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KINETICS AND STRUCTURAL EVOLUTION OF SORBENTS AT HIGH
TEMPERATURES

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

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

Structural evolution studies during sulfation were carried out at 1353 K. The porosity shows a decreasing trend right from the start unlike calcination which shows a increasing porosity initially. In addition to sintering, which causes coalescence of smaller pores into larger ones, deposition of higher volume reaction product (CaSO₄) fills up the CaO pores and reduces the overall porosity. The pore size distribution curves for the partially sulfated sorbent lie below the parent hydrate curve and show the decreasing contribution of the smaller pore sizes and shifting of the entire distribution to the higher sizes.

Modified sorbent studies have yielded results leading to improved understanding

of the mechanism of promotion. Studies were conducted with lignosulfonate as the modifier at a concentration of 1.5 mass% at 1353 K. The modified hydrate possesses higher surface area (about 45 m²/g) as well as internal porosity (32%). Results indicate superior capturability in the initial 50 milliseconds, the extent of sulfation is about 30% more than that of the unmodified hydrate. At higher residence times, the rate of capture attenuates and becomes similar to that of the unmodified hydrate. The initial edge is preserved at the higher residence times studied. The porosity as well as surface area of the partially sulfated lignohydrate drop drastically in the first 50 milliseconds and become similar to that of the unmodified hydrate. The very high surface area leads to high sintering rates (since sintering has been shown to be proportional to the square of surface area) causing rapid reduction of surface area. Calcination and sintering studies will be carried out to probe into this phenomena and gain a better understanding.

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

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. STRUCTURAL EVOLUTION OF $\text{Ca}(\text{OH})_2$ SORBENT

A. Introduction:

Most of the previous efforts involving modeling of short-time sorbent/ SO_2 reaction suffered not only from inadequate ultrafast sorbent conversion data, but also from a lack of knowledge on how the internal structure of the sorbent changes with the simultaneous progression of three rapid mechanisms inside the coal-fired furnace. No experimental attempt was made until this study to explore the transient nature of all the sorbent physical characteristics, namely, surface area, porosity, average pore size, and pore size distribution. However, lack of these much needed information makes it practically impossible to have a clear understanding of the sorbent/ SO_2 interaction phenomena, especially when all the reaction processes greatly affect the resulting sorbent structure and these sorbent structural properties in turn influence the subsequent sulfur capture. Hence, in order to develop a sophisticated and comprehensive reaction model, the importance of short-time sorbent structural data can not be argued. In the 4th year of this project, sorbent structural evolution was the primary focus of the study. Rapid changes in sorbent surface area, porosity, and pore size distribution were investigated for both $\text{Ca}(\text{OH})_2$ calcination and sulfation experiments in the reaction time of 0 to 200 ms.

The internal surface area for $\text{Ca}(\text{OH})_2$ as well as h- CaO lies predominantly in pores of size 20 to 500 Å. Such pores are classified as mesopores and the physical adsorption isotherm exhibited by such mesoporous solids is classified as Type IV isotherm according to the BDDT classification. The exact shape of the pores of mesoporous solids can be cylindrical (tubular), parallel plate-shaped or spherical with narrow opening. Another characteristic feature of the mesoporous solids is the hysteresis loop obtained in the adsorption-desorption isotherm. The exact shape of the hysteresis

loop varies from one adsorption system to another and is determined by the shape of the associated pores. The hysteresis loop is classified into Types A, B and E (Gregg and Sing, 1982), and these are exhibited by cylindrical, parallel-plate and spherical with narrow opening type of pores respectively. Previous researchers have shown that h-CaO possesses a parallel plate pore structure, i. e., it exhibits a Type B hysteresis loop (Gullett and Bruce, 1987). A similar hysteresis diagram for calcium hydroxide is not available in the literature. Hence, the adsorption-desorption isotherm was constructed for Ca(OH)_2 using the B. E. T. apparatus and nitrogen adsorption. It was easily identifiable as a Type B hysteresis loop, indicating a parallel plate pore structure for Ca(OH)_2 . Hence, all the pore size distribution calculations for Ca(OH)_2 as well as h-CaO have been done using the parallel plate model.

B. Calcination and Sintering:

Structural evolution studies were conducted at two temperatures, 1273 K and 1353 K with Linwood Ca(OH)_2 in order to observe the surface area, porosity, pore volume and pore size distribution changes with calcination and sintering.

Figure 1 shows the sorbent surface area and extent of decomposition for the calcination experiment conducted at 1273 K. Both the conversion and evolved surface area data are in good agreement with the calcination results obtained in 3rd year's work. The surface area initially increases to $20 \text{ m}^2/\text{gm}$ at 49% conversion, but rapidly decreases due to rapidly occurring sintering.

Figure 2 shows the sorbent conversion with porosity data for the two temperatures studied. The porosity of the sorbent initially increases with conversion at both the temperatures, indicating that effect of sintering is less severe on porosity than surface

Figure 1: Evolution of surface area and extent of decomposition of $\text{Ca}(\text{OH})_2$ at 1273 K

Figure 2: Evolution of porosity with calcination of Linwood Ca(OH)₂ at two different temperatures.

area. Sintering causes grain coalescence or coalescence of smaller pores into larger pores. As most of the surface area resides in smaller pores, it is readily lost due to sintering. On the other hand, larger pores primarily contribute to the total sorbent porosity, and consequently, the effect of sintering on this sorbent property is less pronounced. In fact, any loss of porosity due to sintering is hidden by the evolving porosity due to further calcination, and the overall porosity increases with increasing sorbent decomposition. Further more, at the higher temperature of 1353 K, initially porosity rises faster and higher; but it also reduces faster at longer residence times. The total pore volume evolution in Figure 3 shows a similar trend. The pore volume remains almost constant at 1273 K, indicating that the pore volume being generated due to calcination is being compensated by its loss due to sintering.

The pore size distribution data shown in Figure 4 for 1273 K provides some further insight into the pore structure evolution phenomenon. The parent Ca(OH)_2 powder exhibits a peak in the pore size distribution at a pore size (plate separation) of 105 Å, and a substantial pore volume in a wide size range of 60 to 300 Å. As a result of calcination reaction, CaO is formed which undergoes rapid sintering to make larger pores. Some small peaks in the size range of 20-60 Å for these partially calcined sorbents probably point to the pores of nascent CaO. However, the pore size distribution clearly shifts to the right due to rapid sintering and a careful comparison of 79.5% and 82% calcined sorbent (not much difference in conversion) would indicate a shift to the larger pores with time, induced by sintering. This shifting of the entire distribution to the right is even clearly elucidated in Figure 5 for 1353 K. As can be observed, the peak pore size shifts appreciably from about 105 Å for parent to about 300 Å for the 91% calcined sorbent. The decreased contribution of the less than 100 Å pore sizes is also

Ca(OH)₂ Calcination: Pore Volume Evolution Influence of Temperature

Figure 3: Influence of temperature on evolution of pore volume with the decomposition of Linwood Ca(OH)₂.

Ca(OH)_2 Calcination: Pore Size Distribution

Temperature: 1273 K.

Figure 4: Pore size distribution of various partially calcined Linwood Ca(OH)_2 at 1273 K.

clearly apparent from comparison of the p.s.d curves in Figure 5.

C. Sulfation Studies:

Evolution of sorbent structural properties during $\text{Ca}(\text{OH})_2$ sulfation was investigated for a reaction temperature of 1353 K. Figure 6 shows the plot of sorbent surface area during sulfation along with the extent of solid conversion. The surface area evolution during calcination & sintering alone is also plotted versus time for the same temperature. As can be seen, the overall surface area decrease with increasing sorbent sulfation and lies below the calcination surface area curve. In this case, all the three mechanisms, namely, calcination, sintering, and sulfation progress simultaneously, and affect the resulting sorbent structural properties.

The porosity evolution with sulfation is shown in Figure 7 along with its evolution during calcination for comparison. Unlike calcination, the porosity decreases continuously from the beginning of sulfation. In addition to sintering, which causes coalescence of smaller pores into larger ones, deposition of higher volume reaction product (CaSO_4) fills up the CaO pores and reduces the overall porosity.

As the smaller pores get filled up faster, the overall pore size distribution shifts to the right much more rapidly than for only calcination reaction. This can be seen from Figure 8. As sulfation conversion increases from 13 to 19.5%, contribution of the pores smaller than 120 Å to the overall pore volume gradually decreases, and maximum volume contribution slowly shifts to the pores of size range between 300-400 Å. The p.s.d. curves of partially sulfated samples lie below the parent $\text{Ca}(\text{OH})_2$ curve.

Ca(OH)₂ Calcination: Pore Size Distribution
Temperature: 1353 K

Figure 5: Pore size distribution of various partially calcined Linwood Ca(OH)₂ at 1353 K.

Ca(OH)₂ Sulphation: Surface area development
Temperature: 1353 K.

Figure 6: Evolution of surface area during sulfation of Ca(OH)₂ at 1353 K.

Ca(OH)₂ Sulphation: Porosity Evolution
Temperature: 1353 K.

Figure 7: Porosity evolution during sulfation of Ca(OH)₂ at 1353 K

Ca(OH)₂ Sulfation: Pore size distribution
Temperature: 1353 K.

Figure 8: Change in Pore Size distribution during sulfation of Ca(OH)₂ at 1353K

III. Modified Sorbent

A. Introduction:

Limited literature results on lignosulfonate modified sorbents indicate that final concentration of lignosulfonate in the modified sorbent is an important parameter in its ability for sulfur capture. In this work, modified hydroxide sorbents have been prepared with varying lignosulfonate conc., from 0.5 to 2%. The modified sorbents have been made by calcining Ca(OH)_2 at 600°C , and then mixing specific amount of lignosite (calcium lignosulfonate) in a known amount of calcined powder and then adding excess water. The slurry was dried overnight in a box furnace at 60°C , which yielded a dried cake of modified sorbent with specific lignosulfonate concentration. The sorbent was then ground and sieved; and particles of less than $38\ \mu\text{m}$ were used for reaction studies.

The 1.5% ligno hydrate was completely characterized and compared with the parent Ca(OH)_2 . Figure 9 shows the p.s.d plot comparison between pure and lignosulfonate (1.5%) modified hydroxide. It can be seen that modified sorbent has much higher pore volume than the pure hydroxide. Furthermore, the surface area of modified sorbent is about $45\ \text{m}^2/\text{gm}$, as opposed to $16.9\ \text{m}^2/\text{gm}$ of that of pure sorbent. Also, the modified hydrate possesses a overall porosity of 32% as compared to the 14% porosity for parent hydrate. In addition to internal structural characteristics, the primary particle size analysis was performed with the modified and the parent Ca(OH)_2 . Figure 10 shows the cumulative particle size distribution curves obtained from Sedigraph analysis. As can be seen, the median primary particle size (at 50% mass finer) of the modified hydrate is about $1.2\ \mu\text{m}$ as compared to almost $2\ \mu\text{m}$ for the parent hydrate.

B. Results & Discussion:

Kinetic and structural evolution studies were then performed with the 1.5% lignohydrate at 1353 K. Figure 11 shows the sulfation versus time plots for the modified as well as the parent hydrate. The lignohydrate shows superior performance in the initial 50 milliseconds, at higher residence times however, the rate of sulfur capture attenuates considerably. The conversion profiles of both the hydrates become parallel to each other at higher times, with the lignohydrate maintaining the initial edge achieved in the first 30 milliseconds. In order to understand and explain this

Pure & 1.5% ligno- $\text{Ca}(\text{OH})_2$
Comparison of initial p.s.d.

Figure 9: Comparison between Pore Size distribution of pure and 1.5% Lignosulfonate modified $\text{Ca}(\text{OH})_2$.

**Cumulative Particle Size Distribution
for pure $\text{Ca}(\text{OH})_2$**

**Cumulative Particle Size Distribution
for 1.5% Ligno-modified $\text{Ca}(\text{OH})_2$**

Figure 10: Comparison between Particle size distribution of pure and 1.5% Lignosulfonate modified $\text{Ca}(\text{OH})_2$.

Pure & 1.5% ligno- $\text{Ca}(\text{OH})_2$ Sulfation

Comparison of extent of sulfation

Temperature: 1353 K, size: 3.9 μm

Figure 11: Comparison between extent of sulfation of pure and 1.5% Lignosulfonate modified $\text{Ca}(\text{OH})_2$ at 1353 K.

characteristic behavior, the internal structure evolution of the partially sulfated lignohydrate was also conducted. Figure 12 shows the comparison of porosity development and extent of sulfation between the two hydrates. The lignohydrate initially possesses about 32% porosity which is rapidly lost within the first 30 milliseconds to approach very close to that of the unmodified hydrate. Thus, the lignohydrate does not seem to hold any advantage over the unmodified hydrate (with respect to internal porosity) beyond about 50 ms. Further insight can be obtained into this phenomena by studying the pore size distribution behavior with sulfation as shown in Figure 13. As seen, the p.s.d. curves of the partially sulfated samples lie much below the initial lignohydrate and the peak can be seen to shift towards the right indicating closure of smaller pores.

Pure & 1.5% ligno- Ca(OH)_2 Sulfation:
Comparison of porosity development
Temperature: 1353 K.

Figure 12: Comparison between porosity development and extent of sulfation of pure and 1.5% Lignosulfonate modified Ca(OH)_2 at 1353 K.

1.5% ligno- $\text{Ca}(\text{OH})_2$ sulfation: Pore size distribution

Figure 13: Pore size distribution of partially sulfated 1.5% Lignosulfonate modified $\text{Ca}(\text{OH})_2$.

IV. MODELING WORK

A. Model Development for Simultaneous Calcination & Sintering:

The mathematical model developed here describes the kinetics and surface area evolution during simultaneous calcination and sintering of very small diameter Ca(OH)_2 particles. The overall concept of the model is illustrated in Figure 14. A single Ca(OH)_2 particle is assumed to be composed of identical, spherical, non-overlapping grains. Calcination takes place on a single grain of Ca(OH)_2 according to the sharp interface model. As hydroxide decomposes, smaller grains of CaO are formed surrounding the unreacted Ca(OH)_2 core, and the H_2O diffuses out through the product CaO layer. The CaO micrograins sinter rapidly, reducing the internal surface area and porosity of the product layer.

The overall reaction progresses according to the following steps: decomposition of Ca(OH)_2 at the CaO/Ca(OH)_2 interface, diffusion of the product gas H_2O through the product shell to the grain surface, and diffusion of H_2O through the inter-grain voids to the bulk gas phase. For small diameter Ca(OH)_2 particles, intraparticle mass and heat transport are not considered to be rate limiting (Beruto and Searcy, 1974). All the grains can be considered to be at same conditions of temperature and gas concentration, and H_2O diffusion from the grain surface to the bulk gas is assumed to experience negligible resistance. On the other hand, the product CaO layer offers resistance to the H_2O transport.

The product shell is composed of CaO grains of varying ages with varying degrees of sintering, it can be described as a multilayered CaO shell, each layer corresponding to CaO of certain age. The most recently formed CaO layer, which surrounds the unreacted hydroxide core possesses the highest surface area and porosity.

Calcination Modeling

The decomposition reaction takes place at the $\text{Ca(OH)}_2/\text{CaO}$ interface and is assumed to be first order with respect to H_2O partial pressure at the hydroxide core surface (Silcox et al., 1989).

Figure 14: Schematic illustration of modified grain mode, (a) Single, spherical Ca(OH)_2 grain at time $t=0$; (b) Partially calcined grain with inner Ca(OH)_2 core and sintered CaO micrograins at time $t=t_i$.

$$R_{Ca(OH)_2} = k_c \frac{(P_e - P_i)}{RT} \quad (3)$$

From solid reactant balance, the calcination rate can be expressed in terms of conversion as:

$$\frac{dx}{dt} = \frac{3r_c^2 k_c (P_e - P_i)}{RT r_{go}^3 C_s} \quad (4)$$

where k_c is the calcination rate constant (in m/s) and C_s is the solid reactant conc. (in gmole/m³). The equilibrium decomposition partial pressure, P_e can be obtained as a function of temperature using standard thermochemical approach (Hartman and Martinovsky, 1992):

$$P_e = \exp (-0.023 \ln T - 0.001771 T - 46300 T^{-2} - 12997.48 T^{-1} + 18.202) \quad (5)$$

The species continuity equation for product gas H₂O diffusing through the product CaO assuming the pseudo-steady state approximation can be written as:

$$\frac{\delta^2 P}{\delta r^2} + \frac{2}{r} \frac{\delta P}{\delta r} = 0 \quad (6)$$

with the following boundary conditions.

$$-D_{eff} \frac{\delta P}{\delta r} \Big|_{r=r_c} = k_c (P_e - P_i) \quad (7)$$

The latter boundary condition assumes negligible bulk H₂O concentration.

Although several researchers have investigated the effect of CO₂ pressure on

$$P|_{r=r_i} = 0 \quad (8)$$

CaCO₃ decomposition kinetics (Darroudi and Searcy, 1981; Silcox et al., 1989) and the diffusion of gaseous CO₂ through the porous lime, similar studies on the effects of H₂O partial pressure and H₂O diffusion are non-existent. Both Knudsen and ordinary diffusion may be important at different stages of reaction. Hence, Knudsen and ordinary diffusion coefficients are estimated and the effective diffusivity is derived from the following equations:

$$D_{AB} = 8.938E-6 (T/273)^{1.5} P_i^{-1} \quad (9)$$

$$D_k = 0.013 \epsilon T^{0.5} S^{-1} \quad (10)$$

and,

$$D_{eff} = (D_k^{-1} + D_{AB}^{-1}) \epsilon^2 \quad (11)$$

S and ϵ are the surface area and porosity of the multilayered product shell. The most sintered CaO layer possesses the lowest surface area and porosity and determines the overall rate of diffusion through the entire product shell. Equation 11 approximates the value of calcine's tortuosity as ϵ^{-1} , (Smith, 1981)

Sintering Modeling

Most of the previous sintering models (Silcox et al., 1989; Mai and Edgar, 1989) have used second-order kinetics proposed by Nicholson (1965), in which rate of sintering is expressed as:

$$\frac{dS}{dt} = -k_s (S - S_a)^2 \quad (12)$$

where S_a is the asymptotic surface area of CaO at the specific sintering temperature, and k_s is the sintering rate constant (in m²/g-s).

The presence of H₂O accelerates the rate of sintering of CaO (Borgwardt et al.,

1986; Mai & Edgar, 1989). In order to account for enhanced sintering in presence of H_2O , the sintering rate constant is modified according to the following correlation proposed by Milne et al., (1990):

$$k_{sm} = k_s (1 + BP^m) \quad (13)$$

Based on their correlation, m and B are taken as 0.17 and 6 respectively.

According to the model, the CaO product shell is divided into multiple layers depending on the time interval in which they are formed. At the end of the i -th time interval, the CaO formed during j -th time interval will have a surface area,

$$S_{j,i+1} = S_a + \frac{1}{\frac{1}{S_o - S_a} + k_{sm}(t_{i+1} - t_j)} \quad (14)$$

where S_o is the surface area of the nascent CaO formed during j -th time interval.

The surface area of the entire product shell and the overall specific surface area of the partially calcined particle are calculated as:

$$S_{CaO} = \sum_{j=1}^{j=i} S_{j,i+1} z_j \quad (15)$$

$$S_s = (x)S_{CaO} + (1-x)S_{Ca(OH)_2} \quad (16)$$

where z_j is the fraction of CaO formed during j -th time interval. Experimental data obtained on surface area evolution reflect the combined surface area of both CaO formed and unreacted $Ca(OH)_2$ solid.

A host of previous studies have indicated a linear relationship between surface area and porosity in the low surface area-porosity range (Gullett and Bruce, 1987; Gullett and Blom, 1987; Bruce et al., 1987, Milne et al., 1990). In this work, it is assumed that $\Delta\epsilon$ is proportional to ΔS and ϵ approaches zero as CaO surface area approaches the asymptotic value. In such a case, the particle porosity results from intergrain voids

alone. The porosity of an individual layer of CaO is written as a function of its surface area as:

$$\epsilon = \epsilon_o \left(\frac{S - S_a}{S_o - S_a} \right) \quad (17)$$

where ϵ_o is the theoretical porosity of the nascent CaO.

The calcination rate equation (4) is coupled with the product H₂O continuity equation (6). The surface area, porosity and effective diffusivity are functions of the fractional conversion x . The core radius r_c is related to the solid conversion as:

$$r_c = r_{go} (1-x)^{1/3} \quad (18)$$

where the initial Ca(OH)₂ grain size is obtained from its BET surface area assuming uniform spheres:

$$r_{go} = \frac{3}{S_{Ca(OH)_2} \rho_{Ca(OH)_2}} \quad (19)$$

The instantaneous grain radius, r_g , decreases due to reaction and sintering causes a porosity reduction and accompanying shrinkage of the entire grain, and can be expressed as:

$$r_g = \left[r_c^3 + \frac{\rho_{Ca(OH)_2} (r_{go}^3 - r_c^3)}{\rho_{CaO} (1 - \epsilon_{eq})} \right]^{1/3} \quad (20)$$

where ϵ_{eq} is the average porosity of the entire CaO product shell.

The H₂O partial pressure profile in the product layer can be obtained analytically by solving the continuity equation (6) with the given boundary conditions. The H₂O partial pressure at the interface of the unreacted Ca(OH)₂/CaO can be expressed in terms of r_c , r_g and D_{eff} :

The calcination rate equation (4) is solved with the initial condition of $x=0$ at time $t=0$ using the 4th order Runge-Kutta integration scheme. This local conversion corresponds

$$P_i = -P_e \frac{\frac{k_c r_c^2}{D_{eff}} \left(\frac{1}{r_g} - \frac{1}{r_c} \right)}{1 - \frac{k_c r_c^2}{D_{eff}} \left(\frac{1}{r_g} - \frac{1}{r_c} \right)} \quad (21)$$

to the overall particle conversion. The S_s value obtained from the model represents the predicted surface area of the partially calcined particle. The reaction constant, k_c and the sintering constant, k_s represent the two specific rate parameters of the model.

B. Model Matching of Experimental Results:

Calcination of Linwood $\text{Ca}(\text{OH})_2$

Figure 15 shows the effect of temperature on calcination of $3.6 \mu\text{m}$ $\text{Ca}(\text{OH})_2$ for residence times ranging from 10 to 300 ms. For all the three temperatures, a similar trend is observed in the calcination behavior. In the initial period of about 50 milliseconds, calcination progresses extremely fast and exhibits a strong influence of temperature. However, at high residence times, the reaction rates attenuate considerably and conversion tends to flatten out.

Nearly 75% of the final extent of calcination is achieved within the first 50 ms at all the temperatures studied. At 1323 K, nearly 85% calcination is completed in this initial 50 ms, while at 1173 K, it is much less at about 45% in the same time period.

The sharp attenuation of reaction rate at higher residence times is seen clearly from the 1323 K data which exhibits virtual ceasing of calcination at about 90%. This near 'die-off' of the reaction at higher residence times is also observed at lower temperatures of 1173 & 1223 K.

The characteristic behavior of high initial rate followed by attenuation with virtual die-off at higher residence times is closely linked with the structural effects accompanying the reaction. In these high temperature studies, sintering holds the key to explaining and modeling these observed features.

The model discussed earlier assumes the reaction proceeds on a single $\text{Ca}(\text{OH})_2$ grain according to the shrinking core model. The strong influence of temperature during the initial stage of reaction and the high porosity of the nascent product layer suggest that chemical reaction at the $\text{CaO}/\text{Ca}(\text{OH})_2$ interface may be the rate limiting step. The

Figure 15: Effect of temperature on calcination of 3.6 μm Linwood $\text{Ca}(\text{OH})_2$. Experimental data and model predictions.

product CaO layer rapidly sinters losing surface area and porosity. This offers increasing resistance for the gaseous product H_2O to diffuse through the product shell. This leads to increasing H_2O concentration in the product layer and at the interface which not only enhances the rate of CaO sintering but also retards the calcination rate. All these phenomena eventually result in the overall calcination reaction being dominated by outward H_2O diffusion through the CaO.

Experimental data is used to establish values of the two parameters, the calcination rate constant, k_c , and the sintering rate constant, k_s . The initial surface area of the nascent CaO produced in the dispersed environment is taken to be $100 \text{ m}^2/\text{g}$ (Milne et al., 1990). The asymptotic CaO surface area is a function of the temperature of study, experimental data is utilized to estimate its value. S_a is estimated to be $15.5 \text{ m}^2/\text{g}$ at 1223 K and $13.5 \text{ m}^2/\text{g}$ at 1323 K. The rate constants are determined by trial and error procedure to obtain the best fit of the experimental data. A statistical sum of squares of error minimization is not attempted. The activation energies and the pre-exponential factors are then calculated from the Arrhenius-type plots.

The model fits the experimental data fairly well, both the initial steep slope and the rate attenuation match closely with the data. At 1173 K, the model underestimates the initial slope while at higher residence times, its prediction lies above the experimental data. The model fits the higher temperature data of 1323 K very well at both short time scales as well as at higher residence times.

Surface area evolution

The overall surface area evolution of the partially calcined $\text{Ca}(\text{OH})_2$ represents the net effect of the two opposing phenomena of calcination and sintering. Figure 16 shows the evolution of overall surface area at the three temperatures studied. For the two lower temperatures of 1173 K and 1223 K, calcination kinetics dominates over the sintering kinetics at short time scales, hence surface area of the partially decomposed $\text{Ca}(\text{OH})_2$ initially rises above the parent hydroxide surface area. The surface area goes through a maxima, then rapidly decreases due to sintering and tends to level off to an asymptotic value at higher residence times. On the other hand, at the higher temperature of 1323 K, the effect of sintering is more pronounced and the observed surface area decreases

Figure 16: Effect of temperature on surface area evolution during calcination of 3.6 μm Linwood $\text{Ca}(\text{OH})_2$. Experimental data and model predictions.

continuously toward the asymptotic value from the very beginning of the decomposition process. For 1323 K, the surface area attains a value of about 14.3 m²/g beyond about 250 ms.

The model predictions qualitatively agree well with the observed trends. At the two lower temperatures, the model predicts the initial rise in surface area and the maxima; the predicted maxima however occurs earlier is lower than the observed value for both the temperatures. The rapid reduction and the asymptotic leveling also matches with the observed trends. At 1323 K however, the model predicts a sharp spike in surface area at very low residence time of about 8 ms before the rapid downward trend toward the asymptotic value. This predicted sharp spike is not observed experimentally, probably to lack of data at the low residence time of 8 ms.

V. CONCLUDING REMARKS

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

Structural evolution during sulfation was carried out at 1353 K. The porosity shows a decreasing trend right from the start unlike calcination which shows a increasing porosity initially. In addition to sintering, which causes coalescence of smaller pores into larger ones, deposition of higher volume reaction product (CaSO_4) fills up the CaO pores and reduces the overall porosity. The pore size distribution curves for the partially sulfated sorbent lie below the parent hydrate curve and show the decreasing contribution of the smaller pore sizes and shifting of the entire distribution to the higher sizes.

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

Modeling work has yielded results which match very well with the experimental data. The model has been developed for simultaneous calcination and sintering of $\text{Ca}(\text{OH})_2$. The model is based on a modified form of the simple grain model (Szekely

& Evans, 1976). The model visualizes these phenomena taking place on a single grain of Ca(OH)_2 with surrounding micrograins of product CaO which undergoes sintering. The model matches the experimental data of calcination kinetics very well. It predicts the two characteristics exhibited by the reaction; very high initial rate followed by attenuation and subsequent 'die-off' at higher residence times. The surface area evolution predictions also match closely with the experimental data. The next task is to take the sulfation reaction into account and model the simultaneous calcination, sintering and sulfation of the Ca(OH)_2 sorbent.

VI. REFERENCES

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