C (1308 K), which compares to a conversion of 26% at 1115°C (1388 K).

The short-time sulfation data reported in this study are first of its kind in the time scale of less than 30 ms. However, a comparison can be made with the available literature data for reaction times greater than 30 ms. Milne et al.[1990] reported sulfation data for 2.5 μm raw Linwood hydrates for temperatures of 990 (1263 K), 1095 (1368 K), and 1175°C (1448 K) and a Ca to S ratio of 2. For a comparable temperature of 1095°C (1368 K), they observed 15% conversion in first 40 ms of the reaction, which compares to a 18% conversion reported here in 11 ms at 1115°C (1388 K). Gullett et al. [1988], working with the same powder and a reaction condition differential with respect to SO_2 , obtained a 16% conversion in 50 ms for a temperature of 1000°C (1273

Figure 16: Effect of temperature on the sulfation of $3.9 \mu\text{m Ca(OH)}_2$.

K). However, for longer reaction times of 200-300 ms, the conversion reported in these past studies are in fair agreement with the results shown here.

C.4 Effect of particle size on Ca(OH)_2 sulfation:

The particle size effect during Ca(OH)_2 sulfation is presented in Figure 17. The reaction temperature is 1115°C (1388 K), and the particles are classified into four size groups of 1.2, 3.9, 4.9, and greater than $9\text{ }\mu\text{m}$ according to their mean aerodynamic diameters. Figure 18 compares the conversion of two particle sizes (1.2 and $3.9\text{ }\mu\text{m}$) for sulfation at 1035°C (1308 K). It can be seen from the figures that for the three low particle sizes, effect of particle size on sorbent conversion is almost non-existent. These results agree with the findings by several researchers [Milne and Pershing, 1987; Cole et al., 1986] that below $2\text{-}5\text{ }\mu\text{m}$, sulfation is no longer influenced by particle size. Elimination of pore diffusional resistances below a certain size has been cited as the possible reason. However, this finding is contrary to the observation by Gullett and Blom [1987], who reported no limit to this particle size effect upon higher reactivity and observed constant effect of size over the range of $0.72\text{ to }12.1\text{ }\mu\text{m}$.

Figure 17: Effect of particle size on sulfation of $\text{Ca}(\text{OH})_2$ at 1115°C .

Figure 18: Effect of particle size on sulfation of $\text{Ca}(\text{OH})_2$ at 1035°C .

V. MODIFIED SORBENT WORK

In the last quarter of this year, work was commenced on studying modified sorbents for their enhanced sulfur capturability. The additive modified sorbent being studied in this project is lignosulfonate-modified calcium hydroxide. Details of the sorbent preparation are discussed in the next section. Sulfation experiments were also carried out with the modified sorbent to compare the kinetics of capture with the unmodified sorbent and preliminary results obtained are discussed.

A. Modified Sorbent Preparation

The parent material used was calcium oxide supplied by the Linwood Mining & Minerals Corporation. The original lime was in the form of pebbles and was crushed and screened to - 38 μm size. The parent lime contains 94% CaO .

The additive chosen is calcium lignosulfonate which was obtained from Pfaltz Bauer Inc., as a dry powder. The material is a anionic surfactant and is extensively discussed by Grayson [1983].

The pulverized calcium oxide powder is loaded in a blending vessel. The lignosulfonate is dissolved in the hydration water in a separate beaker by using a ultrasonic bath. Water is used in a 4:1 molar ratio with respect to the original calcium oxide. The amount of lignosulfonate used is sufficient to make the final $\text{Ca}(\text{OH})_2$ product contain 1.5% lignosulfonate on a mass basis. Kirchgessner and Lorrain [1987] have shown that about 1.5 % lignosulfonate concentration leads to maximum calcium utilization increase. The hydration was conducted by adding this lignosulfonate solution to the calcium oxide at a constant rate using a syringe. The blending vessel is kept

immersed in a water bath in order to absorb the exothermic heat of the hydration reaction. The hydration vessel is then kept in a vacuum oven overnight at about 100° C to purge it of the excess water, leaving a dry product. The product is finally crushed and sieved to -38 μ m before being used for sulfation experiments.

B. Sulfation with lignosulfonate-modified $\text{Ca}(\text{OH})_2$

The experimental procedure and analysis is similar to that discussed in the sulfation section. Some preliminary results of the ongoing sulfation experiments are shown in Table 1. The table compares the conversion-time data for both the modified and the original hydroxide sorbent. Both the original Linwood $\text{Ca}(\text{OH})_2$ powder and the Linwood CaO powder (used to prepare modified $\text{Ca}(\text{OH})_2$) have very similar composition. Hence, the kinetic data can be compared to study the effect of the additive. More work is continuing on sulfation with modified sorbent and should shed more light on the kinetic phenomena and the mechanism itself.

Table 1: Comparison of preliminary sulfation data of ligno-modified $\text{Ca}(\text{OH})_2$ with $\text{Ca}(\text{OH})_2$.

$\text{Ca}(\text{OH})_2$ conversion msec conv	Modified $\text{Ca}(\text{OH})_2$ conversion msec conv.
13	16.9
19	17.5
	30
	13.2
	16.7

VI. CONCLUDING REMARKS

Some of the goals of this work accomplished so far can be explained as follows:

The simultaneous calcination and sintering of calcium hydroxide has been completely and thoroughly studied with some new findings and insights. The change in the controlling regime after about 30 ms of residence time has been demonstrated for the first time. This work has also shed more light on the overall surface area evolution. It has been shown that the surface area is not as high as was previously reported in the available literature. One possible explanation is that heat transfer resistance played an important role in the previous studies due to poor sorbent/gas mixing.

Sulfation has been studied, both in isolation and occurring simultaneously with calcination and sintering. Precalcined and presintered CaO derived from hydroxide has been used to study isolated sulfation for temperature effects and particle size and initial surface area effects. Again, the shifting of the controlling regime after about 30-35 ms is shown clearly for the first time. Initially, chemical reaction is the controlling regime with a high activation energy and the rate being proportional to the initial surface area. As the reaction proceeds and the product rapidly covers the available CaO surface, ionic diffusion through the product layer becomes the rate determining step. This is confirmed by the high activation energy and from the higher sensitivity to surface area at residence times above 30 ms.

Sulfation studies with Ca(OH)_2 show the combined effect of all the three simultaneously occurring processes, calcination, sintering and sulfation. The results show a distinct influence of temperature on sorbent conversion from the very onset of sulfation reaction. Particle size effect studies have confirmed that below a certain

minimum size of about 5 μm (aerodynamic diameter), size has no effect on conversion.

Currently, sulfation with lignosulfonate-modified calcium hydroxide is being studied and preliminary results have been presented here.

Work on modeling the shifting controlling regime observed in both calcination and sulfation studies is also simultaneously being carried out. Some preliminary calculations of activation energies etc have supported the rate limiting step observations. More modeling work has been planned for the fourth year.

Effect of gas phase conditions such as SO_2 concentration etc will also be studied in the fourth year. Finally, the ultimate objective of this entire initiative, a comprehensive understanding and modeling of the complex phenomena by putting together all the pieces of the puzzle, will follow in the coming year.

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