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

Final Report for the Period
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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 the flue gas desulfurization. The goal is to provide fundamental research kinetics and effects of sorbent properties, aimed at improving SO₂ removal and increasing sorbent utilization in a cost effective manner.

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

Modified sorbent studies have yielded results leading to improved understanding of the mechanism of promotion. Studies were conducted with lignosulfonate as the modifier at a concentration of 1.5 weight % at 1353 K. The modified hydrate possesses higher surface area (about 45 m²/g) as well as internal porosity (32%). Results indicate higher capture ability in the initial 50 milliseconds, the extent of sulfation is about 30% more than that of the unmodified hydrate. At higher residence times, the rate of capture attenuates and becomes similar to that of the unmodified hydrate. The initial edge is preserved at the higher residence times studied. Work with modified calcium carbonate sorbent (Forsby carbonate) has generated some very interesting results. Forsby carbonate has shown conversions of 50% while the ligno modified and pure linwood hydrate show only about 36% and 30% respectively. Forsby carbonate has thus shown nearly 70% higher capture than the pure hydrate. The extraordinary sulfur capture ability shown by Forsby carbonate makes it a viable sorbent for Furnace Sorbent Injection (FSI) process. It is evident that Forsby carbonate's initial high surface area and associated pore structure translate into optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. It has been observed in prior studies that not all the limestone samples with initial high surface area exhibit very high sulfation conversion. The pore size distribution of their calcines show a preferential dominance of very small pores, and much like Linwood carbonate sample, such high concentration of small pores leads to premature pore plugging. Therefore, there must

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

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

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

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.

Extensive amount of work done in characterizing the sulfation behavior of pure calcium based sorbents by various researchers [1,2,3] has resulted in a widely accepted conclusion that it is necessary to explore the modified (both physical and chemical) calcium based sorbents in order to make FSI a viable flue gas desulfurization technology.

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. comprehensive microscopic model to account for the above, and,
7. a comprehensive set of guidelines based on this study for achieving the project goal.

II. MODIFIED SORBENT

A. Introduction:

Modified sorbent studies were continued into the fifth year as proposed. Investigations were carried out with two modified sorbents, lignosulfonate modified hydrate and Forsby carbonate powder. Earlier studies with pure calcium based sorbents have revealed that FSI technology can be made very attractive and economically viable if conventionally used natural calcium based sorbents can be modified to increase their reactivity towards sulfur dioxide. Limited literature results have shown that addition of calcium lignosulfonate (an anionic surfactant) to calcium hydroxide moderately increases the sulfur capture. These results also indicate that final concentration of lignosulfonate in the modified sorbent is an important parameter in its ability for sulfur capture and a 1.5% by weight concentration was found to be the optimum lignosulfonate concentration for sulfur dioxide capture [4]. Similar to the modified calcium hydroxide sorbent, calcium carbonate can also be modified using suitable surfactants to yield more effective sorbents. The modified hydroxide sorbent has been made by calcining $\text{Ca}(\text{OH})_2$, 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 to yielded 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 $\text{Ca}(\text{OH})_2$. Modified sorbent work with 1.5% lignommodified hydrate has shown about 20% higher capture than the pure Linwood hydrate. At higher residence times, both the conversion curves run parallel to each other, with the lignohydrate retaining the initial edge acquired over the pure hydrate.

Studies with Forsby limestone, a modified calcium carbonate powder and procured from Dr. Bjerle's research group at Lund University in Sweden have shown amazingly high conversion results. This modified calcium carbonate is prepared by adding an industrial surfactant (Dispex) to a thick slurry of calcium carbonate and subjecting it to a wet grinding process before drying. This modified carbonate shows nearly 70% higher sulfur capture than the pure hydrate at high residence times beyond 400 ms with good reproducibility.

Exhaustive investigations, conducted with Forsby carbonate powder and 1.5% ligno-modified Linwood hydrate have revealed that the unusually high sulfur capture by Forsby carbonate powder is primarily due to its high initial reactivity, confined to first 40 to 50 ms. It was inferred that the relative advantage of Forsby over other solids originates from its early internal structure. The high initial surface and porosity of Forsby carbonate leads to high calcination rate and the slow sintering characteristics leads to the Forsby-CaO retaining a high surface area and porosity for a longer residence time.

B. Results and Discussion:

Kinetic and structural evolution studies with modified sorbent were continued into the fifth year as proposed. Work was focused on investigating lignosulfonate modified hydrate and modified calcium carbonate sorbent obtained from Dr. Bjerle. Some preliminary results were presented in the 4th year Annual Report. This work was continued to study and compare the behavior of pure and modified hydrate at very high residence times. Figure 1 compares the sulfation results for pure and the 1.5% lignohydrate. The 1.5% lignohydrate shows nearly 20% higher conversion after more than 500 ms of exposure. The near parallel nature of the conversion curves at higher residence times suggests a similar deactivation mechanism in case of both the sorbents. This study suggests that with a Ca/S of 2:1, lignohydrate should exhibit a 20% improvement in sulfur capture than pure hydrate.

In addition to lignohydrate, investigations were conducted with another sorbent, namely Forsby carbonate (modified calcium carbonate) powder. This sorbent was procured from Dr. Bjerle's research group in Sweden. Dr. Bjerle's research group had found some interestingly high conversions with Forsby carbonate powder in their laboratory tests. The powder itself was in the form of a slurry, which was vacuum dried at 100°C overnight and then crushed and ground in a ball mill facility in the Materials Science and Engineering Department. The Forsby carbonate was characterized for its surface area, porosity and pore size distribution. It possesses about 12 m²/g of surface area and pore volume of about 0.043 cm³/g. Both the porosity and the surface area of Forsby are about 30% lower than those of the pure Linwood hydrate which has about 16.9 m²/g surface area and about 0.06 cm³/g of

Figure 1: Sulfation of pure Linwood hydrate and 1.5%ligno-modified hydrate at 1353 K for 3.9 micron particles.

pore volume. Figure 2 shows the pore size distribution comparison for Forsby carbonate and pure hydrate. The Forsby carbonate was then tested for sulfation reaction in our entrained flow reactor system. Figure 3 shows the sulfation versus time results for Forsby. The pure hydrate and lignohydrate sulfation results are also shown for comparison. As can be seen, at a residence time of about 535 ms, Forsby shows a conversion of 50% while the ligno and pure show only about 36% and 30% respectively. Forsby has thus shown nearly 70% higher capture than the pure hydrate. These results with Forsby, being so incredibly high, were checked for reproducibility and found to be very consistent. These results have great implications due to the fact that these are one of the highest conversions observed with any sorbent. Figure 4 shows the internal pore structure and pore volume attained by all the three sorbents of the same size cut ($3.9\ \mu\text{m}$) following calcination for 20 ms and sulfation for the same time. Figure 5 shows the development of calcination and the subsequent pore structure evolution at two different residence times, 20 ms and 35 ms. Figure 6 shows the development of sulfation and the subsequent pore structure evolution at 20 ms and 35 ms. Figure 7 shows the pore size distribution changes in Forsby at 46% and 51% conversion.

As already seen with the 1.5% ligno-modified hydroxide the reason for the unusually high sulfur capture by Forsby carbonate powder also lies primarily in its high initial reactivity, confined to first 40 to 50 ms. Conversion curves for all the three sorbents tested thereafter lie almost parallel to one another, indicating similar reaction mechanism. From a comparison of their behaviors, it can be inferred that the relative advantage of Forsby over other solids originates from its early internal structure. This advantage is further elucidated by the cumulative pore size distribution plots of the sorbents resulting from calcination reactions at 20 and 35 ms reaction times (Figure 5). After 20 ms of calcination, all the three sorbents show nearly identical decomposition to CaO , however, the calcines differ widely in terms of the resulting surface area and porosity. CaO generated by Forsby shows maximum pore volume ($0.19\ \text{cc/gm}$) and surface area ($62.1/\text{gm}$). Higher total surface area and porosity values for the Forsby CaO as compared to the other two hydroxide-derived CaO sorbents indicates a relatively smaller drop from their nascent values. Retention of higher surface area and porosity for a longer period probably suggest that the sintering process, which is largely responsible for sorbent deactivation proceeds at a much slower rate for the Forsby- CaO . A

Figure 2: Pore size distribution of Forsby carbonate and Linwood hydrate.

Figure 3: Sulfation of 3.9 μm pure hydrate, 1.5% lignohydrate and Forsby carbonate at 1080°C.

Figure 4: Pore size distribution changes of 3.9 μm Forsby carbonate, pure Linwood hydrate and 1.5% lignommodified hydrate with calcination and sulfation at 1080°C.

Figure 5: Pore size distribution changes of 3.9 μm Forsby carbonate, pure Linwood hydrate and 1.5% lignommodified hydrate with calcination at 1080°C.

Figure 6: Pore size distribution changes of 3.9 μm Forsby carbonate, pure Linwood hydrate and 1.5% lignommodified hydrate with sulfation at 1080°C.

Figure 7: Pore size distribution changes for Forsby carbonate at different extents of sulfation at 1353 K.

possible explanation for this can be found in Borgwardt's work [5], who mentions that due to differences in molar volumes between CaCO_3 and Ca(OH)_2 , packing of CaO grains produced from carbonates is relatively less dense, which offers fewer contact points between these grains, thus reducing the sintering rate. Borgwardt [5] also reported even though the hydroxide and carbonate calcines have comparable activation energies of sintering, the sintering rate constant for the carbonate calcine is one order of magnitude less than that of the hydroxide calcine.

As the Forsby-CaO offers a more open internal structure with higher surface area, the rate of sulfation is faster in its pores, considering that rate of sulfation is directly proportional to the surface area when sulfur capture is chemical reaction controlled. Surface area dependence becomes even more significant when the capture is product-layer diffusion controlled because the rate becomes proportional to the square of the CaO surface area. Only after about 50 ms, reduction in the surface area and porosity values for the Forsby calcine become sufficiently large enough to parallel the deactivation extent of the calcines. Thus the high initial surface and porosity of Forsby carbonate leads to high calcination rate and the slow sintering characteristics leads to the Forsby-CaO retaining a high surface area and porosity for a longer residence time.

Further experiments were also performed in our laboratory to make hydrated lime by a unique rehydration process. The Linwood hydrate was calcined and the CaO was rehydrated with 5 times excess water. The slurry was dried and crushed. The hydrate produced was observed to have a high surface area of about $50 \text{ m}^2/\text{g}$. Thus calcination and rehydration seems to lead to higher surface area and porosity of the hydrate. As mentioned in previous quarterly report, the 1.5% lignommodified hydrate possesses about $62 \text{ m}^2/\text{g}$ which indicates the positive role of surfactant in the hydration process.

As stated earlier, thorough investigations into the Forsby limestone and comparison of its pore structure evolution with the modified and pure Linwood hydroxides and carbonate has shed light on a number of factors that make for a good sorbent. In addition to pore structure evolution during calcination and sintering, SEM studies were also performed to analyze the nature and size of the component grains. Figure 8a shows the structure of 85% calcined $1.2 \mu\text{m}$ Forsby (FC) particles after 20 ms at 1080°C , which possess a BET surface

area of about 60 m²/g. The small grain size and the granular nature of the surface are easily observable. Figure 8b shows the SEM photomicrograph of the 80% calcined Linwood hydroxide (LH) powder of the same size after 20 ms at 1080°C, possessing a much lower surface area of 17 m²/g. From this picture, the surface appears much less granular with reduced apparent porosity. In addition, the grains are larger in size and appear more agglomerated in the case of LH-CaO, most probably an effect of the faster sintering process.

Also, theoretical porosity reduction calculations were performed to compare the experimentally observed pore volumes with the predicted volumes. This would give an indication of the pore filling characteristics of the sorbents. The theoretical pore volume after 20 ms of sulfation is calculated by assuming that the extent of CaO pore reduction due to sintering is identical for both sulfation (with SO₂) and calcination (without SO₂) reactions. Furthermore, it is assumed that the extent of hydroxide or carbonate decomposition to CaO is not affected by the presence of SO₂, i.e., for both the cases, calcination extent can be represented by X_c. The fraction of CaO (w_{CaO}) in a unit weight of partially calcined product can be expressed as:

$$w_{CaO} = \frac{X_c}{\frac{M_s}{M_{CaO}} (1 - X_c) + X_c} \quad 1$$

where M_s and M_{CaO} are molecular weights of the unreacted sorbent (Ca(OH)₂ or CaCO₃) and CaO respectively. During sulfation reaction, a fraction of this w_{CaO} converts to CaSO₄. If the overall sulfation conversion is expressed as X_s, the amount of CaSO₄ can be obtained as:

$$W_p = X_s \left(\frac{w_{CaO}}{M_{CaO}} + \frac{w_s}{M_s} \right) M_p \quad 2$$

where M_p is the molecular weight of the product, CaSO₄. The amount of residual CaO is:

$$W_{CaO} = \left[\frac{w_{CaO}}{M_{CaO}} - X_s \left(\frac{w_{CaO}}{M_{CaO}} + \frac{w_s}{M_s} \right) \right] M_{CaO} \quad 3$$

(a)

(b)

Figure 8: SEM photomicrographs after 20 ms of calcination at 1080°C; mean particle size: 1.2 μm .

(a) FC, 85% calcined, BET surface area of 60 m^2/g .

(b) LH, 80% calcined, BET surface area of 17 m^2/g .

So the theoretical reduction in pore volume can be obtained by calculating the additional volume occupied by the product CaSO_4 due to its higher molar volume (v_p) compared to that of CaO (v_{CaO}). If V_c is the specific pore volume after 20 ms of calcination, then theoretical pore volume after equal duration of sulfation on a unit weight of sulfated sample can be expressed as:

$$V_{\text{theo}} = \frac{[V_c - X_s (v_p - v_{\text{CaO}}) (\frac{W_{\text{CaO}}}{M_{\text{CaO}}} + \frac{W_s}{M_s})]}{(w_s + W_{\text{CaO}} + W_p)} \quad 4$$

These theoretical pore volume values for each sorbent are calculated and plotted in Figure 9 with the experimentally obtained values. The theoretically calculated data lie much below the experimentally obtained values for all the sorbents, suggesting that the effect of sintering on pore volume loss is diminished in presence of SO_2 . Newton et al. [6] performed calcination and sulfation experiments in presence of CO_2 and observed a similar reduction in sintering effect during sulfation. They concluded that during sulfation, the influence of CO_2 in accelerating the rate of sintering is inhibited due to the product layer surrounding the CaO grains.

To conclude from this comparison work, it is evident that Forsby carbonate's initial high surface area and associated pore structure translate into optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. It has been observed in prior studies that not all the limestone samples with initial high surface area exhibit very high sulfation conversion. The pore size distribution of their calcines show a preferential dominance of very small pores, and much like Linwood carbonate sample, such high concentration of small pores leads to premature pore plugging. Therefore, there must exist an optimum pore structure affiliated with the uncalcined carbonate, which on calcination, makes the nascent pore size distribution of CaO favorable for the sulfation reaction. Identifying the optimum pore distribution of original carbonate powder has not been attempted in this study and presents an area for future work.

The results of this investigation bring up an interesting comparison between limestone and hydrated lime sorbents. Some of the earlier studies employed very low surface area (non-

Figure 9: Comparison of experimental pore volumes after 20 ms of sulfation at 1080°C with that predicted from calcination results.

porous) carbonates and also of average size larger than the hydrates. So, the higher conversion shown by the hydrate sorbents most probably has been a result of smaller particle size. When particle size is equally small for both these powders, the advantage of hydroxides may have resulted from a more favorable pore size distribution of its calcine. This can be explained if we consider the initial structure of the hydroxide sorbents, which is more porous with an inherent distribution of pore sizes. As a result, the size distribution of its nascent calcine is shifted to the larger sizes, preventing rapid reaction termination caused by pore-mouth-plugging. In case of carbonates, the small CaO pores experience severe pore-mouth-plugging which restricts its final utilization. However, when the parent carbonate powder is porous and possesses a favorable pore size distribution, the calcine pore structure can make the carbonate powder a more attractive furnace-injection sorbent than typical Ca(OH)_2 powders.

III. MODEL DEVELOPMENT

A. Introduction:

The sulfation reaction has not only been one of the most extensively studied reactions experimentally, it has also posed an enormous challenge to researchers trying to model its conversion and pore structure behavior. In fact, the sulfation reaction can be said to have served as a bench-marking tool for testing and validation of most of the new gas-solid reaction models developed. The experimental data on sulfation is of two types:

- (a) Ca(OH)_2 sulfation, with all the three phenomena occurring concomitantly; or
- (b) independent CaO sulfation, with precalcined and presintered CaO .

Most of the early efforts to model Ca(OH)_2 sulfation assumed the calcination reaction to be instantaneous and neglected the effect of sintering altogether. Most modeled the experimental data of independent CaO-SO_2 reaction. Borgwardt and Bruce [7], as well as Bruce et al. [8] applied the limiting case of product layer control with the grain model to fit their CaO-SO_2 reaction data. They derived the specific rate constants for product layer control from their best fit of the data. Ramachandran and Smith [9] applied the single-pore model to the sulfation reaction data of Hartman and Coughlin [10]. Bhatia and Perlmutter [11] tested their model predictions with experimental CaO-SO_2 data from Borgwardt [12]. They found that a combination of kinetic and diffusional resistances is needed to explain the experimental data. The specific reaction rate constant and the product layer diffusivity were the two model parameters varied to fit the model. Their values of the rate constants compared with those of previous researchers [9]. Christman and Edgar [13] also used the surface reaction rate constant and the product layer diffusivity as the two variable model parameters which they estimated from the kinetic data. They estimated the reaction rate constant from the initial rate data and found their value to be in reasonable agreement with Bhatia and Perlmutter [11]. However, they noted that the values of both the parameters varied over a large range in the literature. Simons and Garman [14] modeled the plugging of the smallest pores as the rate-controlling step in leveling-off of the conversion-time data. Milne et al. [15,16], and Alvfors and Svedberg [17] modeled the sulfation of CaO using the overlapping grain concept.

Comprehensive Ca(OH)_2 sulfation modeling has been attempted by very few researchers due to the complex nature of the various phenomena and the lack of a thorough understanding of their interaction. In Ca(OH)_2 sulfation, there exist consecutive reactions where in the product of the first reaction (CaO) becomes the reactant for the second, as well as concomitantly undergoes structural changes due to sintering. Mai's [18] work used a pore model for the sulfation and second-order kinetics for sintering. Milne and Pershing [19] presented a combined model using the grain model for sulfation, second-order kinetics for sintering and an empirically modified shrinking-core model for the calcination. Alvfors and Svedberg [20] attempted to model the total process occurring when a sorbent particle is injected into the flue gas atmosphere. The calcination is described by first-order kinetics at the reaction surface, similar to the empirically verified model of Borgwardt [21]. The calcination and sintering models together are used to predict the available surface area as a function of time. The predicted area is then used to calculate calcium sulfation. The sulfation itself considers pore diffusion, product layer diffusion and chemical reaction. Alvfors and Svedberg [20] used their PSSM model for predicting the sulfation behavior by adjusting the model parameters. They concluded that qualitative predictions of conversion of limestone to calcium sulfate were possible but quantitative predictions proved to be difficult.

B. Development of Comprehensive Sulfation Model:

A mathematical model was developed earlier (4th year Annual Report) to describe 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 and required mathematical expressions were reported in the fourth year Annual Report. The calcination and sintering model used the grain model as the basis but was largely modified to take into account the sintering of the product CaO layer and the diffusion resistance the porous sintering CaO layer offers to the outward diffusion of H_2O (in case of Ca(OH)_2 calcination). The model thus incorporated a number of unique features and was able to fit both the experimental kinetics and the surface area evolution data extremely well. Hence, it was decided to take advantage of the already existing work in order to develop the comprehensive sulfation model. This also meant taking into consideration some of the already existing features of the calcination model, namely, the conceptualization of the CaO formed as a

multilayered sintering porous product shell on each grain. In order to develop the sulfation model, both the grain model formulation as well as the pore model formulation were studied for a number of factors such as ease of adaptability with the existing work, the solution scheme, and the reliability, robustness etc. The random pore model [22] and the distributed pore model [13] have well-refined formulation and a number of capabilities. Further more, the random pore model has been applied to the sulfation reaction and has been shown to model the experimental data very well. After careful consideration of the various existing models, it was decided to use the random pore model formulation for developing the comprehensive model.

Since the sulfation is restricted to the sintering CaO only, the region of interest is the product CaO shell with its micrograins and associated porosity and surface area. In order to develop the pore model formulation, the reacting solid CaO is now visualized not as grains but rather we represent it as a network of random pores. For the random pore model formulation, the pores are considered to be of the same size and their intersections are taken into account. A schematic illustration of the product CaO layer building during calcination of a Ca(OH)_2 grain is shown in Figure 10. The various diffusion and reaction steps are:

- (a) SO_2 diffusion through the intergrain voids,
- (b) diffusion through the intragrain voids of the sintering and sulfating CaO,
- (c) diffusion through the product layer (after its formation), and finally,
- (d) reaction with CaO.

The inherent assumption involved here is that there is no external diffusion resistance because of the small particle size. Moreover, it is assumed that calcination and sintering proceed unhindered during sulfation. This assumption has been made by several researchers in attempting to model the experimental data. Further, intraparticle (i.e., intergrain) resistance to heat or mass transfer is considered insignificant thus neglecting step (a).

A differential mass balance for diffusion and reaction of SO_2 through the porous CaO product shell of the grain can be written as:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{\text{eff}} r^2 \frac{\partial C}{\partial r} \right) = \frac{\rho(1 - \varepsilon)}{M} \frac{dx_s}{dt} \quad 5$$

(a)

(b)

Figure 10: Schematic of the overlapping pore structure of the random pore model. The blackened area represents the unreacted solid, the dotted area the product layer. (a) early stage, showing product layer around each pore, and (b) intermediate stage, showing some overlapping reaction surfaces (from Bhatia and Perlmutter, 1981a).

Here, r is the radial distance along the grain and D_{eff} represents the effective diffusivity of SO_2 through the pores of CaO product. C is the concentration of SO_2 inside the porous structure of CaO . dx/dt is the local rate of conversion of CaO to CaSO_4 . The boundary conditions are based on radial symmetry and on no mass transfer resistance at the grain boundary.

$$\frac{\partial C}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad 6$$

$$C = C_{\text{bulk}} \quad \text{at} \quad r = r_g \quad 7$$

The local reaction rate, dx/dt at the internal surface of the pores (actually the interface of the CaO and CaSO_4), is obtained from the random pore model which takes into account the growing product layer and the diffusion of the reactant gas through the layer. The pores are considered to be cylindrical in shape and their random overlapping nature is taken into consideration. For the detailed equation development, the reader is referred to Bhatia and Perlmutter [20,23].

$$\frac{dx_s}{dt} = \frac{k_r S_o C (1-x) \sqrt{1-\Psi \ln(1-x)}}{(1-\epsilon_o) \left[1 + \frac{\beta}{\Psi} (\sqrt{1-\Psi \ln(1-x)} - 1) \right]} \quad 8$$

Ψ is a structural parameter defined as

$$\Psi = \frac{4 \Pi L_o (1 - \epsilon_o)}{S_o^2} \quad 9$$

β can be considered as a Biot modulus and takes into account the ratio of chemical reaction rate compared to the rate of product layer diffusion.

$$\beta = \frac{2 k_r \rho (1 - \epsilon_o)}{M D_p S_o} \quad 10$$

Z is the molar volume ratio of the product CaSO_4 to reactant CaO and ρ is the density of the CaO . k_r is the specific reaction rate constant and D_p is the diffusivity through the product layer.

The three parameters, ϵ_o , S_o , and L_o are the core features of the random pore model. The model considers the actual reaction surface to be the result of a random overlapping of a set of cylindrical pore surfaces of distributed sizes. ϵ_o , S_o and L_o are the total enclosed volume, total surface area and total length of the overlapping cylindrical pore system respectively. Bhatia and Perlmutter (1980) [20] have indicated that these quantities can be determined from measurements of the pore volume distribution, $v_o(r)$. Such pore volume distribution data can be obtained from BET measurements.

$$\epsilon_o = \int_0^\infty v_o(r) dr \quad 11$$

$$S_o = 2 \int_0^\infty \frac{v_o(r)}{r} dr \quad 12$$

$$L_o = \frac{1}{\pi} \int_0^\infty \frac{v_o}{r^2} dr \quad 13$$

The conversion-time behavior can be obtained by the simultaneous solution of equations (5) and (8) with boundary conditions (6) and (7). The solution scheme requires the simultaneous solution of two highly non-linear ordinary differential equations. Further, some of the existing models [11] have made a number of simplifying assumptions and have shown reasonable agreement with the experimental data. In this work, the intragrain mass transfer resistance is neglected, then chemical kinetics and product layer diffusion control the overall reaction rate. Equation (8) can be integrated to give the local reaction rate which is also

representative of the global reaction rate for the particle due to insignificant intragrain transport resistances. The solution procedure requires the predictions of ϵ_o , S_o and L_o , which are the structural properties of the porous CaO reactant. The calcination and sintering model calculates the porosity and surface area of the individual layers of the CaO and also the average values of the above by integration over the entire layer structure. In the original random pore model formulation, the properties ϵ_o , S_o and L_o are calculated from experimental data and are invariant since the reactant is not undergoing any sintering induced structural changes. However, in this case, sintering largely affects the values of the above three parameters and their variation cannot be neglected. ϵ_o and S_o are calculated from the calcination and sintering model. L_o itself is not available from the model or any experimental data, an average representative non-variant value is assumed for this parameter. k_r and D_p are the two variable model parameters.

C. Results and Discussion:

In order to test the model, the entrained flow reactor kinetic data for Ca(OH)_2 sulfation at 1080°C and at other temperatures obtained earlier is utilized. The predictions of the model for three temperatures of 950, 1035 and 1080°C are shown in Figure 11. For comparison, experimental data at 1035 and 1080°C is also shown in the figure. The model prediction agree qualitatively with the data, however, the initial high reaction rate is not predicted well by the model. Moreover, the experimental conversion can be seen to be leveling-off even as early as 200 ms, which is not represented well by the model. The variation of the reactant CaO surface area and porosity are shown in Figures 12 and 13 respectively. As can be seen, the steep changes in both these structural characteristics lead to very drastic changes in the non-dimensional parameters, Ψ and β which influence the sulfation rate. The changes in Ψ and β are shown in Figure 14 and Figure 15 respectively.

Figure 11: Comparison of comprehensive model predictions with experimental sulfation data for 3.9 μm Linwood $\text{Ca}(\text{OH})_2$.

Figure 12: Variation of CaO porosity as predicted by the calcination and sintering model and used in the sulfation modeling.

Figure 13: Variation of CaO surface area as predicted by the calcination and sintering model and used in the sulfation modeling.

Figure 14: Variation of the structural parameter Ψ with time; model simulation.

Figure 15: Variation of the parameter with time; model simulation.

As can be seen, both Ψ and β level-off asymptotically after the first 50 ms of reaction and sintering. The value of k_r can be computed from the initial rate data [11] or can be obtained together with D_p by fitting the experimental data at specific temperatures. The values of k_r obtained in this work varied from 1.0×10^{-6} at 950°C to 2.6×10^{-6} at 1080°C (the units of k_r are $\text{m}^4/\text{kmol s}$ throughout this discussion). These values compare with those reported in the literature. Bhatia and Perlmutter (1981b) [11] obtained k_r to be 0.834×10^{-6} at 980°C .

In fitting the model to the experimental data, it was observed that the β has a strong influence on the predictions as well as the stability of the solution scheme. The value of β is seen to level off to about 40 for all the three temperatures studied. The asymptotic value of β was observed to give a better and more robust performance, and the model predictions shown in Figure 11 are using the asymptotic β values. Considering the large value of β , it can be said that this model represents the entire sulfation data using the limiting case of product layer diffusion control. The initial rapid reaction rate occurs during the period in which the extent of sulfation is quite small (less than 5%) and so is the product layer build-up. During this period, both kinetic and diffusion limitations will need to be considered. However, this period lasts for a very short time (less than 25 ms) and therefore, the overall behavior is better explained by the diffusion-control mechanism.

IV. CONCLUDING REMARKS

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. Work with modified calcium carbonate sorbent (Forsby carbonate) has generated some very interesting results. Forsby carbonate has shown conversions of 50% while the ligno modified and pure linwood hydrate show only about 36% and 30% respectively. Forsby carbonate has thus shown nearly 70% higher capture than the pure hydrate. The extraordinary sulfur capture ability shown by Forsby carbonate makes it a viable sorbent for Furnace Sorbent Injection (FSI) process. It is evident that Forsby carbonate's initial high surface area and associated pore structure translate into optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. It has been observed in prior studies that not all the limestone samples with initial high surface area exhibit very high sulfation conversion. The pore size distribution of their calcines show a preferential dominance of very small pores, and much like Linwood carbonate sample, such high concentration of small pores leads to premature pore plugging. Therefore, there must exist an optimum pore structure affiliated with the uncalcined carbonate, which on calcination, makes the nascent pore size distribution of CaO favorable for the sulfation reaction. Identifying the optimum pore distribution of original carbonate powder has not been attempted in this study and presents an area for future work.

The results of this investigation bring up an interesting comparison between limestone and hydrated lime sorbents. Some of the earlier studies employed very low surface area (non-porous) carbonates and also of average size larger than the hydrates. So, the higher conversion shown by the hydrate sorbents most probably has been a result of smaller particle

size. When particle size is equally small for both these powders, the advantage of hydroxides may have resulted from a more favorable pore size distribution of its calcine. This can be explained if we consider the initial structure of the hydroxide sorbents, which is more porous with an inherent distribution of pore sizes. As a result, the size distribution of its nascent calcine is shifted to the larger sizes, preventing rapid reaction termination caused by pore-mouth-plugging. In case of carbonates, the small CaO pores experience severe pore-mouth-plugging which restricts its final utilization. However, when the parent carbonate powder is porous and possesses a favorable pore size distribution, the calcine pore structure can make the carbonate powder a more attractive furnace-injection sorbent than typical $\text{Ca}(\text{OH})_2$ powders.

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

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