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HIGH REACTIVITY Ca-BASED SORBENTS FOR SO₂ AND As₂O₃ REMOVAL AT ELEVATED TEMPERATURES: EXPERIMENTAL & MODELING

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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ABSTRACT

A high reactivity calcium carbonate sorbent with an open initial pore structure is prepared and its calcination, sintering and sulfation characteristics are investigated in an entrained flow reactor system at high temperatures (900-1100°C) and short residence times (20-600 ms) using small particle sizes (<5 μm). The high reactivity carbonate (HRC) shows 70-75% sulfation conversion within 0.5 s, which is substantially higher than any other calcium based sorbents ever reported in the literature. The high initial surface area combined with its open pore structure and pore size distribution of its calcine contribute to its high reactivity. The calcined HRC possesses a significant portion of its pore volume in the 50-200 Å range. This pore size range represents an optimum pore size for sulfation since it provides a reasonably high surface area and is less susceptible than <50 Å pore sizes to pore filling, or pore mouth plugging due to formation of high molar volume CaSO₄. Furthermore, HRC is shown to be resistive to sintering and is able to maintain the favorable pore structure even under extreme conditions favorable for thermal sintering. Investigations with other carbonates reveals that a much higher portion of their calcines' porosity lies in the smaller pores, which leads to premature termination
of sulfation. Results show the impact of internal pore structure on initial reactivity and ultimate sorbent utilization.

Time resolved kinetic data regarding the calcination, sintering and sulfation behavior of calcium-based sorbents is obtained from the experimental investigations conducted in the entrained flow reactor system. Overall sulfation behavior of the calcium sorbent is simulated using a structural model based on grain-micrograin concept. This modified grain model incorporates the structural changes due to thermal and chemical induced sintering of CaO and due to various reactions. The uniqueness of the model lies in its ability to simulate overall sulfation phenomena of calcination, sintering and sulfation and incorporate actual mechanism of sulfation involving ionic diffusion in its formulation. The model predictions are in good agreement with the observed experimental results.

In this research work, investigations are also conducted into determining the effectiveness of some commonly used mineral sorbents for removal arsenic species from hot flue gases. As₂O₃ is used as the source of arsenic species and experimental investigations indicate Ca(OH)₂ to be most effect sorbent and presence of a chemical interaction mechanism between hydrated lime and As₂O₃. X-ray diffraction and ion chromatography analyses of the post-sorption sorbent sample confirm that calcium arsenate is the dominant reaction product. Sorption of arsenic on fly ash is found to be reversible and physical in nature.
To my parents
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PUBLICATIONS


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<td>Surface area of the pore</td>
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<td>A'</td>
<td>Constant of integration</td>
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<tr>
<td>A_t</td>
<td>Total surface area of the pore</td>
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<td>B</td>
<td>Constant to incorporate effect of H₂O partial pressure on sintering</td>
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<tr>
<td>Bi</td>
<td>Biot number, dimensionless</td>
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<tr>
<td>B</td>
<td>Empirical constant</td>
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<tr>
<td>C_{ion}</td>
<td>Concentration of calcium ions</td>
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<td>C_p</td>
<td>Specific heat capacity of particle</td>
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<td>C_s</td>
<td>Ca(OH)₂ concentration</td>
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<td>C</td>
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<td>D_{ion}</td>
<td>Solid state ionic diffusivity</td>
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<tr>
<td>d_p</td>
<td>Diameter of the particle</td>
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<td>d_{50}</td>
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h Convective heat transfer coefficient
kc Specific reaction rate constant for Ca(OH)$_2$ calcination
ksin Specific rate constant for CaO sintering
ksm Modified specific rate constant for CaO sintering
ks Specific rate constant for CaO sulfation
ks Parameter in determining the micrograin surface ion concentration
m Constant to incorporate effect of H$_2$O partial pressure on sintering
m Grain structure parameter in the modified grain model
Ms Molecular weight of the sorbent
M$_{CaO}$ Molecular weight of CaO
M$_p$ Molecular weight of CaSO$_4$
Nu Nusselt number, dimensionless
P Partial pressure of CO$_2$/H$_2$O in the CaO product layer
Pc Partial pressure of CO$_2$/H$_2$O at the CaO/sorbent interface
Pe Equilibrium CO$_2$/H$_2$O dissociation pressure for sorbent calcination
Pt Total pressure
R Universal gas constant
R$_c$ Unreacted grain core radius
R$_g$ Overall grain radius
R$_{go}$ Initial grain radius
R$_p$ Particle radius
rc Instantaneous unreacted micrograin core radius
rg Instantaneous micrograin radius
\( r_{go} \) Initial micrograin radius
\( S \) Specific surface area of product CaO layer
\( S_a \) Asymptotic specific surface area of CaO at a particular temperature
\( S_{\text{CaO}} \) Specific surface area of CaO product shell
\( S_{\text{Ca(OH)}_2} \) instantaneous specific surface area of \( \text{Ca(OH)}_2 \)
\( S_{\text{CaCO}_3} \) instantaneous specific area of \( \text{CaCO}_3 \)
\( S_o \) Specific surface area of nascent CaO
\( S_{j,i} \) Specific surface area of CaO formed in the \( j \)-th time interval at the end of \( i \)-th interval
\( S_s \) Overall specific surface area of the particle
\( T \) Reaction temperature
\( T_b \) Bulk gas temperature
\( T_p \) Particle temperature
\( t \) time
\( V_p \) Pore volume
\( V_c \) Experimental pore volume of the sorbent after calcination
\( V_{\text{theo}} \) Calculated pore volume of the sorbent following sulfation
\( w_{\text{CaO}} \) Weight of CaO per unit weight of partially calcined sorbent
\( w_s \) Weight of unreacted sorbent per unit weight of partially calcined sorbent
\( W_p \) Weight of product \( \text{CaSO}_4 \) per unit weight of partially calcined sorbent
\( W_{\text{CaO}} \) Weight of unsulfated CaO per unit weight of partially calcined sorbent
\( X_c \) Extent of calcination of the sorbent
\( x_s \) Local Extent of sulfation of the sorbent

xx
\( x \) Fractional conversion of sorbent to \( \text{CaSO}_4 \)

\( z_j \) Fraction of total \( \text{CaO} \) formed in the \( j \)-th time interval

\( Z \) Molar volume ratio of \( \text{CaSO}_4 \) to \( \text{CaO} \)

**Greek letters**

\( \gamma_{\text{Ca(OH)}_2} \) Rate of \( \text{Ca(OH)}_2 \) calcination reaction

\( \gamma_{\text{CaCO}_3} \) Rate of \( \text{CaCO}_3 \) calcination reaction

\( \varepsilon \) Product layer porosity

\( \varepsilon_0 \) Initial product layer porosity

\( \varepsilon_p \) Emissivity factor of the particle

\( \rho_p \) Density of the particle

\( \rho \) Overall solid density of the grain

\( \rho_{\text{CaO}} \) Density of \( \text{CaO} \)

\( \rho_{\text{Ca(OH)}_2} \) Density of \( \text{Ca(OH)}_2 \)

\( \rho_{\text{CaCO}_3} \) Density of \( \text{CaCO}_3 \)

\( \sigma \) Stefan-Bolzmann constant

\( \nu_p \) Molar volume of the product \( \text{CaSO}_4 \)

\( \nu_{\text{CaO}} \) Molar volume of \( \text{CaO} \)

\( \psi \) Structural parameter used in random pore model
CHAPTER 1

INTRODUCTION

This research work focuses on various mechanisms of interaction in removal of SO$_2$ and arsenic species by economical Ca-based sorbents from hot flue gases emanating from coal-fired power plants and development of an effective methodology to achieve the same. The originality of the research lies in the fact that it demonstrates and determines the importance of sorbent structure in gaining insights in the overall phenomenon of gas-solid reaction and successfully applies this knowledge in development of a high reactivity Ca-based sorbent for SO$_2$ and As$_2$O$_3$ removal.

Sulfur dioxide and other sulfur compounds, such as hydrogen sulfide, have been identified as the main precursors to the acid rain and their deleterious effects on the environment are well documented. One of the major sources of sulfur species emission into our environment is the burning of fossil fuels, such as coal, for energy. The very nature of origin of coal makes the presence of sulfur essential albeit undesirable. Sulfur in coal is present in both organic and inorganic forms and during any coal combustion process almost all the sulfur present in the coal is transferred into the flue gas. Thus, resulting in significant contribution to the emission of sulfur dioxide by coal-fired utility boilers and coal-fired combustors in power generating facilities. More than two-thirds of the emitted sulfur
dioxide in United States comes from the coal-fired boilers in power generating facilities. In the light of overwhelming evidence pertaining to the damaging effects of acid rain to the eco-system and bio-system, considerable attention has been focused on the control and abatement of sulfur dioxide emissions. The recent focus of various environmental acts puts considerable emphasis in making flue-gas desulfurization technology an integral part of utility and industrial processes with coal-fired boilers. The utilization of vast reserves of coal throughout the world depends critically on the availability of economically feasible means of removing sulfur from it.

Sulfur dioxide control can be effected by various means but broadly these can be classified as pre and post combustion treatments. Removal of sulfur from the coal prior to combustion is one of the more direct methods. Removal of elemental sulfur from coal can be achieved by either chemical leaching process or by catalytic reduction. Both these methods are rather expensive and are associated with other difficulties, such as loss in heating value and generation of other undesirable sulfur products such as hydrogen sulfide. Moreover, the heterogeneity of coal itself presents considerable challenge to its cleaning. The second method of sulfur removal involves the removal of sulfur compounds, mainly the oxides, after the coal combustion. Combustion of coal transfers most of the sulfur present into the flue gas and prior to venting the waste flue gas it is treated to remove sulfur dioxide. Removal of sulfur dioxide from flue gas is mainly accomplished by contacting it with calcium-based (limestone, lime and hydrated lime) sorbents which have shown remarkable sulfur dioxide scavenging ability. Limestone and lime scrubbers are common installations in coal-fired power generating facilities. In industry, removal of sulfur dioxide from flue gases is usually accomplished by either wet scrubbing or by dry scrubbing. There are other
Flue Gas Desulfurization (FGD) processes too, which combine the wet and dry techniques of SO₂ scrubbing. In recent years, other innovative FGD techniques have emerged such as duct injection, dry injection with recycle (R-SOₓ), wet electrostatic precipitator (E-SOₓ), SOₓ, NOₓ, Rocks in a Box (SNRB) etc. Although the most commonly used industrial practice is wet limestone scrubbing process, dry scrubbing processes especially dry sorbent injection (DSI) technology, offer a more economical and retrofittable technology. EPA, under the Lime Injection Multistage Burner (LIMB) programs in mid 1980’s, initiated the development of DSI.

Sulfur dioxide from the flue gas can be removed at various stages. High-temperature removal of sulfur dioxide would be at the upper-furnace region (850-1200°C) where the temperatures are favorable for rapid reaction. At these temperatures only dry scrubbing of the gases by injecting calcium-based sorbents (Furnace sorbent injection, FSI) is possible and the main product formed is calcium sulfate. Reaction scheme for this process is given as:

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (1.1)
\]
\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (1.2)
\]
\[
\text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 \quad (1.3)
\]

Sulfur dioxide capture in the medium temperature range (400-750°C) or in the economizer section results from the formation of calcium sulfite instead of calcium sulfate because at this temperature range calcium sulfite formation is thermodynamically more favorable. Under these conditions SO₂ capture takes place via direct interaction with the sorbent and is given as:

\[
\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} \quad (1.5)
\]
Application of DSI for flue gas desulfurization in high-temperature range of 800-1200°C (temperatures typically found in upper furnace region) involves injection of sorbent powders in the furnace. When Ca-based sorbents are injected into the furnace, it decomposes or calcines to give highly porous, high-surface area CaO (Eq. 1.1 and 1.2). The highly reactive CaO then reacts with SO$_2$ in the presence of oxygen to form solid CaSO$_4$ (Eq. 1.3).

The thermal decomposition of CaSO$_4$ becomes dominant at temperatures above 1200°C whereas at temperatures below 800°C the formation of CaSO$_3$ is favorable, thus restricting the formation of CaSO$_4$ in the temperature window of 800-1200°C. Figure 1.1 gives a simplified schematic of a typical Pulverized Coal Combustor (PCC) unit and indicates various locations where dry sorbent can be injected.

Although the DSI (or FSI) offers an economical solution to the problem of SO$_2$ removal from hot flue gas environments with minimal capital investment it suffers from an inherent drawback. The formation of the reaction product CaSO$_4$, that has nearly 3 times the volume of reactant CaO, leads to a virtual “choking” of the reaction. It has been observed by various researchers (Ghosh-Dastidar et al., 1993) that FSI process can effect only 70-75% removal of SO$_2$ even when the sorbent used is twice the amount that would be needed theoretically. This falls far below the levels of removal mandated by EPA (more than 90% SO$_2$ removal) and would necessitate the additional processes downstream for sulfur removal thus off-setting the gains of using a low-cost FSI technology. The cessation or termination of sulfation reaction is mainly caused by the formation of CaSO$_4$ which leads to a loss of sorbent surface area due to extensive pore plugging and pore-mouth blockage.
In addition to the “deactivating” role played by sulfation, high temperatures also induce sintering of CaO and reduce its reactivity by lowering its surface area.

In most of the gas-solid non-catalytic reactions, generation of surface area is considered to be an activation step and any process which results in a loss of surface area is considered a deactivation step. Calcination of Ca-based sorbents leads to the formation of highly porous CaO and acts as an activation step, the sulfation reaction is a deactivation phenomenon which results in the build-up of CaSO₄ product layer and hence, a loss in available surface area. Along with sulfation, thermal sintering also contributes to deactivation of CaO.

All the three steps mentioned above take place within a very short time of sorbent injection (a few hundred milliseconds). Researchers (Milne et al., 1990) have reported that about 30% of sulfur capture by calcium hydrates takes place within 50 ms at 1090°C. Time-scales for calcination, sintering, and sulfation are not very different and these processes overlap to a considerable degree depending on the furnace conditions. Literature is replete with studies done to explain the sulfation behavior of CaO under high temperatures but a thorough understanding of the overall process is still elusive and interplay of each of the three phenomenon is not clear. One of the reasons for that is the “ultra-fast” nature of these processes and lack of understanding of the effect played by each process on solid surface area. In addition to that the low residence times available for SO₂ capture in the temperature range of interest for FSI (800-1200°C), typically less than 1 second, are not only a testimony to the “ultra-fast” nature of the process but also add to the complexity of the overall process. Therefore, it is important to understand each of the three steps independently and simultaneously at very short contact times and apply that understanding to suitably “tailor”
Ca-based sorbents in order to attain high level of SO$_2$ removal. Development of inexpensive and highly reactive calcium sorbents holds the key to improving the furnace sorbent injection technique.

The main objectives of this study can be classified as:

(a) determine the independent calcination characteristics of a high reactivity CaCO$_3$ (HRC) under upper-furnace conditions (850-1200°C) and at very small residence times; investigate the influence of calcination on internal pore structure development; simulate calcination and sintering behavior using a grain-micrograin mathematical model.

(b) investigate the sulfation activity of the high reactivity CaCO$_3$ (HRC) at short residence times and in the temperature window of 850-1200°C; determine the effect of sulfation on sorbent structure and develop a fundamental understanding for its enhanced reactivity.

(c) propose a comprehensive model to simulate simultaneous calcination, sintering and sulfation, taking into account various dominating mechanisms.

(d) extend the methodology developed for making high reactivity CaCO$_3$ (HRC) to reactivation of partially utilized/spent Ca-based sorbents.

(e) develop a methodology for removal of arsenic species (specifically oxides) from flue gases at elevated temperatures and propose a mechanism for its interaction with calcium-based sorbents.

The following delineates the organization of the subject matter into different chapters and their significance/relevance.
Chapter II lays the foundation for chapters III, IV, V, and VI. It details the “chain of events” and the overall “thought process” that lead to the effort of making a high-reactivity calcium-based sorbent. It gives details of how the sorbent is prepared and summarizes some of its physical characteristics that distinguish it from other Ca-based sorbents. It also provides a snapshot of its capabilities. Chapter II provides answers to questions such as: Can modified sorbents improve the fate of DSI/FSI techniques? What needs to be modified in conventional sorbents to improve their reactivity? Why and how does one modify limestone particles? Furthermore it provides the foundation for answering the question, in chapters III to V, if indeed these modifications make an impact on flue gas desulfurization by DSI/FSI?

Chapter III describes the operation and design of the experimental set-up used for studying the calcination, sintering and sulfation characteristics of the high-reactivity CaCO₃ (HRC) sorbent at very short-contact times. Study of HRC calcination behavior and the kinetics of the calcination reaction form the backbone of this chapter. The interaction of calcination and sintering and their opposing effects on the surface area evolution and pore structure development is illustrated to provide an insight into subsequent sulfation characteristics (Chapter IV) of this sorbent. Effect of sorbent particle size and reaction parameter, viz. temperature, on the overall surface area development is also featured in Chapter III. The results of calcination and sintering behavior of HRC are simulated using a mathematical model (Ghosh-Dastidar et al. 1995). The model visualizes the CaCO₃ particles to be composed of spherical non-porous grains. The calcination product, CaO, is visualized as micrograins surrounding the uncalcined core of CaCO₃ in each of the grains. The sintering phenomena is taken into account by
allowing the micrograins to coalesce to form bigger micrograin and thus reducing the overall surface area of the particle. The model fit of the experimental kinetic and surface area data, along with predicted kinetic parameters, such as activation energies for calcination and sintering steps, are also presented in Chapter III.

Chapter IV is devoted to studying the sulfation characteristics of HRC. This chapter identifies various factors that contribute to the phenomenally high reaction rates and reactivity shown by HRC. Simultaneous calcination and sulfation studies at short contact times are the main focus of this chapter. Reactivity of Ca-based sorbents towards SO$_2$ is dependent on the pore-volume, pore-size and surface area distribution changes that occur with calcination and sulfation. The distribution of pore sizes and surface area play a crucial role since the filling and pore mouth plugging of small pores (high surface area contribution) leads to tremendous resistance to SO$_2$ diffusion into the particles and causes eventual termination of the reaction.

In Chapter IV special emphasis is placed on studying the overall sulfation characteristics of the sorbent against a backdrop of structural changes. This chapter discusses some of the advantages of having mesoporous sorbent particles and tries to explain the high reactivity shown by HRC on the basis of its pore structure which mimics the mesoporous structure. For the sake of comparison and to further illustrate the important role of internal structure, sulfation characteristics of similar size conventional calcium-based sorbents particles, under identical reaction conditions, are also given in Chapter IV. Since sulfation reaction of sorbent particles is extremely fast ("damage" to particle reactivity is done very early and quickly) and leads to its own termination, degenerative effects of sulfation on particle internal structure are tracked for short
reaction times. Sulfation characteristics are studied under isothermal conditions with particular attention given to the first 100 milliseconds of the reaction. The influence of sulfation in lowering the porosity and the possible particle expansion is theoretically analyzed.

Chapter V describes the development of a comprehensive calcination, sintering and sulfation model to simulate the kinetics of the overall sulfation process of calcium-based sorbents. The model is built upon the concept of grain-micrograin calcination and sintering model (developed by Ghosh-Dastidar et al., 1995). Model visualizes the sulfation reaction to be taking place on the surface of micrograins developed during the calcination step. Unlike other sulfation models in literature this comprehensive model takes into account the "physics" of the reaction. Models previously proposed in the literature assume that the sulfation reaction on the CaO surface involved ionic diffusion of $SO_4^{2-}$ ions through the CaSO$_4$ product layer and the reaction takes place at the CaSO$_4$/CaO boundary. Hsia et al. (1993, 1995) have conclusively shown, through isotope and marker experiments, that the actual mechanism of the ionic diffusion involves movement of $Ca^{2+}$ and $O^{2-}$ ions outward from the unreacted CaO core, though the CaSO$_4$ product layer, and the reaction takes place at the gas/CaSO$_4$ boundary. Comprehensive model developed in this chapter accounts for the actual reaction mechanism and unlike most of the other models, is capable of simulating all the three steps, viz. calcination, sintering and sulfation, involved in the process. The model assumptions, mathematical development, solution scheme and model limitations are discussed in this chapter. The model is used to predict the sulfation characteristics of
HRC and its predictions are also compared with experimental data available in the literature for other Ca-based sorbents.

Chapters II through VI dealt with removal of SO$_2$ from hot flue gases. In Chapter II details of making HRC in the laboratory are given and Chapters III and IV explored the short time high temperature calcination and sulfation characteristics of the sorbent. Special emphasis is placed on the development of internal pore structure of the sorbent. Chapter V describes the efforts to develop a mathematical model which is capable of simulating comprehensive sulfation behavior of these sorbents and in particular, HRC.

In recent years, trace air pollutants other than SO$_2$ and NO$_x$ have come to the limelight and vigorous efforts are being made to develop a viable control technology for removal of these trace pollutants. Arsenic and arsenic species are emitted from coal-fired power plants and utility boilers in trace amounts and are being targeted for removal due to their toxic effects on both plants and animals.

Issues pertaining to the removal of trace toxic emissions from coal-fired combustors are subject of attention in Chapters VI and VII. Arsenic is chosen as the representative trace toxin found in coal. Due to the volatile nature of arsenic, it is emitted into the atmosphere in either vapor form or as condensate on the fly ash particles. Chapter VI gives the background and literature review on various trace pollutants that are emitted from fossil fuel fired power plants. This chapter discusses various trace toxins and their classification based on their volatility, their concentrations in the flue gas, their interactions with other flue gas species, and their speciation before and after emission from the stack. Some trace emission control methodologies are also discussed along with the possible mechanisms that could enhance the removal of these trace pollutants.
Chapter VII describes design and development of a differential bed reactor system for studying interaction of vapor phase arsenic species with different mineral sorbents. One of the unique features of the system is a high sensitivity microbalance equipped vapor-generating unit. A high temperature furnace and valve arrangement along with a custom designed sorbent bed holder, improve reactor differential conditions and reduce external mass transfer resistance. Sorbent screening tests are performed with various mineral sorbents including alumino-silicates, silicates, and calcium-based sorbents in the medium and high temperature ranges. Results of thorough arsenic sorption studies with Ca(OH)$_2$ and various analytical investigations are discussed to identify interaction mechanism between lime and arsenic oxide in Chapter VII.

Conclusions and contribution of this research work are delineated in Chapter VIII. Some recommendations for the future work are also suggested in this chapter.
Figure 1.1: Schematic of a typical Pulverized Coal Combustion (PCC) unit.
CHAPTER 2

HIGH REACTIVITY CaCO₃: BACKGROUND

The contents of this chapter have been published as an article in *Ind. Eng. Chem. Res.* (S.-H. Wei, S. Mahuli, R. Agnihotri, and L.-S. Fan; Vol. 36, 1997).

2.1 Introduction

Injection of calcium-based sorbents to the upper-furnace region of a coal-fired boiler has been widely studied as a potential cost-effective alternative to more expensive SO₂ emission control techniques for utility plants. In spite of the many attractive features it offers, interest in this technology has been declining in recent years due to findings by a number of researchers that sulfur capture with known pure and modified sorbents falls short of the 90 to 95% sulfur removal goal. Even though promoting hydroxide or carbonate sorbents with chemical or structural modifiers has resulted in improved sulfur capture, only a maximum of about 70% sulfur removal (at Ca/S = 2) has been achieved with such modified sorbents in laboratory and pilot scale studies (Bortz and Flament, 1985; Overmoe et al., 1985; Beittel et al., 1985). However, recent studies by Bjerle et al. (1991a; 1991b) have demonstrated that use of a particular high surface-area limestone (Forsby Carbonate, FC) resulted in more than 95% sulfur removal within 2 seconds in an entrained-flow reactor for a Ca/S ratio of 2, indicating a sorbent utilization of about 50%. A comparison with other
sorbents reveals the true significance of this finding, since most other sorbents, pure or modified, have been reported to achieve a sorbent utilization of only 35% or less under the entrained condition of the upper furnace, which allows a maximum of 1-2 s for the reaction to occur in the favorable temperature range of 800-1200 °C.

The reasons for such superior reactivity exhibited by this particular carbonate powder are not fully understood. One property which distinguishes this sorbent from most other carbonate powders is its relatively high initial surface area measuring to be around 12 m²/g, compared to only 1-3 m²/g for most other calcium carbonates. However, a number of calcium hydroxide powders possess initial surface areas equal or more than that of Forsby carbonate, but fail to match its high reactivity. Ye (1994) compared Forsby’s sulfation rate with other high surface-area carbonates and concluded that smaller particle size is responsible for higher utilization of the former. In contrast, some prior reaction studies with less than 1-3 μm particles, failed to produce high conversions for various hydroxide, carbonate, and dolomitic sorbents, suggesting that small particle size alone probably can not explain such high utilization of the carbonate powder.

A review of the prior work in the field of high-temperature sorbent injection reveals that there are a number of factors, all of which play crucial roles to determine the overall reactivity (conversion of Ca to CaSO₄) of a sorbent. Particle size is a significant parameter because larger size induces transport limitations for both calcination and sulfation reactions, which severely retards the reaction rate. Calcium oxide generated from sorbent decomposition also sinters at different rates depending on the initial sorbent type and foreign ion concentration in the parent solid (Borgwardt, 1989). Sintering, being a deactivation phenomenon reduces the available surface area and porosity for sulfation reaction and
therefore the rate at which CaO sinters greatly influences the rate of sulfation. Equally important for the sulfation rate and final sorbent utilization is the pore size distribution of the nascent CaO and possibly of its sintered form. Gullett and Bruce (1987) propose that there exists an optimum pore size range (100-200 Å diameter) which provides sufficient surface area for the sulfation reaction without causing rapid pore filling and pore-mouth plugging, a major reason for premature reaction termination in very small pores. On the other hand, for pores larger than 200 Å, surface area to pore volume ratio progressively diminishes, and their contribution to the overall sulfation rate becomes insignificant. Hence, relative advantage of one sorbent over another may be caused by one or more of these important chemical and structural parameters. For a highly reactive sorbent, all these factors are expected to work in unison to maximize the extent of final sulfur capture. In other words, the most effective sorbent should meet the necessary criteria of small particle size, slower sintering rate, and a favorable pore structure.

Considering Forsby Carbonate (FC) as the blueprint for an effective Ca-base sorbent for SO\textsubscript{2} removal Fan et al. (1995) have developed a high reactivity CaCO\textsubscript{3} sorbent (HRC) on the basis of criteria mentioned above. Such calcium carbonate powder with maximization of the surface area and of the surface area to pore volume ratio leads to generation of CaO with maximization of pores in the 50-200 Å size range. This powder is prepared by precipitation process in a three-phase reactor system by bubbling CO\textsubscript{2} through a Ca(OH)\textsubscript{2} suspension in the presence of certain additives.

Precipitated calcium carbonate is extensively produced for industrial uses such as fillers, extenders, diluents and inerts in the paper, paints, cosmetics, pesticides, pharmaceuticals, and plastics manufacturing industries. The behavior of CaCO\textsubscript{3}
precipitation using CO$_2$ bubbling through Ca(OH)$_2$ solution has been reported in the literature. However, most of the studies were directed towards optimizing the properties of the carbonate that are crucial for the above applications, such as the fineness of particle size, uniformity of product size distribution, optical properties and product purity. Moreover, a number of studies are conducted in a stirred tank mixed suspension, mixed product removal (MSMPR) crystallizer which is based on a liquid-liquid phase reaction (Maruscak et al., 1971; Swinney et al., 1982; Hostomoskey and Jones, 1991; Tai and Chen, 1995). Although the influence of different operating parameters on the properties of the precipitated calcium carbonate has been studied, an understanding of the surface area and porosity aspects of the precipitated products is generally lacking. This lack of investigation is attributed to the knowledge gap regarding the influence of pore structure properties on sulfation.

2.2 Making of High Reactivity CaCO$_3$ (HRC)

The high surface area CaCO$_3$ (HRC) is produced from an aqueous suspension of calcium hydroxide by bubbling CO$_2$ (Wei, 1996). Carbonate particles with surface areas in the range of 10-70 m$^2$/g have been generated, and the influence of the suspension concentration, the gas flow rate and surfactant has been studied. The BET surface area of the product is seen to increase with increasing Ca(OH)$_2$ concentration in the slurry in the range of 0.16 wt.% to 2.56 wt.%. Pure CO$_2$ is used to generate these particles and the gas flow varies in the range of 2-5 scfh depending on the solids loading. The presence of a small quantity of anionic surfactant is seen to dramatically increase the surface area and porosity (Wei et al., 1997).
A schematic of the set-up used for carbonation is shown in Figure 2.1. The Pyrex reactor is 64 mm in diameter and 380 mm high. A sintered glass plate with a pore opening of 25 to 50 \(\mu m\) (ASTM Por C) is used as the gas distributor. An aqueous suspension of calcium hydroxide (industrial grade) of various concentrations is prepared and reacted batchwise with pure CO\(_2\) gas which is introduced from the bottom of the reactor. Dispex N40V, Dispex A40 (Allied Colloids) and Lignosite 100 (Georgia Pacific) are the surfactants used ranging in concentrations from 2 to 16 wt\% (based on the weight of calcium hydroxide used).

### 2.3 Characterization of High Reactivity CaCO\(_3\) (HRC)

High reactivity CaCO\(_3\) (HRC) is characterized for various physical properties that are known to play an important part in gas-solid reactions details of which are given elsewhere (Wei, 1996). The particle size distributions of carbonation products are measured by Sedigraph 5100 (Micromeritics). The particles sampled from the reactor are filtered by #1 filter paper and dried in a vacuum oven at 75°C for 24 hours. Figure 2.2 gives the particle size distribution of precipitated CaCO\(_3\) produced under specific conditions. A thermogravimetric analyzer (Perkin Elmer) is used to determine the conversions of calcium hydroxide during the carbonation reaction. The surface areas are measured by the low temperature nitrogen adsorption using the BET technique (Quantachrome). Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) are used to study the crystal structure and composition of the precipitated CaCO\(_3\). Surface morphology and crystal structure of HRC suggest a predominantly calcitic structure as shown in Figure 2.3.
2.4 High Reactivity CaCO₃ (HRC) utilization during sulfation

The reactivity and sorbent utilization of the precipitated CaCO₃ is investigated and compared with commercially available carbonates and hydrates under identical conditions. The chemical composition and internal pore properties of 3 high reactivity CaCO₃ sorbents (HRC1, HRC2, and HRC3), commercial Linwood calcium carbonate (LC), and Linwood hydrate (LH) are given in Table 2.1. Sulfation investigations are conducted in a differential fixed-bed reactor assembly shown in Figure 2.2. The main components include a 2.5 cm o.d. ceramic reactor tube housed in a single zone vertical hinge furnace (Thermcraft). The reactor accommodates a custom-designed sorbent bed holder (0.5 cm i.d.) which enters from the bottom. The sulfation experiments are conducted by dispersing a very small amount of sorbent (about 20 mg) on quartz wool and using a high reactant gas flow rate of 1.6 lpm through the sorbent bed. This ensures minimal external transport resistances. The sorbent is precalcined by maintaining the sorbent at the desired reaction temperature (800-1000°C) inside the reactor under inert nitrogen flow for 10 minutes before exposing to SO₂. The composition of the reactant gas used is 3900 ppm SO₂, 5.45% O₂ and balance N₂. The sorbent utilization following 30 min of sulfation at 900°C are presented in Figure 2.5. The precipitated carbonates exhibit conversion much higher than the commercial sorbents. The HRC1 shows nearly complete sorbent conversion of 98% while the commercial hydrate and carbonate show only 51% and 42% respectively. The HRC3 carbonate, with the surface area and pore volume similar to the Linwood hydrate exhibits much higher conversion than the commercial sorbents. Thus, for similar pore properties, carbonate shows higher conversion than hydrate, which can be explained as follows. Borgwardt and Bruce
(1986) have shown that at high temperatures, CaO derived from carbonate exhibits less surface area loss than hydrate-derived CaO due to lower sintering rate. Ghosh-Dastidar et al. (1996) compared the calcination and sulfation characteristics of Linwood carbonate and hydrate and showed greater surface area retention by carbonate at 1080°C. However, most of the surface area of the calcined carbonate resides in the small pores (< 50 Å”) which are prone to pore filling and clogging. As a result, the low surface area Linwood carbonate shows lower sulfation than the hydrate. The precipitated carbonates, with their higher surface area and a more open pore structure therefore exhibit higher utilization.

In order to further illustrate the role of structural properties in imparting high reactivity to precipitated CaCO₃ (HRC), short-time calcination and sulfation studies are carried out in a high-temperature, entrained-flow reactor and results are compared with the performances of more conventional Ca-based sorbents under identical experimental conditions. Structural evolution and subsequent reaction effects on surface area, pore volume, and pore size distribution are examined for reaction times less than 100 ms, which are used to elucidate the reasons for high reactivity. Details of these studies are presented in the subsequent chapters. Chapter III describes the calcination characteristics of high reactivity CaCO₃ and traces the development of porous structure, which is conducive to high reactivity towards SO₂. A grain-micrograin model is proposed to simulate the calcination behavior. Chapter IV discusses the sulfation characteristics of CaCO₃ and explores the effect of sulfation on the structure of CaCO₃.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Linwood hydrate&lt;sup&gt;a&lt;/sup&gt; (LH)</th>
<th>Linwood carbonate (LC)</th>
<th>Forsby carbonate&lt;sup&gt;b&lt;/sup&gt; (FC)</th>
<th>In-house Carbonate (HRC1)</th>
<th>In-house carbonate (HRC2)</th>
<th>In-house carbonate (HRC3)</th>
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<tr>
<td>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>94.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>CaO</td>
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<td>-</td>
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<tr>
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<tr>
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<td>-</td>
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<td>0.044</td>
<td>0.180</td>
<td>0.085</td>
<td>0.108</td>
</tr>
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<sup>a</sup> Linwood Mining and Minerals Co.
<sup>b</sup> Carbital Co., Sweden.

Table 2.1: Chemical composition & initial structural properties of sorbents investigated.
Figure 2.1: Schematic of experimental set-up for HRC production.
Figure 2.2: Particle size distribution of different CaCO$_3$ sorbents prepared under different carbonation conditions.
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Figure 2.4: Schematics of differential bed reactor system for sorbent utilization studies.
Figure 2.5: Comparison of sorbent utilization of various sorbents following 30 min. of sulfation in a differential bed reactor.

Reaction temp.: 900°C; Particle size: <45 μm; SO₂ conc.: 3900 ppm
CHAPTER 3

CALCINATION AND SINTERING OF HIGH REACTIVITY CaCO$_3$ (HRC):
EXPERIMENTAL AND MODELING

Most of the contents of this chapter (except for the section 3.5 describing the Simulation of Calcination and Sintering Behavior) have been published as a paper in the *AIChE Journal* (with S. Mahuli, S. Chauk, S. Wei, A. Ghosh-Dastidar, and L.-S. Fan, Vol. 43, No. 9, 1997).

3.1 Introduction

In this chapter, results of short-time calcination studies carried out in a high-temperature, entrained-flow reactor for an in-house developed CaCO$_3$ (HRC) are presented. Structural evolution and subsequent reaction effects on surface area, pore volume, and pore size distribution are examined for reaction times less than 100 ms, which are used to elucidate the reasons for high reactivity.

Calcium-based sorbent powders (carbonate, CaCO$_3$ or hydrate, Ca(OH)$_2$) used in the high temperature removal of SO$_2$ from combustion systems suffer from rapid loss of reactivity and incomplete utilization. The calcium conversion reaches a maximum of only about 35% under the high temperature conditions (850-1100°C) of the combustor.
Even though promoting these pure sorbents with chemical or structural modifiers has resulted in improved sulfur capture, only a maximum of about 75% sulfur removal (at Ca/S = 2) has been achieved with such modified sorbents in laboratory and pilot scale studies.

Sintering of CaO is a concomitant deactivation phenomenon which reduces the available surface area and porosity of the calcined sorbent for sulfation reaction. There are a number of factors involved, all of which play a crucial role, in determining the rate of sulfation and the overall conversion of the sorbent. The particle size is a significant parameter since larger sizes induce transport limitations for both calcination and sulfation reactions. For particles smaller than 5 μm, the size ceases to be a determining factor in the overall reactivity (Milne et al., 1990). The CaO sintering rate is strongly influenced by the initial sorbent type and the foreign ions or impurities in the solid (Borgwardt, 1989). The CaO derived from carbonate (c-CaO) sinters slower than hydroxide-derived CaO (h-CaO), and the presence of certain foreign (aliovalent) ions accelerates the rate of sintering. Equally important is the pore size distribution of the parent sorbent and of the CaO. Gullet and Bruce (1987) proposed that there exists an optimum pore size range which provides sufficient surface area for the sulfation reaction, without causing rapid pore-filling and pore-mouth plugging, reasons for the premature reaction termination in small pores. On the other hand, for large pores, the surface area to pore volume ratio progressively diminishes, and their contribution to overall sulfation rate becomes less significant. Hence, the relative advantage of one sorbent over another may be caused by one or more of these important chemical and structural parameters. An effective sorbent should meet the necessary criteria of small particle size, slow sintering rate, and a favorable pore size structure.
In both laboratory and pilot-scale studies (Milne et al., 1990), hydroxides have shown consistently higher sulfur capture than the carbonates. The commercial limestone powder used in the SO$_2$ capture is usually non-porous and possesses a very low surface area (less than 3 m$^2$/g). On the other hand, the typical calcium hydroxide sorbents possess an initial surface area of 12-18 m$^2$/g. Ghosh-Dastidar et al. (1996) have shown that the calcines (c-CaO) generated by the calcination of the CaCO$_3$ possess high surface area but their pores lie predominantly in the less than 50 Å range. These pores are very susceptible to blockage and plugging leading to premature termination of sulfation. Calcine (h-CaO) derived from Ca(OH)$_2$ exhibits larger pore sizes, however, it also sinters at a much faster rate than c-CaO leading to rapid loss of surface area and subsequent deactivation (Ghosh-Dastidar et al., 1996). As a result, both calcium-based sorbents exhibit rapid deactivation and incomplete utilization. Investigations with promoted hydrates with high surface area did not exhibit much improvement in overall reactivity either (Kirchgessner and Jozewicz, 1989). Sintering is proportional to the surface area so the high surface area hydrate-derived CaO also deactivated faster (Mahuli, 1995).

The arguments made above suggest that if the calcium carbonate could be modified to a more open initial pore structure, it would lose its surface area due to sintering at a lower rate and could yield higher sulfur capture than the hydrate particles. Ghosh-Dastidar et al. (1996) demonstrated that a particular high surface-area limestone (Forsby, 12 m$^2$/g) exhibited very high sorbent conversion of about 50% in about 0.5 seconds. They showed that the Forsby carbonate’s initial high surface area and associated pore structure translated into an optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity.
Ye et al. (1995) also compared Forsby with another high surface area carbonate and concluded that the Forsby's high reactivity was due to its large surface area and pore volume located in pores >50 Å.

A high reactivity calcium carbonated is produced in the laboratory from precipitation process that has shown very high reactivity towards SO$_2$ (described in Chapter II). Since one of the applications of this high reactivity sorbent is in removal of SO$_2$ from pulverized coal combustors where the typical residence time in the desired temperature window is less than 1 s the sorbent needs to be characterized for its short-contact time behavior. Further more, it is known that the calcination of calcium-based sorbents is an extremely fast reaction with more than 80% completion in less than 100 ms at temperatures greater than 900°C. Thus, in order to gather any meaningful information it is pertinent that this reaction and its subsequent effects be studied in time-scales that are in the order of milliseconds.

Before delving into the sulfation characteristics of HRC, the calcination and sintering behavior of the sorbent (HRC) are studied and compared with the other conventional Ca-based sorbents under entrained flow conditions. Surface and pore structure, which holds the key to the reactivity of the sorbent, evolves during calcination step and is greatly influenced by sintering (both thermal and CO$_2$/H$_2$O induced). In the next section details of the experimental set-up, used for obtaining short-contact time calcination and sintering kinetic data, are presented. The calcination and sintering behavior of high reactivity sorbent is reported in section 3.4. Particular emphasis is placed on analyzing short-contact time data (less than 200 ms) to reveal the time-resolved evolution of internal
pore structure. A grain-micrograin model is applied to simulate the calcination and sintering characteristics.

3.2 Experimental set-up

In this section, the experimental set-up used for studying the ultra-fast calcination and sintering behavior of calcium-based sorbent is described in details. The rationale behind the development of a new high-temperature, short-contact time flow reactor is to examine gas-sorbent reaction kinetics for short residence times. The high-temperature, short contact-time reactor system used to accomplish the kinetic study is shown schematically in Figure 3.1 and details of the reactor system are presented elsewhere (Raghunathan et al., 1992, 1993; Ghosh-Dastidar, 1993; Mahuli, 1995). The reactor set-up consists of a furnace, the reactor tubes, a particle feeder, an injection probe, a collection probe, and a particle separation/classification system. Same experimental set-up is also used for studying the sulfation behavior of various other Ca-based sorbents but with different operating conditions. Various components of the experimental system are discussed below in detail.

3.2.1 The powder feeder system

The sorbents powders used in furnace sorbent injection are generally <10 μm in size and belong to Geldart’s Group C category. Due to their small particle size and adhesive nature these particles possess highly undesirable flow properties. Transportation of these powders to obtain a steady and stable flow is quite a difficult task. Furthermore, the sorbent powders need to be injected in high enough quantity to be easily detected by the optical techniques employed for their residence time measurement. Various feeder designs are
available in the literature (Hamor and Smith, 1971; Gullett and Gillis, 1987). While one design fails to produce a stable flow of the powders, the other provides powder concentrations too low to be detected by the optical systems. In this work, a novel powder feeder is used which performs quite satisfactorily in providing steady and low flow of powder when operated under pulse or continuous injection mode.

The feeder used in the high-temperature reactor system is a Plexiglas column with cylindrical top and conical bottom. Schematic of powder feed system is given in Figure 3.2. At the bottom of the conical section is a 1.2 cm i.d. tube fitted with a porous filter disc, which helps in distributing the feeder/fluidizing flow. Located above the powder bed is an off-take tube extending outside the column. Position of the off-take tube above the powder bed can be adjusted depending upon the height of the powder bed and the desired rate of powder feeding. The whole powder feeder assembly is attached to a vibrator. The entrained sorbent particles from the powder bed are transported by the off-take tube into the reactor. The flow through the porous disc and random vibrations from the vibrator maintain the powder in a "loosened" or locally fluidized state. The vibrator which provides irregular vibrations to the vessel also prevents channeling of fluidizing gas in the powder bed.

The sorbent particles can be fed continuously or in pulses into the reactor by means of a modified solenoid valve, adopted and modified from the design available in the literature (Hamor and Smith, 1971). In continuous operation mode, powder bed is fluidized and the entrained sorbent particles are carried into the reactor through the off-take tube. In pulse feeding mode, the outlet from the solenoid valve is connected to the injection probe of the reactor. When the solenoid is open, the powder is ejected from the feeder into the valve chamber and swept by the transport gas to the reactor. When the solenoid is closed, the
运输气体冲洗阀门以及连接到反应器的运输管，防止粉末积聚。同时，从分配器取出管的积聚通过吹扫线消除，该线会引起反向流回到分配器。因此，当电磁阀开合时，一脉冲的吸附剂粉末被注入反应器。粉末在实验中作为脉冲的列车被注射。脉冲的持续时间和脉冲的频率由连接到电磁阀的计时器控制。在粉末输送的两种模式（连续和脉冲）中，输送速率是这样的，使得粉末在反应器中的滞留时间小于0.1%。粉末输送器还有一个手动脉冲输送粉末的装置，通过注射器，来确定连续粉末输送模式下的粉末滞留时间。

3.2.2 高温流态化反应器（EFR）

高温反应器由两个同心的氧化铝管（外径分别为5.08 cm和7.62 cm）组成，它们被安置在一个3区，1500°C的林德伯格垂直炉中。炉子的加热由每个区单独控制的控制台控制。反应物气体从底部进入两管间的环形区域。气体在36英寸的加热长度上向上升，被加热到所需的反应温度，然后在顶部以120°的转弯进入内管，形成两股热气流。脉冲的吸附剂颗粒通过注射器被引入反应器，其尖端位于进入气流的上方。因此，吸附剂流由注射器尖端被热反应物气流所冲击。冲击喷射技术，被早期的研究者（Sonnet et al., 1988）成功地使用，造成显著的动量损失，创建了32

transport gas flushes the valve as well as the transport tube connected to the reactor, preventing powder accumulation. At the same time, accumulation in the off-take tube from the feeder is eliminated by the purge line which causes a reverse flow back into the feeder. Thus, as the solenoid opens and closes, a pulse of sorbent powder is injected into the reactor. The powder is injected as a train of pulses during experiments. Duration of a pulse and frequency of pulsing are controlled by a timer connected to the solenoid. In both modes of powder feeding (continuous and pulse), feeding rate is such that the powder hold-up inside the reactor is less than 0.1%. Powder feeder also has a provision for manual pulse injection of the powder, by a syringe, to determine the residence time during continuous powder feeding mode.

3.2.2 High-temperature Entrained-Flow-Reactor (EFR)

The high-temperature reactor consists of two concentric alumina tubes (5.08 cm and 7.62 cm o.d. respectively) which are housed within a 3-zone, 1500°C, Lindberg vertical furnace. Furnace heating is controlled for each zone separately by a control console. The reactant gas enters from the bottom into the annular region between the two alumina tubes. While travelling upwards through a heated length of 91.4 cm (36 inches), gases are heated up to the desired reaction temperature, and at the top make a 120° turn to enter into the inner tube as two hot jets. The details of the entrance block design are shown in Figure 3.3. Pulses of sorbent particles are introduced into the reactor by the injection probe, whose tip is located just above the incoming jets. Thus the sorbent stream from the injection probe is impacted by the hot reactant gas jets. The jet impaction technique, successfully employed by earlier researchers (Sonnet et al., 1988), causes substantial loss of momentum, creating
severe turbulence, which in turn causes rapid heating of the sorbents. Heat transfer calculations, indicate that sorbent particles of less than 10 μm size, heat up within a few milliseconds after injection into the reactor, provided the gas and solid phases are well mixed. Optical fibers housed within the injection probe detect a spike for each pulse of incoming powder, and similar optical fiber system in the collection probe detects another spike as particles are sampled. The collection probe can be moved up and down along the axis of the reactor, and hence, particles can be intercepted at various residence times. The sorbents are cooled down very rapidly in the collection probe to prevent any further reaction and eventually collected in the particle collection/classification system. The alumina reactor tubes are cooled by several cooling fans at both ends of the reactor column, which also serve to provide external convection currents.

To obtain accurate kinetic information it is necessary that the temperature profile in the reaction zone be as uniform as possible. Figure 3.4 shows the axial temperature profile in the reaction zone at two different axial locations. As can be seen from the profiles near the tip of the injection and collection points there is substantial drop in the temperature this is due to the cooling effects from the specially designed injection and collection probes. It is also evident that away from collection and injection probes the temperature profile is rather stable. Cooling effects from the injection and collection probe put a restriction on the minimum length of the reaction zone which in turn puts restriction on minimum reaction time attainable. Test runs have revealed that a reaction zone length of less than 8.75 cm (residence time of about 10 ms) doesn't give a stable uniform temperature profile and kinetic data obtained under these conditions is not reliable.
3.2.3 The probe system

Design of the probes is critical for obtaining short contact time measurements. The schematic of the collection probe assembly is shown in Figure 3.5. Figure 3.6 details the design of the collection probe assembly. The injection probe is almost similar in design with minor differences needed for probe specific operation. Each probe has an o.d. of 2.5 cm and although the injection probe remains fixed at a particular position, the collection probe can be moved up and down along the axis of the reactor tube. The sorbent particles are injected (injection probe) and sampled (collection probe) through a 3.2 mm hole along the probe center, and pass through the optical path created by an optical fiber assembly as they exit or enter the probe. Two 4.7 mm holes are located diametrically opposite to each other and each is at a distance of 7.1 mm from the probe central axis and aligned parallel to it. These two holes and the central hole are connected by a 1.6 mm opening radially to create the optical path near the probe tip. Inserted in each 4.7 mm hole is a light guide consisting of a stainless steel tube of 3.2 mm o.d., a fiber optic cable inside the steel tube and a miniature 2 mm right angle prism which is located at the top of the fiber optic cable. Each light guide can be withdrawn from the probe in case of any accidental particle deposition on the prism surface. One of the cables is connected to an illumination source, while the other is connected to a high-speed microcomputer-based data acquisition system via a photomultiplier. The optical guide design is shown in Figure 3.7 in detail. The prisms are assembled in such a way that their vertical sides face each other. The light from the illumination source travels through the fiber optic cable to the base of the prism. The prism causes a 90° turn in the light transmission at its hypotenuse due to total internal reflection, directing the light to the face of the other prism radially, where again a 90° turn directs the
light to the photomultiplier-microcomputer data acquisition system. With this optical arrangement, the solid laden gas entering the collection probe crosses the optical path between the two prisms, causing attenuation of the light transmitted.

Dry nitrogen is purged through the annular space surrounding the fiber optic cable past the prism and mixes with the central gas-solid stream. The purge gas quenches the reaction as soon as the sampled stream enters the collection probe. It also prevents powder from depositing on the prism surface and helps maintain fiber optic systems at a lower temperature. Cooling water also circulates through the probes to prevent any undesirable heating of the various parts of the probe assembly.

It has been mentioned before that the injection probe is fixed in a particular position and the collection probe is free to move along the axial path of the reactor tube. This provision makes it possible to collect particles at different residence times from the reactor. Among other differences between the two probes, there is an extra path for thermocouple insertion in the injection probe. A 1.83 m long thermocouple goes through the injection probe head and is free to move up and down inside the reactor, thus making it possible to measure temperature at different axial locations during experiments. The tips of the two probes are also of different configuration. The collection probe tip is made like a funnel to facilitate particle collection, whereas, such an arrangement is neither required nor provided in the injection probe head.

The main premise behind the design of injection and collection probe is to limit the reaction only within the reaction zone which lies between the tips of injection and collection probe. Particles coming out of the injection probe should be instantaneously heated upto the reaction temperature and the reaction should be quenched as soon as the particles enter the
collection probe. Reaction quenching is effected by cooling the particles as well as the gases coming out of the reaction zone.

The heat-up rate of particles is estimated for Ca(OH)$_2$ particles subjected to an increase in the surrounding temperature. Heat balance on a single, spherical Ca(OH)$_2$ particle accounting for convection from bulk gas, radiation from wall, and the endothermic heat of calcination reaction gives:

\[
\frac{\rho_p V_p C_p}{4\pi R_p^2} \frac{dT_p}{dt} = h(T_b - T_p) + \sigma \varepsilon_p (T_b^4 - T_p^4) - \gamma_{\text{Ca(OH)}_2} \Delta H_c \quad (3.1)
\]

The Ca(OH)$_2$ particles are assumed to be initially at room temperature as these are transported by the feeder gas (nitrogen) through the water-cooled injection probe. The hot bulk gas impinges upon the Ca(OH)$_2$ particles and due to the high bulk/transport gas ratio, the resulting feeder gas is assumed to reach the final temperature instantaneously, implying a step increase in the particle surrounding temperature to $T_b$. The surrounding gas is assumed to be stagnant (creeping flow) and the internal temperature gradients in the particle are assumed to be insignificant, since the Biot number for the small particles of interest is less than 0.1 (Holman, 1972). Earlier researchers (Alvfors and Svedberg, 1992) have also justified the assumption of a flat temperature profile for small diameter particles.

Equation (3.1) and calcination reaction rate equation are simultaneously solved for a bulk gas temperature of 1000°C, and a particle initial temperature of 27°C. The results indicate that the particles which are less than 10 μm in diameter are heated to the final temperature (1000°C) within 2 ms of injection into the hot gas stream. The cooling effect of endothermic calcination reaction is observed to be insignificant for such small particle sizes. Calculations done by other researchers (Gullett et al., 1988; Alvfors and Svedberg, 1992)
also estimated negligible heat-up times for such small particles. Additional heat transfer calculations confirm that the assumption of neglecting temperature gradient inside the particle is indeed valid.

Quenching of the reaction is achieved by rapid mixing of the hot particle/gas stream with cold nitrogen purge and by the water-cooling of the collection probe. Sufficient flow of circulating water is used to maintain the collection probe assembly at about 50°C. Considering a reaction temperature of 1100°C, temperature of the gas-particle stream drops to about 1000°C at the probe tip as seen in Figure 3.4. Upon entering the collection probe, the hot stream is mixed with two cold N₂ purge jets. Heat balance calculations are performed using reactant gas conditions of 12 lpm (STP) and 1000°C, nitrogen purge of 3 lpm (STP) at 50°C and inside wall temperature of 50°C. Further simplifying assumptions of instantaneous gas mixing, flat particle temperature and no entrance effects are similar to heat-up calculations. It is seen that the desired cooling of the gas/particle stream is also achieved within about 2 ms. Sufficient quenching of the reaction is believed to have been achieved when the gas/solid mixture attains a temperature below 500°C, since no appreciable conversion of CaO to CaSO₄ occurs below 800°C, and Ca(OH)₂ calcination is reasonably slow at temperatures less than 500°C. Experimental verification of quenching is also carried out by studying the effect of increasing purge flow on calcination. Increasing the flow rate of the cold purge from 3 lpm to 5 lpm results in no significant difference in the extent of decomposition which confirms that adequate quenching of calcination reaction is achieved with 3 lpm of nitrogen flow.

3.2.4 Particle collection/classification system
The particle collection assembly constitutes of a filter and a train of cyclones or a cascade impactor. For pulses with low solid feed, just a filter made of quartz wool is placed after the collection probe, which catches all the particles including fines. The filter is subsequently taken out of the filter holder for kinetic measurements and analysis. For pulses with higher solid feed, a train of cyclones is employed to achieve the preliminary gas-solid separation. In this case, the particles are collected/classified in both the cyclone and the filter and are analyzed for sorbent conversion. For each experimental condition, a cascade impactor can also be used instead of the cyclone train to obtain in-situ particle size distribution. The particle size distribution data is useful for investigating the particle size effect on reactivity. During sulfation experiments, the collection path stretching from the probe outlet to the filter assembly is kept heated to about 350°C to avoid any SO_{3}/H_{2}SO_{4} condensation in the line or 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’s 2-stage vacuum pump, at the end of the sampling system facilitates particle collection in the collection probe. Both the bulk outlet and collection probe outlet gas streams are monitored by flowmeters to account for the total distribution of flow.

Rehydration or recarbonation of partially calcined sorbent particles could drastically change the internal structural morphology. Since the collected sorbent particles are constantly exposed to the outgoing gases carrying some amount of CO_{2} or H_{2}O, present as a
result of calcination of CaCO₃ or Ca(OH)₂ respectively, it is important to make sure that no significant rehydration or recarbonation of collected sample takes place. In order to verify that no significant rehydration of the collected sorbent has occurred in the cascade cyclone sampler, samples of high-surface area CaO are placed in all stages of the sampler. H₂O-laden N₂ gas is passed over the CaO samples for about 30 minutes, which is the typical duration for calcination experiment. The H₂O concentration in the gas is representative of the experimental calcination conditions (based on sorbent feed rate and assuming 100% calcination). A maximum of 3-5% rehydration is observed with this high-surface area CaO, which confirms that during calcination run, rehydration is not significant in the collection system. Similar investigations are also performed to determine the extent of recarbonation of CaO.

3.2.5 Data acquisition system

The fiber optic cables are connected to photomultiplier which convert the light intensity to a voltage signal. These photomultiplier are interfaced with Laser 80386 AT computer via a Metrabyte DAS-16 data acquisition system. Typical frequency of sampling of the optical signals is 1000 to 2000 Hz.

3.3 Experimental procedure and operating conditions

3.3.1 Sorbent preparation

Apart from high reactivity carbonate (HRC), three other calcium based sorbents are studied. The calcination characteristics of high reactivity carbonate sorbent are compared with a commercial carbonate (Linwood CaCO₃, obtained from Linwood Mineral and
Mining Co.) and another high surface area carbonate (Forsby carbonate). In addition, a modified calcium hydroxide with pore properties similar to the high reactivity calcium carbonate is also studied for comparison.

The Forsby carbonate (FC) is received as slurry from Carbitol Co. in Sweden, and is dried and ground, while Linwood carbonate (LC) is used in its as-received form. In order to prepare the modified hydroxide (MH), the as-received Linwood calcium hydroxide powder (from Linwood Mineral and mining Co.) is calcined at 600°C and then rehydrated in excess water containing dissolved calcium lignosulfonate surfactant (from Georgia-Pacific Corp.). The surfactant is added in such a quantity that the final hydroxide product has 1.5% mass concentration of the lignosulfonate, reported to be optimum by previous investigators (Kirchgessner and Lorrain, 1987). Preparation method of high reactivity carbonate is described in Chapter II and in Wei et al. (1997).

3.3.2 Calcination experiments

During calcination experiments, bulk gas constitutes only of nitrogen. 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 the reaction temperature. After a desired residence time, the partially reacted mixture is sampled by the collection probe, immediately quenched, and passes 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.
For all the calcination experiments, 10 lpm (STP) of bulk gas (nitrogen) is preheated by passing it through the annular region of the reactor assembly as illustrated in Figure 3.8. 1 lpm (STP) of N₂ gas flow is used for each of the feeder fluidizing flow and the injection probe purge. 2 lpm (STP) and 3 lpm (STP) of N₂ are used as quench gases and purges through the injection and the collection probes respectively. The bulk outlet of the reactor is kept closed during the experiment and all the 15 lpm (STP) of gas is drawn through the sampling line.

3.3.3 On-line estimation of particle residence time

As mentioned before, for the purpose of determining the particle residence time during reactor operation, the sorbent particles are injected into the high-temperature environment as a train of pulses through the injection probe. During continuous powder feeding mode, for residence time measurements, the fluidizing flow is diverted through a by-pass line, and pulse injection of solids is done manually by a syringe in the feeder line. Just before a pulse of particles enters the reaction zone, it crosses optical path located at the tip of the injection probe. Since these solids cause attenuation of the transmitted light, the flowing powder pulse produces a spike in the optical signals measured. After a certain residence time in the reactor column, the pulse enters the collection probe, and during entry produces another spike in the signal. The time delay between these two spikes is the residence time of the solids in the reactor.

A statistically sound procedure for estimation of time lag is through cross-correlation functions. The cross-correlation \( r_{xy}(\tau) \) between two signals \( x(t) \) and \( y(t+\tau) \) is given by:

\[
r_{xy} = \int_{0}^{\infty} x(t)y(t+\tau)\,dt
\]  

(3.2)
The first maximum in $r_{xy}(\tau)$ occurs at the value of $\tau$ which is the time lag between the two signals. For signals with large number of data points, $r_{xy}$ can be computed rapidly via Fast Fourier Transforms (FFT). The Fourier transform of Equation (3.2) gives:

$$R_{xy}(f) = X(f)Y^*(f)$$  \hspace{1cm} (3.3)

Where, $X(f)$, $Y(f)$ and $R_{xy}(f)$ are the Fourier transforms of $x(t)$, $y(t)$ and $r_{xy}(t)$, respectively, $f$ is the frequency variable, and $Y^*(f)$ is the complex conjugate of $Y(f)$. Thus, from the FFT of $x(t)$ and $y(t)$, $R_{xy}(f)$ is evaluated using Equation (3.3). Inverse FFT of $R_{xy}(f)$ yields $r_{xy}(t)$. Since the first maximum in $r_{xy}(t)$ occurs at the time lag between the two probe signals $x(t)$ and $y(t)$, the residence time of solids in the reactor is known. Computation of cross-correlation using FFT is much faster than direct evaluation using Equation (3.3), hence is preferred for on-line estimation.

Optical signal assembly and data acquisition system are used to collect residence time data for various experimental runs. For a representative run, using the conventional entrance configurations, the two probe signals and their cross-correlation functions are shown in Figure 3.9. The maximum in the cross-correlation function occurs at 40 milliseconds, measuring the residence time of solids in the reactor for this run. The accuracy of estimation of the residence time is about 0.5 ms, which can be further improved by increasing the sampling frequency of the signals. As seen from this figure, time lag between the signals is too small to be estimated from a visual observation of the two signals.

With this approach for short contact time measurements, iso-kinetic sampling is not necessary, nor is the precise knowledge of the fluid dynamics in the reactor required. This method is accurate and imposes no restrictions or assumptions regarding the flow patterns.
3.3.4 Post-reaction analyses of data for reaction kinetics

The particle collection system has already been discussed in detail in the previous section. Conducting the experiments at a specific particle residence time, enough sample is collected for subsequent kinetic analysis. Thermogravimetric analyzer (TGA) is used for obtaining the extent of calcination reaction and other information pertaining to reaction kinetics. The partially calcined sample is further calcined to 100% decomposition in a TGA, and the back calculation gives the degree of calcination achieved within the entrained flow reactor. Using the cascade cyclone sampler for each experimental condition particles of various sizes are collected, and from the analysis of particles of different size groups, information on particle size effect is obtained.

In any gas-solid non-catalytic reaction study, particle morphology plays an important part. Determination of particle structural properties, such as specific surface area of the particle, its porosity and pore size distribution is essential to a better understanding of the reaction mechanism. Quantitative information regarding structural properties (such as, surface area, pore volume, and pore size distribution) of sorbent particles is obtained by using BET low-temperature nitrogen adsorption method. Scanning Electron Microscopy (SEM) is used to get qualitative information regarding sorbent particle structure and surface morphology.

3.4 Calcination and sintering characteristics: Kinetics and structural evolution

Since the external diffusional limitations do not play any role in dictating the sulfation characteristics of these small size particles, the factors influencing the sulfation behavior must be associated with CaO internal structure which develops from the
decomposition reaction and alters with sintering and sulfation. Of primary interest should be the pore structure data of first 50 ms, in which bulk of the sorbent conversion is completed and also the extent of succeeding sulfation reaction rate is determined.

3.4.1 Calcination and structure pore evolution of HRC

The calcination kinetics and surface area and pore structure distribution changes are studied for HRC in order to gain insights into its high reactivity and to quantize the effects of temperature. Figure 3.10 shows the extents of calcination and Figure 3.11 shows the corresponding surface area of the partially calcined HRC particles. Calcination of HRC exhibits a very high initial rate of decomposition and nearly 75% of the ultimate calcination is achieved in the first 50 ms. Almost complete calcination is achieved at 1080 and 1000°C, but 900°C exhibits a slower rate of calcination and reaches only about 85% calcination even after 600 ms. The strong influence of sintering is clearly visible at 1080°C which shows a very high rate of surface area loss even at short contact times. This indicates that the surface area loss due to sintering more than compensates for the additional surface area being produced by the calcination reaction. The rate of sintering is strongly dependent on the surface area of the sintering CaO and is accepted to follow second-order kinetics as proposed by Nicholson’s (1965) model (Ghosh-Dastidar et al., 1995; Mai and Edgar, 1989; Silcox et al., 1989):

\[ \frac{dS}{dt} = -k_{\text{sin}}(S - S_a)^2 \]  

(3.4)

where, S is the surface area at time t, \( S_a \) is the asymptotic surface area, and \( k_{\text{sin}} \) is the specific sintering rate constant. Due to the high surface area of the HRC itself, the surface area of its
nascent calcine can be expected to be very high. As a result, the rate of surface area
reduction is the highest in the initial few milliseconds, when the surface area of the nascent
calcine is the greatest. At higher residence times, the surface area approaches the
asymptotic value and the rate of sintering is much slower. On the contrary, 900°C shows a
maxima in the surface area at about 34 ms in spite of the calcination extent being 76%.

Figure 3.12 shows the variation of the total pore volume with time. The pore
volume is seen to increase for all the three temperatures initially. However, the increase is
not commensurate with the theoretically predicted amount of pore volume based on the
molar volumes of CaCO₃ and CaO. This indicates that sintering does consume a substantial
amount of the pore volume. Moreover, sintering also leads to a disappearance of the small
pores which combine to yield larger pores, thus shifting the pore size distribution towards
larger sizes. This might give rise to pores larger than 500 Å in diameter. Measurement of
such large pore sizes would entail interference with the interparticle voids and moreover,
such large pores contribute negligible surface area for the sulfation reaction. The desorption
isotherm is used for pore size distribution calculations and the Kelvin equation forms the
basis for determining the pore size distribution:

\[ r_p - t = \frac{2 \gamma V_L}{RT \ln \left( \frac{P_o}{P} \right)} \quad (3.5) \]

where \( r_p \) indicates the actual radius of the pore in which condensation occurs at a relative
pressure of \( P/P_o \) and \( t \) is the thickness of the adsorbed film. At the relative \( N_2 \) pressure of
0.96, all the pores of sizes up to 252 Å are assumed to be completely filled and this
corresponds to the total pore volume of the solid. The pore volume distribution after 20 ms
of calcination is similar at all the three temperatures. This indicates that the primary
difference between the 3 temperatures is due to the surface area evolution. The results
obtained at 1000°C show a similar rate of calcination and a higher surface area retention
when compared to 1080°C results which would lead to comparable rates of sulfation in the
initial 50 ms. At longer times, HRC calcined at 1000°C is seen to possess higher surface
area (Fig. 3.11) as well as pore volume (Fig. 3.12) than at 1080°C.

SEM analyses are conducted to complement the studies of structural changes
accompanying the simultaneous calcination and sintering. Figure 3.13 shows the scanning
electron micrographs of original HRC and HRC calcined at 900°C for 600 ms. The
calcium-based sorbents undergo size variations due to fragmentation and/or agglomeration
in the high temperature reaction environment. In order to analyze the mechanical strength
and fracturability of the HRC particles, the effect of high temperature environment on the
particle size distribution of the HRC is studied using Sedigraph analysis of the original HRC
and of the partially calcined HRC following 170 ms of calcination at 1000°C. Hu and
Scaroni (1995) have shown that calcination and subsequent CO₂ pressure build-up within
the particles can lead to fragmentation. They studied particle sizes between 37-105 μm and
found that the dolomitic carbonates were more susceptible to fragmentation than the
carbonate particles. However, in the case of small particle sizes (< 10 μm), agglomeration
can take place during fluidization in the particle feeder unit and break-up may occur during
transport due to the fluid-shear (Ghosh-Dastidar et al., 1994; Lee and Fan, 1993). All these
factors together dictate the particle size distribution and its variations. The particle size
distribution of calcined HRC is found to change only slightly from the original HRC. The
fragmentation tendency due to CO\textsubscript{2} pressure build-up can be discounted in the case of HRC due to its small particle size and its high porosity.

### 3.4.2 Comparison with other sorbents

In order to explain the high reactivity of the HRC, its pore structure evolution is studied with calcination and compared with FC, LC and MH. Figure 3.14 shows the initial pore volume distributions for the sorbents. The modified hydrate and the high reactivity carbonate possess similar pore volume as well as surface area. In addition to the pore volume distribution, the distribution of surface area in various pore sizes is also investigated for the calcines. The surface area distribution is theoretically calculated from the pore size distribution (Gregg and Sing, 1982). The cumulative surface area value at any pore radius, \( r \), represents the total amount of surface area residing in the pores of radius, \( r \), or larger. The overall surface area of the calcine (\( A \)) can be calculated by summation over all size intervals as:

\[
A = \sum \frac{2V_p}{r_p}
\]

where \( V_p \) represents the actual pore volume in each size interval. For the hydrate sorbent, it is accepted that its calcine possesses a parallel-plate shaped pore structure (Gullett and Bruce, 1987). The pore volume distribution and the surface area distribution procedure for the hydrate is similar to the carbonate except the pore radius, \( r_p \), is replaced by the plate width, \( d \), and \((r_p-t)\) is replaced by \((d-2t)\) in Eq. (3.5) and (3.6) (Innes, 1957).
Figure 3.15 corresponds to the pore volume distributions after 34 ms of calcination at 1080°C and Figure 3.16 shows the corresponding surface area distributions. Calcination conversion data show that for high temperature and small particle size, there is no appreciable difference between the three carbonates and modified hydroxide in CaO generation rate (Ghosh-Dastidar et al., 1996), with all the sorbents exhibiting between 85 to 95% decomposition after 34 ms. Upon comparing the carbonates, the surface area of FC-CaO is greater than HRC-CaO and the LC-CaO also shows a high surface area. Yet the sulfation extents of the carbonates are considerably different from each other, which indicates that the surface area of the calcine alone cannot be used to predict their sulfation behavior.

Only about 35% of total pore volume of LC-calcine lies in pores > 50 Å in size, while the surface area distribution indicates only about 10% of surface area in > 50 Å pores for LC. The FC-calcine possesses about 45% of its pore volume and about 15% of its surface area in pore sizes greater than 50 Å. On the contrary, nearly 75% of the HRC-calcine pore volume lies in the 50-200 Å size range. This leads to nearly 50% of surface area in this pore size range for the HRC-calcine.

Upon comparison of the original sorbent pore volume distributions (Figure 3.14) and the distribution in their calcines after 34 ms (Figure 3.15), it can be seen that the FC shows a 4-times addition to the pore volume in the < 50 Å sizes, while the HRC shows that the pore volume in the < 50 Å sizes remains nearly unaltered. The total surface area of the HRC-CaO has reduced from 61 m²/g (original sorbent) to 42 m²/g which is lower than the FC-CaO (54 m²/g). Since the HRC-, FC- and LC-CaO are derived from carbonates of similar chemical composition, and show similar extent of decomposition, a probable explanation for
the differences in their pore volume and surface area distributions can be as follows: the original HRC possesses substantial pore volume and surface area in the smaller sizes. The nascent HRC-CaO formed in the pores < 50 Å in the initial few milliseconds possesses extremely high surface area, which cannot be sustained and is consumed rapidly by sintering. As a result, the pore structure data of HRC-calcine at 34 ms does not exhibit high surface area. The FC and the LC on the other hand, do not possess high volumes in the < 50 Å sizes and upon calcination generate pore volume and surface area which can be sustained. As a result, all the 3 carbonate calcines possess similar pore volumes in the < 50 Å range as seen in Figure 3.15.

In comparison, the MH-CaO has the lowest surface area of all the calcines and unlike the carbonate calcines its pore volume decreases from the parent sorbent. Both of these observations indicate extremely high degree of sintering. MH-CaO also shows a reduction in the 50-200 Å pores over its parent sorbent while all the three carbonate calcines exhibit an increase. In the case of MH, the high nascent surface area of its calcine combined with the higher sintering of hydrate-derived calcines lead to the poor pore properties. One possible explanation for the lower sintering rate of carbonate derived calcines, as proposed by Borgwardt (1989), is that due to differences in molar volumes between CaCO₃ and Ca(OH)₂, packing of CaO grains produced from carbonates is relatively less dense, which offers fewer contact points between these grains. Borgwardt (1989) further reported that even though the activation energies of sintering for hydroxide and carbonate calcines are comparable, the sintering rate constant for the latter is one order of magnitude less than that of the former.
Figures 3.15 and 3.16 elucidate two contributing factors which lead to the higher reactivity of HRC. Firstly, its calcine provide a high surface area and pore volume. Secondly, HRC-CaO also possesses a favorable pore size distribution, which distinguishes this sorbent from other carbonates. More than 90% of the LC calcine surface area resides in the pores smaller than 50 Å. In spite of the relatively high surface area to volume ratio this pore structure offers, pore filling and pore-mouth plugging occur predominantly in these small pores. In the event of pore-mouth plugging, further SO$_2$ access into the inner pore region is severely limited, and the sulfation rapidly dies-off (Simons and Garman, 1986; Milne and Pershing, 1987).

3.4.3 Analysis of the sorbent properties for maximizing 50-200 Å pores

Theoretical analyses of parent CaCO$_3$ pore size distribution for maximization of 50-200 Å pores in its calcine is presented below. Following discussion elucidates the importance of mesoporous calcium sorbents with regards to maintaining a favorable pore structure for sulfation even under severe sintering. Assume CaCO$_3$ with a total pore volume of $V_o$ (cc/gmol) calcines completely to CaO. Let $f_r$ be the fraction of the total pore volume in a specific size range, with $r_f$ being the average pore radius and $l_f$ being the total pore length used to represent the pore volume, $V_f$=$f_rV_o$ in that pore size range. Assuming no change in the pore length and no effect of sintering, the void volume balance for the given pore size range can be written as:

$$\pi(r_f + \Delta r)^2 l_f - \pi r_f^2 l_f = v_s - v_c \quad (3.7)$$

Since $V_f$ can be expressed as:

$$V_f = f_r V_o = \pi r_f^2 l_f \quad (3.8)$$
The equation (3.7) can then be rewritten to express the change in pore radius, $\Delta r$:

$$\Delta r = r_f \left[ \frac{1}{1 + \frac{(V_s - V_o)}{f_o V_o}} - 1 \right]$$  \hspace{1cm} (3.9)

The above analysis represents the increase in the average pore radius of a specific pore size range. For a given $V_o$, $\Delta r$ increases with decreasing $f_v$, as seen in Figure 3.17. Since maximization of the pores in the 50-200 Å in the calcine formed is desired, the above analysis can be used to provide guidelines for the sorbent pore distribution characteristics.

Consider two original sorbents of identical pore volumes $V_o$, but having different fractions of their total pore volume in the 50-200 Å size range. The sorbent with higher $f_v$ would show lower $\Delta r$, thus retaining more of the pores in the 50-200 Å size range. On the other hand, for the pores in the < 50 Å range in the original sorbent, a low $f_v$ would shift these small pores into the higher size range. Thus, a large fraction of pores in the 50-200 Å and a small fraction of pores in the < 50 Å pore sizes would represent optimum pore distribution for a sorbent.

### 3.5 Simulation of calcination and sintering behavior

#### 3.5.1 Model development

Calcination and sintering model developed by Ghosh-Dastidar et al. (1995) is used to simulate the calcination behavior of HRC. This model is based on grain-micrograin concept and assumes that each sorbent particle is made up of spherical non-porous grains of CaCO$_3$. As the sorbent calcines it forms micrograins of CaO surrounding the uncalcined CaCO$_3$ grain core. In order to take sintering into account the history of micrograin is considered and CaO micrograins that are formed at an earlier time are sintered to a larger
extent (according to Nicholson's model) thus forming different layers of micrograins which are sintered to different extents. A schematic of this model concept is given in Figure 3.18 and mathematical development of the model is briefly described below (detail development is given in Ghosh-Dastidar et al., 1995).

The calcination reaction takes place at the CaCO$_3$/CaO interface and is assumed to be first order with respect to CO$_2$ partial pressure at the carbonate core surface (Silcox et al., 1989):

$$y_{CaCO_3} = k_c \frac{(P_e - P_c)}{RT}$$  \hspace{1cm} (3.10)

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

$$\frac{dx}{dt} = \frac{3R_c^2 k_c (P_e - P_c)}{RT R_\infty^3 C_s}$$ \hspace{1cm} (3.11)

where, $k_c$ is the calcination rate constant (in m/s) and $C_s$ is the solid reactant concentration (in gmole/m$^3$). The equilibrium dissociation pressure, $P_e$ can be obtained as a function of temperature using standard thermochemical approach (Hartman and Martinovski, 1992).

The species continuity equation for product gas CO$_2$ diffusion through the product CaO, assuming the pseudo-steady state approximation can be written as:

$$\frac{\partial^2 P}{\partial r^2} + \frac{2}{r} \frac{\partial P}{\partial r} = 0$$ \hspace{1cm} (3.12)

with the following boundary conditions:

$$-D_{eff} \frac{\partial P}{\partial r} |_{r=R_c} = k_c (P_e - P_c)$$
and, \[ P_{r=R_s} = 0 \] (3.13)

Several researchers have investigated the effect of CO\textsubscript{2} pressure on CaCO\textsubscript{3} decomposition kinetics (Silcox et al., 1989; Darroudi and Searcy, 1981) and the diffusion of gaseous CO\textsubscript{2} through the porous lime. Both Knudsen and ordinary diffusion are considered important at different stages of reaction. Hence, Knudsen and ordinary diffusion coefficients are estimated and the effective diffusivity is derived from the following equations:

\[ D_{\text{eff}} = (D_k^{-1} - D_{ab}^{-1}) \varepsilon^2 \] (3.14)

S and \( \varepsilon \) are the surface area and porosity of the multilayered product shell respectively. 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 (3.14) approximates the value of calcine's tortuosity as \( \varepsilon^{-1} \), (Smith, 1981).

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

\[ \frac{dS}{dt} = -k_{\text{sin}} (S - S_a)^2 \] (3.15)

where, \( S_a \) is the asymptotic surface area of CaO at the specific sintering temperature, and \( k_{\text{sin}} \) is the sintering rate constant (in m\textsuperscript{2}/g-s).

The presence of CO\textsubscript{2} accelerates the rate of sintering of CaO (Mai and Edgar, 1989; Borwardt and Bruce, 1986). In order to account for enhanced sintering in presence of CO\textsubscript{2},
the sintering rate constant is modified according to the following proposed correlation (Milne et al., 1990):

\[
k_{sn} = k_{sn} (1 + B P^m)
\]  

(3.16)

Based on the reported work, \( m \) and \( B \) are taken as 0.6 and 1.25 respectively for \( \text{CaCO}_3 \) in this correlation.

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,

\[
S_{j,i} = S_o - \frac{l}{S_o - S_a} \left( k_{sn}(t_i - t_j) \right)
\]  

(3.17)

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:

\[
S_{\text{CaO}} = \sum_{j=1}^{\infty} S_{j,i} \times z_j
\]  

(3.18)

\[
S_s(x,t) = (x)S_{\text{CaO}} + (1-x)S_{\text{CaCO}_3}
\]  

(3.19)

where, \( z_j \) is the fraction of CaO formed during \( j \)-th time interval.

The porosity of an individual layer of CaO is assumed to be a linear function of its surface area and can be represented as:
\[ e = \varepsilon_0 \left( \frac{S - S_a}{S_o - S_a} \right) \]  \hspace{2cm} (3.20)  

where, \( \varepsilon_0 \) is the theoretical porosity of the nascent CaO.

The calcination rate Eq. (3.11) is coupled with the product CO\(_2\) continuity Eq. (3.12) and the core radius \( R_c \) is related to the solid conversion as:

\[ R_c = R_o (1 - x)^{1/3} \]  \hspace{2cm} (3.21)

The instantaneous grain radius, \( R_g \), changes as a result of both calcination and sintering which work to oppose each other. Sintering alone causes the micrograins in the grain shell to grow by combining with adjacent micrograins. The model simulates the unreacted core of each small grain to remain at the center of the new grain (Ranade and Harrison, 1981). Further, the grain size is not a function of the radial position since the model assumes negligible concentration gradients within the particle. At a given instance the grain radius can be calculated from:

\[ R_g = \frac{3}{S_i(x,t) \rho(x,t)} \]  \hspace{2cm} (3.22)

The CO\(_2\) partial pressure profile in the product layer can be obtained analytically by solving the continuity equation (3.12) with the given boundary conditions. The CO\(_2\) partial pressure at the interface of the unreacted CaCO\(_3\)/CaO can be expressed in terms of \( R_c \), \( R_g \) and \( D_{eff} \).
The calcination rate equation (3.11) is solved with the initial condition of $x=0$ at time $t=0$ using the fourth order Runge-Kutta integration scheme. This local conversion corresponds 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, $k_{	ext{sin}}$ represent the two specific rate parameters of the model.

3.5.2 Comparison of experimental data and model predictions

Figure 3.19 shows the experimental data and model prediction for calcination of 3.6 $\mu$m CaCO$_3$ particles at three different temperatures for residence times ranging from 10 to 300 ms. A similar trend is observed in all the calcination curves. Initially, calcination progresses extremely fast and exhibits a strong influence of temperature. At higher residence times, the reaction rates attenuate considerably and conversion tends to flatten out. The sharp attenuation of reaction rate at higher residence times is seen clearly from the 1353 K data which exhibits virtual ceasing of calcination at about 97%. This near 'die-off' of the reaction at higher residence times is also observed at lower temperatures of 1173 & 1273 K.

The model discussed earlier assumes that the reaction proceeds on a single CaCO$_3$ 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 CaO/CaCO$_3$ interface may be the rate limiting step. The product
CaO layer rapidly sinters losing surface area and porosity, thus offering increasing resistance for the gaseous product CO$_2$ to diffuse out through the product shell. This leads to an increase in CO$_2$ 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 CO$_2$ 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, $k_{sin}$. These rate constants are determined by trial and error procedure to obtain the best fit of the experimental data. The activation energies for calcination and sintering, obtained from the Arrhenius-type plots as shown in Figure 3.20, are 29.5 and 75.5 kcal/mole, respectively and match very well with reported values in literature (Mai and Edgar, 1989; Bortz et al, 1986).

The model fits the experimental data extremely well, closely predicting both the initial steep slope and the rate attenuation of the experimental data. The overall surface area evolution of the partially calcined HRC and model predicted values are shown in Figure 3.21. At 1173 K, surface area first increases and attains a maxima, then rapidly decreases due to sintering and tends to level off to an asymptotic value at higher residence times. At the higher temperatures of 1273 and 1353 K, experimentally observed surface area values show a monotonous decrease indicating a strong effect of sintering. The model predictions agree well with the observed trends at all temperatures. At the two lower temperatures, the model predicts an initial rise in surface area and the maxima; the predicted maxima are higher than the observed values for both the temperatures. The rapid reduction and the asymptotic leveling also match with the observed trends. At 1273 K however, the model
predicts a sharp spike in surface area at very low residence time of about 5 ms before the rapid downward trend towards the asymptotic value. This predicted sharp spike is not observed experimentally, probably due to lack of data at residence times of 10 ms or less. Surface area is predicted to decrease monotonically for calcination temperature of 1353 K.

The model also simulates the build-up of CO$_2$ partial pressure at the CaO-CaCO$_3$ interface with increasing reaction time as shown in Figure 3.22. With increasing decomposition temperature, the CO$_2$ partial pressure approaches the equilibrium dissociation value sooner, which results in an early drop in the calcination rate. This prediction is in agreement with the calcination experimental data of Figure 3.10 and 3.19, where attenuation in reaction rate is exhibited earlier at higher temperatures.

### 3.6 Conclusions

In order to fully understand the calcination and sintering behavior of calcium-based sorbents and in particular the high reactivity carbonate (HRC) it is imperative that short-contact time studies be undertaken. A novel entrained flow reactor system, capable of providing time resolved reaction kinetic data, is used to conduct extensive investigations into the calcination and sintering behavior of HRC. The results thus obtained suggest that the calcination reaction is extremely fast and is accompanied by equally fast sintering (both thermal and CO$_2$ induced). More than 90% of the final calcination conversion is obtained within the first 50 ms at all reaction temperatures.

The development of internal structural properties such as surface area, pore volume and the distributions of surface and pore volumes are critical in determining the sorbent reactivity towards SO$_2$. Initial surface area and pore volume for HRC are
significantly higher than any conventionally used calcium carbonates thus providing an initial open structure. Upon calcination HRC is found to retain its open structure thus indicating less susceptibility to sintering. Furthermore, compared to other high surface area calcium sorbents such as modified calcium hydroxides, which has very similar initial structure, HRC still exhibits better surface and pore retention properties. Pore structure evolution studies shed considerable light on the existence of “favorable” pore size distribution with show considerable pore volume in meso pores. This is manifested in providing high pore surface area for eventual sulfation with lessened pore plugging and blockage that smaller pores tend to suffer from. Results presented in this chapter suggest that the initial sorbent internal structure of HRC and its evolution during calcination step lead to formation of calcines, which would have high reactivity towards SO$_2$.

Calcination and sintering behavior of HRC is simulated fairly well by a grain-micrograin model (developed by Ghosh-Dastidar et al., 1995). The model predicted calcination extents and surface area evolution closely match the experimental results. Values of kinetic parameters, such as activation energies for calcination and sintering, obtained from the model fitting are 29.5 and 75.5 kcal/mole respectively which compare well with the values reported in the literature.
Figure 3.1: Schematic of the high temperature Entrained Flow Reactor (EFR) system.
Figure 3.2: Schematic of continuous powder feed system.
Thermocouple

Figure 3.3 Details of reactor entrance block.

Front View

Side View

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Distance of collection probe tip from entrance block bottom:
- ■ 10.16 cm
- • 20.32 cm

Figure 3.4: Typical axial temperature profile inside the reactor with an average temperature of 1323 K.
Figure 3.5: Schematic of the collection probe.
Figure 3.6: Details of collection probe design.
Figure 3.7: Design of optical guide system.
Figure 3.8: Gas flow scheme for calcination and sulfation experiments.
Figure 3.9: Schematic of cross-correlation analysis for on-line estimation of particle residence time.
Figure 3.10: Influence of temperature on calcination of HRC.
Figure 3.11: Effect of temperature on surface area evolution during calcination of HRC. Particle size: 3.6 μm
Figure 3.12: Influence of temperature on pore volume evolution during calcination of HRC. Particle size: 3.6 μm
Figure 3.13: SEM pictures; (a) Parent HRC, and (b) HRC calcined at 900°c for 600 ms.

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Figure 3.14: Comparison of initial pore volume distribution of sorbents before calcination.
Figure 3.15: Comparison of pore volume distributions after 34 ms of calcination of various sorbents at 1080 °C. Particle Size: 3.6 μm
Figure 3.16: Specific surface area distribution after 34 ms of calcination at 1080°C. Particle size: 3.6 μm
Figure 3.17: Increase in pore radius upon calcination as a function of the average pore radius. Initial volume, $V_o = 12 \text{ cc/gmol}$. 
Figure 3.18: Schematic of calcination and sintering model concept.
(a) Sorbent grain before calcination; (b) Partially calcined sorbent grain with multi-layered CaO product shell.
Figure 3.19: Experimental and modeling results showing effects of temperature on extent of HRC calcination.
Figure 3.20: Calculation of activation energies for calcination and cintering for HRC.

$E_{\text{cal}} = 29.5 \text{ Kcal/mole}$

$E_{\text{sin}} = 75.5 \text{ Kcal/mole}$
Figure 3.21: Experimental and modeling results showing effects of temperature on surface area development during HRC calcination.
Figure 3.22: Model predicted ratio of partial pressure of CO₂ and its equilibrium calcination pressure at a given temperature.
CHAPTER 4

SULFATION CHARACTERISTICS OF HIGH REACTIVITY CaCO₃

Contents of this chapter have been published as a paper in the *AIChE Journal* (with S. Mahuli, S. Chauk, S. Wei, A. Ghosh-Dastidar, and L.-S. Fan, Vol. 43, No. 9, 1997).

4.1 Introduction

In chapters II and III it was mentioned that there are a number of factors, all of which together play a crucial role in determining the rate of sulfation and the overall conversion of the sorbent. The particle size is a significant parameter since larger sizes impose transport limitations on both calcination and sulfation reactions. For particles smaller than 5 μm, the size ceases to be a determining factor in the overall reactivity (Milne et al., 1990). Equally important is the pore size distribution of the parent sorbent and of the CaO. Gullet and Bruce (1987) proposed that there exists an optimum pore size range, between 50-200 Å, which provides sufficient surface area for the sulfation reaction, without causing rapid pore filling and pore-mouth plugging which results in the premature reaction termination in small pores. For large pores, the surface area to pore volume ratio progressively diminishes, and their contribution to overall sulfation rate becomes less significant. Hence, the relative advantage of one sorbent over another may
be caused by one or more of these important chemical and structural parameters. An effective sorbent would meet the necessary criteria of slow sintering rate, small particle size, and a favorable pore size structure.

In previous laboratory studies, hydroxides have shown consistently higher sulfur capture than carbonates (Milne et al., 1990; Bruce et al., 1989). The commercial limestone powders used in the \( \text{SO}_2 \) capture are usually non-porous and possess a very low surface area (less than 3 m\(^2\)/g). On the other hand, typical calcium hydroxide sorbents possess an initial surface area of 12-18 m\(^2\)/g. Ghosh-Dastidar et al. (1996) have shown that the CaO generated by the calcination of limestone possesses high surface area but its pores lie predominantly in the less than 50 Å range. These pores are very susceptible to pore blockage and plugging leading to premature termination of sulfation. The CaO derived from Ca(OH)\(_2\) exhibits larger pore sizes; however, it also sinters at a much faster rate leading to rapid loss of surface area and subsequent deactivation (Ghosh-Dastidar et al., 1996). As a result, both calcium-based sorbents exhibit rapid deactivation and incomplete utilization.

Earlier attempts at improving sorbent reactivity focused on either reducing the CaO particle size or modifying the Ca(OH)\(_2\) with structural or chemical promoters to increase its surface area. Investigations with promoted hydrates with high surface area did not exhibit much improvement in overall reactivity (Kirchgessner and Jozewicz, 1989). Sadakata et al. (1994) produced CaO of ultrafine (UF) size of diameter < 0.1 μm by employing a laser ablation method. They reported that the reaction rate of UF CaO particles increased by a factor of \(10^2-10^3\) in comparison with CaO particles of >1 μm size. This UF size gave rise to high surface area of CaO which was mainly external surface area. Steciak et al. (1995)
reported calcium magnesium acetate (CMA) as an effective sorbent for combined SO$_2$-NOx removal. They observed more than 90% SO$_2$ removal at 950-1200°C and Ca:S of 2:1. Calcination of CMA produces thin-walled cenospheres of CaO and MgO with porosities of nearly 70% and surface area of 27 m$^2$/g. The MgO enhances dispersion of the CaO thereby reducing its sintering and increasing its accessibility.

The above discussion suggests that if the calcium carbonate could be modified to a more open initial pore structure, it could yield higher sulfur capture than the hydrate sorbent particles. Ghosh-Dastidar et al. (1996) have demonstrated that a particular high surface-area limestone (Forsby Carbonate, 12 m$^2$/g) exhibited high sorbent conversion of about 50%. They showed that the Forsby carbonate's initial high surface area and associated pore structure translated into an optimum pore size distribution in its calcine, which, combined with the effect of slower sintering contributed to its remarkable sulfation capacity. Ye et al. (1995) also compared Forsby with another high surface area carbonate and concluded that the Forsby's high reactivity was due to its surface area and pore volume located in pores > 50 Å. As mentioned in Chapters II and III, a calcium carbonate powder with high surface area and pore volume is prepared by carbonation-precipitation of a calcium hydroxide suspension in a slurry bubble column reactor in the presence of a small amount of surfactant. The operating parameters of the slurry bubble column reactor are optimized to generate carbonate particles of desired pore structural properties.

Sulfation of calcium-based sorbent takes place through two reaction steps:

\[
\text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O} \quad (4.1)
\]

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 \quad (4.2)
\]

\[
\text{CaO} + \text{SO}_2 + 0.5 \text{O}_2 = \text{CaSO}_4 \quad (4.3)
\]
Calcination (decomposition) of the sorbent produces high surface area and high porosity CaO, which reacts with SO\textsubscript{2} (sulfation) in the presence of O\textsubscript{2} to form the higher molar volume solid product, CaSO\textsubscript{4}.

The sintering of CaO is a concomitant deactivation phenomenon, which reduces the available surface area and porosity for sulfation reaction. The CaO sintering rate is strongly influenced by the initial sorbent type and the foreign ions or impurities in the solid.

The calcination characteristics of HRC sorbent are compared with a commercial carbonate and another high surface area carbonate (Forsby carbonate) in Chapter III. In addition, a modified calcium hydroxide with pore properties similar to the high reactivity calcium carbonate is also studied for comparison. Evolution of pore structure and the subsequent calcination and sintering effects on surface area, pore volume, and pore size distribution are also examined for reaction times less than 100 ms and are described/discussed in Chapter III. In this chapter, studies exploring the sulfation characteristics of high reactivity carbonate and comparison of its sulfation behavior with above mentioned other calcium-based sorbents are reported. The sulfation experiments are carried out in a high-temperature, entrained-flow reactor system, described in detail in chapter III. Sulfation behavior of Ca-based sorbents is elucidated on the basis of the results obtained in Chapter III.

4.2 Experimental

4.2.1 Experimental set-up and sorbent preparation
Sulfation experiments are performed in a high temperature entrained-flow reactor system. This reactor system is described in details in Chapter III along with its capabilities. Sulfation experiments are performed to gather short-contact time (upto 600 ms) time-resolved kinetic and structural data. As mentioned earlier, sulfation behavior of high reactivity carbonate is compared with three other calcium-based sorbents. Preparation procedure and procurement of these sorbents is discussed in Chapter III.

4.2.2 Experimental procedure

Sulfation studies are performed at a fixed reaction temperature (three representative temperatures are chosen- 900, 1000, and 1080°C). For the sulfation runs, the gas composition is maintained at 5.45% O₂, 3900 ppmv SO₂ and balance N₂. The partially reacted sorbents are classified into various size fractions in a cascade cyclone sampler (Andersen Instruments). The sorbents of a particular size group, having a mean aerodynamic diameter of 3.9 μm, are analyzed for determining reaction conversion and performing structural evolution studies. Obtaining information from particles of the same size fraction eliminates particle size as a variable.

4.2.3 Conversion and structural analysis

The extent of calcination in the flow reactor is measured by heating a portion of the collected sorbent to its calcination temperature in the TGA and allowing it to decompose to CaO completely. The conversion for sulfation studies is obtained from SO₄²⁻ ion concentration analysis by Alltech Ion Chromatography (IC) system. The surface area, pore volume, and pore size distribution of the collected samples are measured by low-
temperature nitrogen adsorption in a Quantachrome BET apparatus. In order to include the largest intraparticle pores in the measurement of pore volume, it is necessary to achieve N₂ condensation at a partial pressure close to its saturation pressure. The pore volume measurement is made at a relative pressure of 0.96, at which the Kelvin equation predicts that pores up to 252 Å in radius are filled. This ensures inclusion of most of the intraparticle pores while omitting the interparticle voids. Another significant point to note is that while the pore sizes of carbonate-calcines are presented in terms of pore radius, those for the hydroxide-calcines are reported as separation between plates. This accounts for the difference in pore shape between carbonate and hydroxide calcines. Gullette and Bruce (1987) suggest that while carbonate CaO possess cylindrical pores, hydrate CaO can be best represented by a parallel-plate pore structure.

4.3 Results of sulfation studies

4.3.1 Sulfation kinetics of HRC

The short-time sulfation kinetics of 3.9 µm (aerodynamic size) HRC particles is investigated at three temperatures, 900, 1000 and 1080°C for residence times ranging from 20 to 600 ms. As shown in Figure 4.1, the most distinguishing feature of the HRC sulfation is its 70-75% conversion which is much higher than the conversion of any other sorbent reported in the literature under similar particle size and reaction conditions. HRC does exhibit both the characteristics typical of sulfation reaction, namely, the very high initial reaction rate and the severe attenuation at longer contact times. Both 1000 and 1080°C show similar conversions achieving nearly 50% conversion in the first 40 ms. At higher residence times, however, there is a considerable reduction in overall reaction rate.
especially at 1080°C which shows a flat conversion profile, and 1000°C exhibits higher conversions than 1080°C beyond 200 ms. At 900°C, the conversion increases initially at a slower rate but the flattening of the conversion profile is not as severe as at the higher temperatures and about 50% conversion is achieved at 600 ms.

For small particles it is generally accepted that the sulfation rate increases with increasing temperature till the equilibrium limitation becomes evident. However, sintering also becomes very significant above 1000°C depleting the surface area and pore volume available for the sulfation reaction. These two opposing mechanisms together yield an optimum temperature which exhibits the highest ultimate conversion. As seen in Figure 4.1, there is a dramatic increase in reactivity between 900 and 1000°C, evidently, the increase in sulfation kinetics compensates for any increase in rate of sintering. In order to investigate the optimum temperature for HRC, the extent of conversion after 530 ms of sulfation is analyzed at various temperatures between 900-1115°C for 3.9 µm particles. Figure 4.2 shows that a maxima in the conversion exists at 1000°C with a sulfation extent of about 78. This temperature trend compares well with results previously reported in the literature for other carbonate sorbents of similar particle sizes (Ye et al., 1995; Cole et al., 1985).

4.3.2 Comparison of sulfation characteristics of HRC with other sorbents

The sulfation characteristics of HRC are compared with three other sorbents, the Forsby carbonate (FC), the Linwood carbonate (LC), and the modified Linwood hydrate (MH), under identical reaction conditions. The chemical composition and the initial surface area and pore volume of all the sorbents are shown in Table 4.1. The primary particle size
distribution of the sorbents, as shown in Figure 4.3, illustrates that all the sorbents possess a similar unimodal distribution and their $d_{50}$ lie in the narrow range between 1-2 μm, except for Linwood carbonate which is significantly coarser. As shown in Figure 4.4, the initial reaction rate of HRC is more than two times that of LC, while its ultimate conversion is nearly 3-times that of the commercial Linwood carbonate. The LC shows a virtual reaction die-off beyond 100 ms and its long-time conversion values of about 28% match with those reported by previous researchers (Milne et al., 1990; Gullett et al., 1988). The modified hydrate (MH) possesses a surface area and porosity similar to the modified carbonate and yet shows a final conversion of only about 35%. These conversion data for MH corroborate the findings by Kirchgessner and Jozewicz (1989) that addition of lignosulfonate additive results in about 35% final sorbent conversion. The only sorbent which exhibits an initial reaction rate comparable with the HRC is the Forsby carbonate (FC). The ultimate conversion exhibited by FC is about 50% and compares well with the observations of Ye (1994) and Wang et al. (1995).

In order to confirm that the particle size is small enough to eliminate intraparticle diffusional and heat transfer limitations, sulfation conversions of various particle sizes at 1000°C are analyzed as shown in Figure 4.5 for HRC. The 3.9 μm and 1.7 μm particles do not exhibit any difference in the initial rate or the longer-time conversion. Ghosh-Dastidar et al. (1996) showed that the FC and MH also do not show significant particle size effect for particles smaller than 5 μm. Similar observation was made by other investigators (Milne and Pershing, 1987; Cole et al., 1986) studying particle size effect on sulfation.

4.3.3 Porosity changes during sulfation of HRC
The formation of the larger molar volume product CaSO₄ leads to loss of pore volume through pore filling or pore-mouth closure. Theoretical analyses regarding porosity changes during sulfation is discussed below. In the case of pre-sintered CaO, the porosity change is due to the sulfation reaction alone and can be obtained from a volume balance (Bhatia and Perlmutter, 1981a):

\[ \frac{\varepsilon}{\varepsilon_o} = 1 - (z - 1)(1 - \varepsilon_o)X_s \]  

(4.4)

where \( \varepsilon_o \) represents the porosity of the calcined and sintered CaO. In actuality, the sulfating sorbent is undergoing concomitant porosity changes due to calcination and sintering. The predicted porosity of the sorbent is calculated with the assumption that the extent of CaO pore reduction due to sintering is identical for both sulfation (with SO₂) and calcination (without SO₂) reactions. Furthermore, the extent of hydroxide or carbonate decomposition to CaO is assumed to be unaffected by the presence of SO₂. The fraction of CaO (\( w_c \)) per unit weight of partially calcined product can be expressed as:

\[ w_c = \frac{X_c}{M_s (1 - X_c) + X_c} \]  

(4.5)

where \( M_s \) and \( M_c \) are molecular weights of the sorbent and CaO respectively. During sulfation reaction, a fraction of \( w_c \) converts to CaSO₄. If the overall sulfation conversion is expressed as \( X_s \), the amount of CaSO₄ can be obtained as:

\[ W_p = X_s (\frac{w_c}{M_c} + \frac{w_s}{M_s}) M_p \]  

(4.6)
where $M_p$ is the molecular weight of the product, CaSO$_4$. The amount of residual CaO is:

$$W_c = \left[ \frac{w_c}{M_c} - X_s \left( \frac{w_c}{M_c} + \frac{w_s}{M_s} \right) \right] M_c \tag{4.7}$$

The additional volume occupied by the product CaSO$_4$ is due to its higher molar volume ($v_p$) compared to that of CaO ($v_c$). If $V_c$ is the specific pore volume after calcination, then the predicted pore volume after equal duration of sulfation per unit weight of sulfated sample can be expressed as:

$$V_{pred} = \frac{[V_c - X_s (v_p - v_c) \left( \frac{w_c}{M_c} + \frac{w_s}{M_s} \right)]}{(w_s + w_c + w_p)} \tag{4.8}$$

The pore volume values for HRC thus calculated are plotted in Figure 4.6 with the experimentally obtained values. The negative values of the predicted pore volumes can be interpreted as higher-than-theoretically-predicted sulfation of HRC. Gullett and Bruce (1987) investigated sulfation by h-CaO and c-CaO and attributed the higher-than-theoretically-predicted sulfation by h-CaO to particle expansion. Their tests with mercury porosimetry indicated expansion in the interparticle region of h-CaO, and tests with nitrogen adsorption/desorption indicated that nitrogen is capable of expanding the h-CaO and increasing the void space by as much as 25%. They concluded that the formation of CaSO$_4$ must be able to produce even greater expansion than indicated by nitrogen adsorption/desorption and hence be able to show conversions which indicate about 30% particle expansion. Theoretical analysis for HRC after 520 ms of sulfation indicates that a particle expansion of nearly 35% would be needed to accommodate the higher molar
volume product formed. Another possible factor is that the effect of sintering on pore volume is diminished in presence of SO$_2$. Newton et al. (1989) performed calcination and sulfation experiments in the presence of CO$_2$ and observed a 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.

4.3.4 Product-layer diffusion

It is accepted that the solid-state ionic diffusion through the product CaSO$_4$ layer is the controlling mechanism for the sulfation reaction (Bhatia and Perlmutter, 1981b; Sotirchos and Yu, 1985). This is based on the activation energy of diffusion as well as the surface area dependence (Borgwardt and Bruce, 1986; Borgwardt et al., 1987). The conversion verses time data is used to evaluate the product layer diffusivity as follows. Bhatia and Perlmutter (1981a, 1983) have formulated the random pore model that accounts for product layer expansion due to the larger molar volume of CaSO$_4$ relative to CaO. In the case of product layer diffusion controlling, the model gives:

$$\left\{ \frac{1}{\Psi} \left[ \sqrt{1 - \Psi \ln(1 - X_s)} - 1 \right] \right\}^2 = k_d t \quad (4.9)$$

where,

$$k_d = \frac{M_e D_p C_s S_o^2}{2 \rho z (1 - \varepsilon_o)^2} \quad (4.10)$$

and

$$S_o = \rho (1 - \varepsilon_o) S_g \quad (4.11)$$

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The values of the pore structure parameter $\Psi$ typically vary from 1.2 to 2.5 (Borgwardt et al., 1987). The time required to reach a given conversion decreases with the square of the surface area. The value of $k_d$ is calculated by fitting the $X_s$ vs. $t$ experimental data to the left-hand side of equation (4.9) to minimize the deviation. The $D_p$ value is calculated from equation (4.10) using $S_g$ values from the calcination experimental data and $M=56 \text{ g/gmol}$, $C_s=1.7 \times 10^{-7} \text{ g/mol/cm}^3$ (3900 ppm), $\rho=3.32 \text{ g/cm}^3$, and $z=3.09$. Using a value of $\Psi=1.2$ (Borgwardt et al., 1987) and using only the experimental data beyond the initial 30 ms, it is found that the value of $D_p$ is $30 \times 10^{-12} \text{ m}^2/\text{s}$ at 1000°C, which compares well with $69 \times 10^{-12} \text{ m}^2/\text{s}$ obtained by Bhatia and Perlmutter (1981b) at 980°C.

The reported values of activation energy for product layer diffusion vary from 30 kcal/mol to nearly 40 kcal/mol (Borgwardt et al., 1987). The activation energy is calculated to be 37.5 kcal/mol in this study for product layer diffusion controlled sulfation of HRC. Borgwardt and Bruce (1986) obtained 36.6 kcal/mol, Bruce et al. (1989) obtained 39 kcal/mol for $c$-CaO particles and Hartman and Trnka (1980) obtained 34 kcal/mol for limestone particles. The reported value lies within the range normally observed for diffusion of ions by thermally induced lattice defects (Bruce et al., 1987).

The above calculations are based on the $\text{SO}_3^{2-}$ ions diffusing through the product layer to the CaO/CaSO$_4$ interface. Recently, Hsia et al. (1993, 1995) examined the mechanism of diffusion by conducting inert marker experiments and $^{34}$S isotope experiments. They established that the ionic diffusion takes place by the outward diffusion
of Ca\(^{2+}\) ions and O\(^{2-}\) ions in a coupled manner from the CaO/CaSO\(_4\) interface to the CaSO\(_4\)/gas interface. At the CaSO\(_4\)/gas interface, the sulfation reaction takes place as

\[
\text{Ca}^{2+} + \text{O}^{2-} + \frac{1}{2}\text{O}_2 + \text{SO}_2 \leftrightarrow \text{CaSO}_4
\]  

\text{(4.13)}

4.3.4 Effect of sulfation on pore volume distribution

Figure 4.7 shows the pore volume distribution after 34 ms of sulfation at 1080\(^\circ\)C to perform a comparative analysis between different sorbents. The sulfation extents for HRC, FC, LC and MH are 46%, 38%, 18% and 23% respectively. All the sorbents show a drastic reduction in total pore volume as well as in the contribution of the < 50 Å° pores. The HRC shows the highest consumption of pore volume due to its highest conversion. The sulfation conversion curves shown in Figure 4.4 indicate that beyond initial 34 ms of reaction, HRC, FC and MH show about 26%, 12% and 15% additional conversions in the maximum allowed reaction time of about 550 ms, while only about 6 to 7% further utilization is observed in case of Linwood carbonate (LC). Figure 4.7 shows that the residual pore volume available for subsequent reaction is the least for LC-CaO and furthermore, most of it resides in less than 50 Å° pores.

4.4 Conclusions

Most of the previous work in improving calcium-based sorbents have maximized the surface area of the parent sorbent in order to produce a high surface area and high reactivity CaO. However, such modifications fail to overcome the blockage and plugging of internal pores which lead to premature termination of sulfation. In order to maximize the sulfation
capacity of calcium-based sorbents, it is established that the pores of their calcines have to lie predominantly in the 50-200 Å sizes.

In this work, the internal pore properties (surface area and pore size distribution) of calcium carbonate sorbent are modified to improve its SO$_2$ reactivity. The modified carbonate (HRC) exhibits exceptionally high conversion of 70-75%, which represents a nearly three-fold enhancement over the commercial carbonates and hydrates. The high initial surface area and the open pore structure of the high reactivity carbonate translates into an optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. The surface area and the pore volume in the 50-200 Å range of its calcine are maximized which distinguishes the modified carbonate from other sorbents. Comparative investigation with other carbonates reveals that in spite of the high surface area of their calcines', the pore size distribution shows a preferential dominance of very small pores which leads to pore plugging and premature termination of sulfation. A modified hydrate of high surface area and porosity comparable to the high reactivity carbonate is also investigated. The ultimate conversion as well as the initial reaction rate of the high reactivity carbonate are nearly twice as high when compared to the modified hydrate.

The results of this study illustrate the impact of internal pore structure on initial reactivity and ultimate sulfation conversion of calcium-based sorbents. It also demonstrates the potential of 'tailoring' the internal pore structure of sorbents to increase their effectiveness.
## Table 4.1: Composition & initial structural properties of sorbents investigated for their sulfation characteristics.

<table>
<thead>
<tr>
<th>Composition (wt %)</th>
<th>Modified Hydrate (MH)</th>
<th>Linwood Carbonate (^a) (LC)</th>
<th>Forsby Carbonate (^b) (FC)</th>
<th>High Reactivity Carbonate (HRC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)(_2)</td>
<td>93.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>1.0</td>
<td>97.0</td>
<td>95.6</td>
<td>97.0</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.9</td>
<td>0.8</td>
<td>0.26</td>
<td>0.9</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.6</td>
<td>0.5</td>
<td>0.30</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>1.0</td>
<td>-</td>
<td>0.88</td>
<td>1.0</td>
</tr>
<tr>
<td>CaO</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.23</td>
<td>0.5</td>
</tr>
<tr>
<td>MgCO(_3)</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cal. Lignosulfonate(^c)</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>BET surface area</strong></td>
<td><strong>(m(^3)/g)</strong></td>
<td><strong>(m(^3)/g)</strong></td>
<td><strong>(m(^3)/g)</strong></td>
<td><strong>(m(^3)/g)</strong></td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>62.0</td>
<td>1.9</td>
<td>12.0</td>
<td>61.0</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>-</td>
<td>0.004</td>
<td>0.044</td>
<td>0.180</td>
</tr>
</tbody>
</table>

\(^a\) Linwood Mining and Minerals Co.  
\(^b\) Carbital Co., Sweden.  
\(^c\) Georgia-Pacific Co.
Figure 4.1: Influence of temperature on sulfation of HRC. Particle size: 3.6 μm; SO₂ Conc.: 3900 ppm
Figure 4.2: Temperature variation in sulfation of HRC.
Residence time: 510 ms; Particle size: 3.6 μm
Figure 4.3: Primary particle size distribution from sedigraph analysis.
Figure 4.4: Sulfation of MH, LC, FC and HRC.

Reaction temperature: 1080 °C
Particle size: 3.6 μm
Figure 4.5: Effect of particle size on sulfation conversion of HRC.
Reaction temperature: 1000°C; SO$_2$ conc.: 3900 ppm
Figure 4.6: Comparison of experimental pore volume of HRC after sulfation at various residence times with that predicted from calcination results.

Reaction temperature: 1080 °C
Figure 4.7: Pore volume distribution after 34 ms of sulfation at 1080°C. Particle size: 3.6 μm; SO₂ conc.: 3900 ppm
CHAPTER 5

COMPREHENSIVE MODEL FOR SULFATION OF Ca-BASED SORBENTS

Contents of this chapter have been submitted as a paper to the *AIChE Journal* (With S. Mahuli, R. Jadhav, and L.-S. Fan). This paper is under review.

5.1 Introduction

The potential of injecting dry calcium based sorbents (CaCO$_3$ and Ca(OH)$_2$) into above the flame region of a coal fired furnace has been extensively studied as an economical alternative to more expensive flue gas desulfurization processes. When Ca-based sorbents are injected into the furnace they decompose to give high porosity and surface area CaO:

$$\text{CaCO}_3/\text{Ca(OH)}_2 = \text{CaO} + \text{CO}_2/\text{H}_2\text{O} \quad (5.1)$$

The highly reactive CaO then reacts with SO$_2$ in presence of O$_2$ to form solid CaSO$_4$:

$$\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 = \text{CaSO}_4 \quad (5.2)$$

Contrary to calcination, which acts as an activation step, the sulfation reaction is a deactivation phenomenon which results in the build-up of CaSO$_4$ product layer and hence, a loss in available surface area. Another mechanism by which active surface area
is lost is thermal sintering. The grains coalesce to form larger grains due to sintering, reducing the surface area and porosity of reactive CaO (Borgwardt, 1989).

The earliest sulfation models were set-up either for calcined sorbent or assumed calcination to be instantaneous. These models also assumed sintering to have negligible effect. These sulfation models followed the grain model approach suggested by Szekly and Evans (1971). These models considered the particle to be formulated of a number of small nonporous spherical grains. The size of these grains is assumed invariant with reaction and the reaction occurred on the ash/sorbent boundary. Wen and Ishida (1973) applied the simple grain model to simulate sulfation of CaO and concluded that at low temperatures the overall rate was controlled by the rate of reaction taking place on each of the CaO grains and intraparticle diffusion to be dominating at high temperatures. Formulation and solution procedure for sharp interface shrinking core models are discussed in detail elsewhere (Sohn and Szekly, 1974; Szekely and Evans, 1976). A number of researchers have modified the original grain model to account for structural changes either empirically or through theoretical considerations. Borgwardt and Bruce (1986) and Bruce et al. (1989) applied the limiting case of product layer diffusion control with the grain model to fit the CaO sulfation data. They concluded from the best fit of the data that the solid-state product layer diffusion was the controlling phenomena. Pigford and Sliger (1973) applied the grain model, assuming that the rate of reaction was governed by either the diffusion of sulfur dioxide through the pores of the particle (inter-grain voids) or through the developing nonporous product layer, to sulfation of lime. Hartman and Coughlin (1976) applied shrinking core model to predict sulfation behavior of CaO particles. In their model development, porosity changes due to the sulfation were
incorporated but thermal sintering was not accounted for. In order to predict on-going sulfation even after the porosity of the particle has dropped to zero they correlated the changing particle porosity empirically to the extent of conversion, thus introducing the concept of residual porosity. On the basis of their analyses, they concluded that calcium carbonates and their calcines were best suited for SO$_2$ removal. Georgakis et al. (1979) modified the grain model by manifesting the lost particle porosity as an increase in grain size with extent of reaction. Ranade and Harrison (1981) also modified the constant property grain model to account for both the sintering and reaction. They suggested that the role of sintering can be depicted as coalescence of grains to form bigger grains.

Sulfation models mentioned above assumed non-overlapping grains which lead to a monotonically decreasing surface area with progress of reaction. Another class of modified grain models represents the solid phase as an aggregate of spherical grains in the initial state of sintering. Partially sintered spheres models (PSSM) developed by Lindner and Simonsson (1981) visualized the particle as an aggregate of truncated spheres in contact with each other simulating initial stages of sintering. Model involved a structural parameter, $\lambda$ and showed the importance of decreasing gas-solid interfacial area due the growing and overlapping product layers. Alvfors and Svedberg (1992) modified the PSS model to determine the influence of presence of inert material in the solid matrix on the sulfation behavior of CaO. Sotirchos (1987), Sotirchos and Yu (1988), and Mine et al. (1990a, 1990b) also developed models based on overlapping grains.

Pore models represent another class of mathematical models for gas/solid non-catalytic reactions. The structural changes due to the reactions are manifested as the changes in the overall geometry (length and radius) of the single pore. Random Pore
model developed by Bhatia and Pertlmutter (1980, 1981a, 1981b) take into account the changes in pore structure due to formation of solid product and it also considers the overlapping and intersections among the pores. They introduced a pore structure parameter $\psi$, which is dependent on the length and diameter of the pore and showed it to be intimately related to the effective grain shape factor, $m$, proposed in earlier grain models (Szekely and Evans, 1970; Calvelo and Smith, 1971). They applied their model to $\text{SO}_2$-$\text{CaO}$ reaction and determined that sulfation behavior strongly depended on the surface area and porosity rather than the pore structure parameter, $\psi$. By fitting their model to experimental data of Borgwardt (1970) and Hartman and Coughlin (1976) they estimated product layer diffusivity of $\text{SO}_2$ and determined that product layer diffusivity showed an Arrhenius type temperature dependence that might be expected of a solid-state diffusion mechanism. Christman and Edgar (1983) proposed a distributed pore-size model which takes into account the reaction and structural changes in pores of all the sizes. Applying sulfation data from Ulerich (1977) their model is able to predict that kinetic behavior of different calcined limestones is attributed to differences in their pore structure. Sotirchos and Zarkantis (1993) developed a structural model for $\text{CaO}$ sulfation behavior with structural changes due to sulfation without considering the effects of sintering. In their model they conceptualized the porous structure to be a network of pores with distributed sizes and length. A number of other sulfation models have been proposed in the literature that consider the porous structure of the solid as a network of pores (Simon and Garman, 1986; Simon et al., 1987). Simon and Garman (1986) applied pore model to sulfation of $\text{CaO}$. They developed their model without considering the
product layer diffusion and concluded that deactivation of the sorbent particles is due to plugging of the smaller pores.

Comprehensive Ca(OH)$_2$/CaCO$_3$ sulfation has been attempted by very few researchers due to the complex nature of the various phenomena and the lack of thorough understanding of their interplay. In earlier efforts at simulating comprehensive sulfation, assumptions of instantaneous calcination and negligible effect of sintering, allowed the use of CaO-SO$_2$ reaction experimental data for modeling. Mai (1987) applied pore model for the sulfation step and a second order kinetics for the sintering step. Alvors and Svedberg (1988) attempted to model the overall sulfation of the Ca(OH)$_2$ particle using PSS model. They assumed a first order kinetics for the calcination surface reaction, on the basis of empirical verification by Borwardt (1985) and modeled sintering on the basis of German and Munir's (1976) work. Calcination and sintering were taken together to predict the surface area available for the sulfation. Pore diffusion, product layer diffusion and chemical reactions were considered for the sulfation step. Milne and Pershing (1988) presented a combined model using a grain model for sulfation, second-order kinetics for the sintering and an empirically modified shrinking-core model for calcination. Milne et al. (1990a, 1990b) applied the PSS model to simulate calcination, sintering and sulfation of CaCO$_3$ particles under non-isothermal conditions. They assumed sulfation reaction to be limited by product layer diffusion and diffusion of SO$_2$ through the pores. In their model sintering is defined as a function of surface area and takes into account the presence of CO$_2$ and H$_2$O on sintering.

Most of the mathematical models mentioned above considered the solid state product layer diffusion in one form or the other, with the reaction taking place at the
CaO/CaSO₄ interface. Alvfors and Svedberg (1992) developed comprehensive sulfation model for sulfation of limestone and dolomite assuming SO₂ diffusion through the nonporous CaSO₄ layer with the reaction taking place at the CaO/CaSO₄ interface. Bhatia and Permutter (1981b) determined from experimental data fit to their random pore model that product layer diffusivity of SO₂ is ionic in nature. They further postulated formation of charged species on the surface of CaSO₄ by SO₂ and O₂ and inwards movement of sulfate ions through the product layer with reaction at the CaO/CaSO₄ interface. Borgwardt et al (1987) determined the effects on impurities on the reaction rate of CaO sulfation. They observed lower product layer diffusivities and slower reaction rates for pure CaO as compared to CaO doped with impurities. On the basis of these observations they concluded that diffusion process through the product layer involves ion transport rather than gas transport with inwards diffusion of SO₄²⁻ ions through the product layer. Hsia et al. (1993, 1995) clearly illustrated, using marker and isotope experiments, that the reaction front is not at the CaO-CaSO₄ interface but at the SO₂-CaSO₄ interface, with outward migration of Ca²⁺ and O⁻ ions through the CaSO₄ product layer (Figures 5.1 and 5.2) instead of inwards SO₄²⁻ ions movement, as presumed to be the case earlier. Entrained-flow reactor systems are typically used to obtain time-resolved kinetic data for such short reaction time scale of interest (Milne et al., 1990; Gullett et al. 1988). Few researchers (Mai and Edgar, 1989; Bortz et al., 1986) have made efforts to obtain calcination and sintering data in less than 100 ms time scale. However, previous short-contact time studies used an assumed gas flow profile to calculate an approximate solid residence time and some studies had inadequate particle heating and quenching provisions upon sorbent injection and sampling.
In this work, an attempt is made to develop a comprehensive mathematical model describing simultaneous calcination, sintering and sulfation phenomena for small calcium-based sorbent particles (less than 5 μm). This chapter describes the effort to mathematically simulate the structural and chemical changes that a sorbent particle undergoes when injected into the boiler furnace. The model is based on the concept of grain-micrograin and includes first order calcination kinetics, the structural changes because of thermal and CO₂/H₂O induced sintering as proposed by Milne et al. (1990) and sulfation reaction. The model incorporates the actual mechanism of product layer diffusion, as proposed by Hsia et al. (1993, 1995). Experimental sulfation data for a highly reactive CaCO₃ (HRC), prepared using a novel approach, is reported in Chapter IV and the calcination and sulfation behavior of calcium-based sorbents for very short contact times (less than 300 ms) is simulated using this model and results are compared with actual experimental data.

The residence time of the small sorbent particles in the desire thermal window of 800-1200°C inside the furnace is less than 1.0 second and it is imperative to experimental study and mathematically simulate the reaction for very short contact times. Sulfation and calcination behavior of small calcium-based sorbents is studied in a specially designed high-temperature, entrained flow reactor (described in Chapter III, and in Raghunathan et al., 1993).

5.2 Comprehensive sulfation model development

5.2.1 Model concept
The overall concept of the model is illustrated in Figure 5.3. A single Ca(OH)$_2$/CaCO$_3$ particle is assumed to be composed of identical, spherical, non-overlapping grains. Calcination takes place on a single grain according to the sharp interface model. As Ca(OH)$_2$/CaCO$_3$ decomposes, smaller micrograins of CaO are formed surrounding the unreacted Ca(OH)$_2$/CaCO$_3$ grain core, and the product gas. H$_2$O/CO$_2$ diffuses out through the porous CaO product layer. All the grains can be considered to be at the same conditions of temperature and gas concentration, and SO$_2$ and/or CO$_2$/H$_2$O diffuse from the bulk gas phase to the grain surface and from grain surface to the bulk, respectively. Diffusing gaseous species are assumed to experience negligible resistance. The CaO micrograins sinter rapidly and simultaneously undergo sulfation, thus reducing the internal surface area and porosity of the product layer. The SO$_2$ diffuses through inter-micrograin voids to the micrograin surface. The micrograin could be partially sulfated or a newly formed CaO micrograin. Sulfation takes place at the outer boundary of the micrograins (CaSO$_4$/gas interface). Ca$^{2+}$ and O$^-$ ions diffuse outwards through the non-porous layer of CaSO$_4$ surrounding the CaO micrograins (Hsia et al., 1993) to react with SO$_2$. The product shell is composed of CaO micrograins of varying ages with varying degrees of sintering and sulfation, and hence, it can be described as a multi-layered partially sulfated CaO shell, each layer corresponding to CaO formed at a certain time. The most recently formed CaO layer, which immediately surrounds the uncalcined sorbent core possesses the highest surface area and porosity and would be least sintered and sulfated whereas the outermost layer would have the lowest surface area and would be highly sulfated. Varying degree of sulfation and sintering of layers of micrograins would give transient porosity and surface area. The multi-layered
partially sulfated CaO shell offers resistance to the transport of both $H_2O/CO_2$ and $SO_2$. The diffusion and concentration profiles of $H_2O/CO_2$ and $SO_2$ through the multi-layered product shell are constantly changing and the rate of calcination/sulfation at the micrograins surface, at a given radial position inside the grain, would decrease with time. At any given time and depending on the radial position of the micrograin, the thickness of the CaSO$_4$ layer surrounding the micrograin would vary. Ca$^{++}$ and O$^-$ ions concentration at the surface of the micrograin is strongly dependent on the CaSO$_4$ layer thickness and $SO_2$ concentration at the micrograin surface.

5.2.2 Calcination and sintering

Development of calcination and sintering model is described in details in Chapter III. The calcination reaction takes place at the sorbent/CaO interface and is assumed to be first order with respect to $H_2O/CO_2$ partial pressure at the sorbent/CaO interface (Silcox et al., 1989):

$$
\gamma_s = k_e \frac{(P_e - P_c)}{RT}
$$

(5.3)

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

$$
\frac{dx}{dt} = \frac{3R_e^2k_e(P_e - P_c)}{RTR_{g0}^3C_s}
$$

(5.4)

where, $k_e$ is the calcination rate constant (in m/s) and $C_s$ is the solid reactant concentration (in gmol/m$^3$). The equilibrium dissociation pressure, $P_e$ for Ca(OH)$_2$ or
CaCO₃ can be obtained as a function of temperature using standard thermo-chemical approach (Hartman and Martinovsky, 1992).

The species continuity equation for product gas H₂O/CO₂ diffusing through the product CaO assuming the pseudo-steady state approximation can be written as:

\[
\frac{\delta^2 P}{\delta R^2} + \frac{2}{R} \frac{\delta P}{\delta R} = 0 \quad (5.5)
\]

with the following boundary conditions:

\[
-D_{\text{eff}} \frac{\delta P}{\delta R} \bigg|_{R = R_e} = k_e (P_e - P_c) \quad (5.6)
\]

\[
P \bigg|_{R = R_e} = 0 \quad (5.7)
\]

The latter boundary condition assumes negligible bulk H₂O/CO₂ concentration and no resistance to intra-particle gaseous diffusion. Both Knudsen and ordinary diffusion may be important at different stages of reaction.

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

\[
\frac{dS}{dt} = -k_{\text{sn}} \left(S - S_e\right)^2 \quad (5.8)
\]

The presence of H₂O/CO₂ accelerates the rate of sintering of CaO (Borgwardt et al., 1986; Mai & Edgar, 1989). The sintering rate constant is modified according to the following correlation proposed by Milne et al., (1990):

\[
k_{\text{sm}} = k_{\text{sn}} \left(1 + BP^m\right) \quad (5.9)
\]

Based on their correlation, m and B are taken as 0.17 and 6 for Ca(OH)₂ and 0.7 and 1.25 for CaCO₃ respectively and k_{\text{sm}} is the modified sintering rate constant.
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:

$$S_{i,j} = S_o + \frac{1}{[1/(S_o - S_a)] + k_m(t_i - t_j)}$$

(5.10)

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 by summation (Ghosh-Dastidar et al., 1995).

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 $\varepsilon$ is proportional to $S$ and approaches zero as CaO surface area approaches the asymptotic value. In such a case, the particle porosity results from inter-grain voids alone. With such an assumption, the porosity of an individual layer of CaO can be written as a linear function of its surface area.

$$\varepsilon = \varepsilon_o \left( \frac{S - S_o}{S_o - S_a} \right)$$

(5.11)

The calcination rate equation (5.4) is coupled with the product $H_2O/CO_2$ continuity equation (5.5). The core radius $R_c$ is related to the solid conversion as:

$$R_c = R_g (1 - x)^{1/3}$$

(5.12)

The instantaneous grain radius, $R_g$, changes as a result of both calcination and sintering which work to oppose each other. Sintering alone causes the grains to grow by combination of adjacent grains. The model simulates the unreacted core of each small grain to remain at the center of the new grain (Ranade and Harrison, 1981). Further, the
grain size is not a function of the radial position since the model assumes negligible concentration gradients within the particle.

5.2.3 Sulfation step

The SO\textsubscript{2} balance in the calcined portion can be written as,

\[
\frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 D_{SO_2} \frac{\partial C_{SO_2}}{\partial R} \right) - \frac{3k_s}{R_g} (1 - \varepsilon) C_{\text{ion}} C_{SO_2} = 0 \quad (5.13)
\]

with the following boundary conditions:

\[
C_{SO_2} \bigg|_{R=R_g} = C_{\text{bulk}}
\]

and,

\[
\left. \frac{\partial C_{SO_2}}{\partial R} \right|_{R=R_c} = 0 \quad (5.14)
\]

where, \(k_s\) is sulfation reaction rate constant, \(\varepsilon\) is the porosity of the partially calcined and sulfated grain, \(R\) is the radial position inside the grain and \(C_{\text{ion}}\) represents the concentration of ions at the reaction interface (surface of the micrograin).

As mentioned earlier the reaction between \(SO_2\) and \(Ca^{2+}\) in the presence of oxygen takes place at the surface of micrograins created as a result of calcination. \(Ca^{2+}\) ions migrate through the \(CaSO_4\) layer to the surface. Assuming pseudo-steady-state, the radial concentration profile of the ions in the \(CaSO_4\) layer is given by,

\[
\frac{\partial}{\partial r} \left( r^2 \frac{\partial C_{\text{ion}}}{\partial r} \right) = 0 \quad (5.15)
\]

with the following boundary conditions

\[
C_{\text{ion}} \big|_{r=r_c} = \rho_{CaO}
\]
and,
\[-D_{\text{ion}} \left( \frac{\partial C_{\text{ion}}}{\partial r} \right) \bigg|_{r_{\text{in}}} = k_s C_{\text{ion}} C_{\text{SO}_2} \quad (5.16)\]

\(r_g\) and \(r_c\) represent overall radius and the radius of the unreacted core of the micrograin.

Both Knudson and molecular diffusivities are considered to calculate the effective diffusivity of \(\text{SO}_2\). Porosity following sulfation step is given as:
\[\varepsilon_s = \varepsilon - (z - 1)(1 - \varepsilon)x_s \quad (5.17)\]

Extent of sulfation for a given micrograin can be determined by performing a solid reactant balance for the micrograin as:
\[\frac{d}{dt} \left( \frac{1}{3} \right) r_c^3 \rho_{\text{CaO}} = k_s C_{\text{ion}} C_{\text{SO}_2} r_c^2 \quad (5.18)\]

Conversion for a micrograin at a specific radial location inside the grain (local conversion) is given by:
\[x_s = 1 - \left( \frac{r_c}{r_{c,0}} \right)^3 \quad (5.19)\]

The change in overall micrograin size is then obtained by taking into account the volume expansion due to sulfation, as given by:
\[r_g^3 = r_c^3 + \frac{3x_s}{4\pi \rho_{\text{CaO}}} \quad (5.20)\]

The overall conversion for the entire grain is calculated by integrating the local conversion over all the layers of micrograins:
\[x_{\text{tot}} = \frac{\int_0^{r_g} x_s r^2 dr}{r_g^3} \quad (5.21)\]

5.3 Model solution

The \(\text{CO}_2\) or \(\text{H}_2\text{O}\) partial pressure profile in the product layer can be obtained analytically by solving the continuity equation (5.5) with the given boundary conditions.
The calcination product gas partial pressure at the interface of the unreacted sorbent/CaO can be expressed in terms of $R_C$, $R_g$ and $D_{\text{eff}}$.

The calcination rate equation (5.4) is solved with the initial condition of $x=0$ at time $t=0$. If particle size is assumed to be small (less than 5\(\mu\)m) the transport resistances inside the particle can be neglected and conversion for a single grain would correspond to the overall particle conversion. The $S_g$ value obtained from the model represents the predicted surface area of the partially calcined particle and is used to obtain the porosity of the grain (Equation 5.10). The reaction constant, $k_C$ and the sintering constant, $k_{\text{sin}}$, represent the two calcination specific rate parameters of the model.

Concentration profile of Ca\(^{2+}\) ions is obtained by solving the equation (5.15) with the boundary conditions given in equation (5.16). The concentration of ions at the surface of the micrograin is obtained as:

\[
C_{\text{ion}}\Big|_{r=r_g} = \rho_{\text{CaO}} + A' \left( \frac{1}{r_c} + \frac{1}{r_g} \right)
\]

(5.22)

where $A'$ is the constant of integration given by:

\[
A' = \frac{k_s'' \rho_{\text{CaO}}}{1 - k_s'' \left( \frac{1}{r_c} - \frac{1}{r_g} \right)}
\]

(5.23)

and,

\[
k_s'' = -\frac{k_s C_{\text{SO}_2}}{D_{\text{ion}}}
\]

(5.24)

As can be seen, the ionic concentration on the surface is a function of SO\(_2\) concentration outside of the micrograin. SO\(_2\) concentration profile inside the multilayered micrograin product shell is obtained by solving equations (5.13) and (5.22)
simultaneously for the boundary conditions given in equation (5.14). The sulfation reaction constant $k$, and product layer diffusivity $D_{ion}$ are the two sulfation specific model parameters are a function of temperature. Once the $SO_2$ and surface ion concentration for a given micrograin is determined the extent of sulfation for that micrograin at a particular time increment can be calculated from equation (5.18) and the local conversion is obtained from equation (5.19). The overall porosity of the grain is adjusted for incremental increase in calcination, sintering and sulfation after each time step according to the equations (5.11) and (5.17). Radius of micrograins are adjusted to accommodate the volume of $CaSO_4$ formed during the time interval and the overall conversion for the grain is determined by adding (integrating) conversions of all the micrograins as shown in equation (5.21). Fourth order Runge-Kutta method is used to solve various differential equations and the overall numerical scheme (FORTRAN CODE) is given in Appendix B.

5.4 Results and discussion

5.4.1 Sulfation of CaO

Experiments were conducted using the EFR to obtain sulfation characteristics of laboratory generated CaO. A batch of $Ca(OH)_2$ powder was calcined in a horizontal furnace at a temperature of 1000°C for a period of 1 hr under flowing nitrogen gas stream to generate highly sintered CaO particles of surface area less than 5 m2/g. Independent sulfation of these CaO particles was conducted and the experimental results were compared with the model predictions. In case of CaO sulfation simulation, the calcination subroutine was not invoked.
Figure 5.4 presents the experimental and simulation results of CaO sulfation obtained for reaction times of less than 400 ms. As can be seen the experimental results and model simulations both show an initial period of very high reactivity which is followed by leveling-off of the reaction. This behavior is typical of sulfation of calcium based sorbents and suggests that the reaction proceeds extremely fast at the beginning and at later stages is retarded severely due to product layer build-up and sulfation induced particle deactivation.

In order to determine the versatility of the model and compare its results with a pore model (random pore model developed by Bhatia and Perlmutter, 1981a, 1981b, 1984), experimental data reported in literature (Borgwardt, 1970) was simulated. Borgwardt reported sulfation of CaO particles in the time-scales of less than 120 seconds at various temperatures in the range of 923 to 1253 K. The same experimental data is also simulated by Bhatia and Perlmutter (1984) using a random pore model (discussed in section 5.1). Figure 5.5 shows the simulations results obtained from the model discussed above along with the experimental data obtained by Borgwardt (1970). For the sake of comparison simulations of random pore model are also presented in Figure 5.6 and as can be seen, both the models are capable of simulating the experimental data extremely well. The obvious advantage of the proposed model is its ability to simulate not only the overall sulfation (simultaneous calcination and sintering) but also in predicting the sulfation behavior for more realistic residence times. Basic kinetic parameters such as activation energy values of the reaction and activation energy values of the product layer diffusivity are calculated using Arrhenius-type plots and are shown in Figures 5.7 and 5.8 respectively. Parameters are determined for both the laboratory generated and literature
reported (Borwardt, 1970) sulfation behavior of CaO. As can be seen the reaction activation energy values predicted for the two types of CaO particles are nearly the same and match closely with the values reported by other researchers using the same data (Table 5.1). Activation energy values obtained for product layer diffusion are approximately 30 kcal/mole for both the types of CaO and are typical of solid-state diffusion processes.

Figure 5.9 shows the predicted radial concentration profile for SO$_2$ inside the calcined grain, at various times. As can be seen from the figure, with increasing radial distance from the center the SO$_2$ concentration increases, this would suggest that the SO$_2$ concentration is depleted as it diffuses inwards. This behavior is also reflected by the local conversion plot, as shown in Figure 5.10. Furthermore, with increasing reaction time the local conversion at a given radial distance increases (Figure 5.10) resulting in reduction in porosity which further reduces the amount of SO$_2$ transported into the grain (Figure 5.9).

Radial surface Ca$^{2+}$ ion concentration profile is shown in Figure 5.11. Concentration of Ca$^{2+}$ ions at the surface of a micrograin is strongly dependent on the SO$_2$ concentration. At lower reaction times the porosity reduction due to sulfation is still not drastic and a significant amount of SO$_2$ can diffuse to the center of the grain thus, consuming the surface ions and lowering their concentration. As the reaction proceeds the SO$_2$ concentration at the center reduces because of loss in porosity (CaSO$_4$ product build-up) thus, resulting in less consumption of Ca$^{2+}$ ions and subsequent increase in surface ionic concentration. This behavior is simulated in Figure 5.12. Simulation results show that the surface ion concentration for micrograins at or near the center of the
grain goes through a minimum, indicating the transition of controlling regimes from reaction controlled phenomena to a diffusion controlled phenomena. Compared to the surface Ca\(^{2+}\) ion concentration of micrograins at the center of the grain, outermost micrograins are constantly exposed to bulk SO\(_2\) concentration and show (Figure 5.12) a monotonous decrease in surface ion concentration.

5.4.2 Sulfation of Linwood Ca(OH)\(_2\)

Figure 5.13 shows the experimental data and model predictions for simultaneous calcination and sulfation of Ca(OH)\(_2\) particles of size 3.6 \(\mu\)m at three different temperatures for residence times varying from 10 to 300 ms. As can be seen from the experimental results the sulfation of Ca(OH)\(_2\) proceeds extremely fast initially reaching upto 20% conversion, which represents nearly 70% of the final conversion attained, within the first 50 ms at all temperatures studied. At higher residence times, the reaction rate is considerably attenuated and the sulfation conversion tends to flatten. The proposed model predicts this behavior very well.

The "virtual die-off" of the reaction at higher residence times is seen at all the temperatures investigated. The characteristic high initial rate followed by considerable drop in the reaction rate can be attributed to various structural changes that accompany the overall sulfation phenomenon. The proposed model considers the sulfation reaction to take place on the outer surface of the micrograins formed during calcination. In a strict sense, calcination does proceed sulfation, as it provides the micrograins of CaO needed for sulfation but the process of "creation" of micrograins and their subsequent
"consumption" by sulfation take place simultaneously in a single grain of Ca(OH)$_2$. The high reaction rate during the initial stages of the reaction suggests that the transport resistances initially do not restrain the reaction. This explanation is further strengthened by the high initial porosity and surface area of nascent calcined Ca(OH)$_2$ as reported by Ghosh-Dastidar et al. (1996) and others (Milne et al., 1990). The CaO layer, consisting of micrograins, surrounding the uncalcined Ca(OH)$_2$ core rapidly sinters while simultaneously undergoing sulfation, thus losing the overall porosity and surface area and increasing the transport resistances for diffusing species (both SO$_2$ and H$_2$O). Furthermore, the build-up of CaSO$_4$ layer over individual micrograins leads to sulfation being dominated by diffusion of ionic species (Ca$^{2+}$ and O$^{2-}$) through this layer. All these phenomena eventually result in the overall sulfation process being dominated by transport resistances and are manifested as drastic drop in overall reaction rate at higher residence times.

Experimental data is used to establish values of the two parameters, the sulfation rate constant, $k_s$, and the product layer solid state diffusivity, $D_{\text{ion}}$. Other model parameters include calcination reaction rate constant, $k_c$, and sintering rate constant $k_{\text{sin}}$, are obtained from the calcination subroutine and details of which are given in Chapter III. The sulfation reaction rate constant and product layer diffusivity are determined by trial and error procedure to obtain the best fit to the experimental data. The activation energies and the pre-exponential factors are obtained from the Arrhenius-type plots shown in Figure 5.14. The activation energy value for sulfation reaction is calculated to be 14 kcal/mole, while for ionic diffusivity it is 32.1 kcal/mol. The sulfation activation energy obtained in this study compares well with 13.4 kcal/mol estimated by Bhatia and
Permutter (1981a) from sulfation data of Borgwardt (1970) of CaO in a differential bed reactor. They determined the activation energy of 28.9 kcal/mol for ionic diffusivity. Borgwardt and Bruce (1986) estimated the apparent activation energy for CaO sulfation at later stages of the reaction to be about 36.6 kcal/mole. They concluded that the high value of activation energy was indicative of ionic product layer diffusion.

The model simulates the experimental data extremely well, closely predicting both the initial steep slope and the rate attenuation of the experimental data. However, for the reaction temperature of 1223 K, only the model simulations are shown. The model fits the higher temperature data of 1308 and 1353 K very well at both short time scales as well as at higher residence times. At 1353 K model simulates a slightly higher initial reaction rate than shown by the experimental results.

5.4.3 Sulfation of HRC

Figure 5.15 shows the experimental data and model prediction for simultaneous calcination, sintering and sulfation of 3.9 μm CaCO\(_3\) (HRC) particles at three different temperatures for residence times ranging from 10 to 300 ms. A similar trend is observed in all the sulfation curves. Initially, sulfation progresses extremely fast and exhibits a strong influence of temperature. At higher residence times, the reaction rates attenuate considerably and conversion tends to flatten out. Nearly 75% of the final extent of calcination (at about 300 ms) is achieved within the first 50 ms at all the temperatures studied. At 1273 and 1353 K reaction temperatures the initial sulfation behavior of HRC is found to be very similar. At higher reaction times HRC exhibits higher sulfation extents at 1273 K temperature than at 1353 K as explained in Chapter IV.
The characteristic behavior of high initial rate followed by attenuation with virtual die-off is closely linked with the structural effects accompanying the reaction, as outlined in Chapters III and IV. For the high temperature studies, sintering and sulfation of product CaO holds the key to explaining and modeling these observed features.

The model discussed earlier assumes that the calcination reaction proceeds on a single CaCO$_3$ grain according to the shrinking core model resulting in the formation of a porous multi-layered CaO surrounding shell comprising of micrograins of CaO. The sulfation reaction takes place at the surface of these micrograins between diffusing SO$_2$ and Ca$^{2+}$ and O$^{2-}$ ions. 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 micrograin surface may be the rate limiting step. The multi-layered CaO product rapidly sinters and sulfates thereby losing surface area and porosity. This offers increasing resistance for the gaseous SO$_2$ to diffuse through the CaO product shell of the grain. This leads to increasing relatively higher sulfation of the outermost CaO micrograin layer and negligible sulfation of the inner micrograin layers. All these phenomena eventually result in the overall sulfation reaction being dominated by diffusion of SO$_2$ through the CaO shell. Furthermore, once the micrograins in the outermost layer have sulfated to a considerable extent the solid state product layer diffusion of ions starts to dominate and retards the sulfation of these micrograins.

As explained earlier the experimental data is used to establish values of the two sulfation reaction rate constant, $k_s$, and the product layer diffusivity. The activation energies and the pre-exponential factors are obtained from the Arrhenius-type plots shown in Figure 5.16. The activation energy value for sulfation reaction is calculated to
be 16.6 kcal/mole, while that for ionic diffusion it is 32.1 Kcal/mol. These values compare well with values reported in the literature (Bhatia and Perlmutter, 1981a, Milne et al., 1990, Borwardt et al., 1986).

The model fits the experimental data fairly well, closely predicting both the initial steep slope and the rate attenuation of the experimental data. However, for the reaction temperature of $1353 \text{ K}$, the model overestimates the initial rate but at higher residence times, its prediction match very well with the experimental data. The model also predicts the “cross-over” between sulfation extents at $1273$ and $1353 \text{ K}$, predicting higher conversions at $1273\text{K}$ temperature than at $1353\text{K}$ for later stages of the reaction, thereby successfully simulating the experimental observations.

5.5 Conclusions

Experimental data for simultaneous calcination, sintering and sulfation of small Ca(OH)$_2$ and CaCO$_3$ particles are obtained for high temperatures and short reaction times. A mathematical model is developed based on first order decomposition kinetics (proposed by Borgwardt, 1970), second order sintering rate equation (proposed by Nicholson, 1965), and sulfation reaction between SO$_2$ and Ca$^{2+}$ and O$^{2-}$ ions, diffusing outwards through the CaSO$_4$ product layer (Hsia et al., 1993, 1995), which satisfactorily describes the time-resolved experimental data. The proposed mathematical model is based on a grain-micrograin concept and includes the initial particle structural properties (surface area and porosity) and structural changes due to sintering and reactions (calcination and sulfation).
The mathematical model successfully predicts the sulfation behavior of three different types of calcium-based sorbents, including laboratory generated CaO, commercially used Linwood Ca(OH)$_2$, and high reactivity carbonate (HRC), at different temperatures, accurately representing the experimental observation that sulfation reaction is extremely fast with more than 75% of the final conversion occurring in the first 50 ms. The model successfully predicts the high initial reaction rate and virtual reaction "die-off" at later stages. Versatility of the model is demonstrated by simulating sulfation behavior of laboratory generated CaO (obtained from pre-calcination of Ca(OH)$_2$) and data reported in the literature. Model predictions compare well with random pore model when applied to the same experimental data. Model predicted kinetic parameters are in significant agreement with the values reported in the literature.

The simulation and experimental results demonstrate the severity of sulfation and sintering on sorbent reactivity at high temperatures and influence of initial sorbent particle structure as an important parameter for SO$_2$ capture. In view of this, the results of this study can be utilized to determine an optimum sorbent structure for sorbent injection, with an objective to achieve superior sorbent utilization and high sulfur capture.
Table 5.1: Comparison of Random Pore Model and proposed Grain-Micrograin Model.
Gas-Phase (G), Containing Gaseous Reactant

(a) Original Sorbent (Solid phase S)

Marker

(b) Product Layer

Unreacted Sorbent

(c)

Figure 5.1: Principle of marker studies; (a) Original specimen with inert marker (preferably Pt); (b) Inward growth reactants move from G/S interface to S/S interface; and (c) Outward growth with reactant moving from S/S interface to G/S interface (adapted from Hsia et al., 1993).
Figure 5.2: Sulfur atom concentration profiles on the sulfation sample (marker experiments); (a) inward growth mode; MX* layer is found next to the S/S interface, (b) mixed growth mode; one additional interface is present, the MX* layer is sandwiched between two MX layers, and (c) outward growth mode; the MX* layer is found next to the G/S interface (adapted from, Hsia et al., 1995).
Figure 5.3: Schematic illustration of the sulfation model: (a) Single, spherical sorbent grain; (b) Partially calcined and sulfated grain with inner unreacted core and partially sintered and sulfated CaO micrograins; (c) Partially sulfated CaO micrograin.
Figure 5.4: Experimental and predicted sulfation extent for CaO at different temperatures. Particle size: 3.6 μm; SO$_2$ conc.: 3900 ppm
Figure 5.5: Experimental data and proposed model predictions on CaO sulfation (experimental data from Borwardt, 1970).
Particle size: 46 μm; SO$_2$ conc.: 3000 ppm
Figure 5.6: Experimental data and random pore model predictions for 46 μm CaO particles (Bhatia and Perlmutter, 1981b).
Figure 5.7: Determination of activation energy for sulfation of laboratory generated CaO and data from literature (Borgwardt 1970).
Figure 5.8: Determination of activation energy of solid-state product layer diffusion during sulfation of laboratory generated CaO and literature values (Borgwardt, 1970).
Figure 5.9: Model predicted $\text{SO}_2$ concentration profile at various radial positions and reaction times during CaO sulfation.
Figure 5.10: Model predicted variation in local conversion with radial distance and time for CaO sulfation.
Figure 5.11: Model predicted ion concentration profile at various radial positions and reaction times during CaO sulfation.
Figure 5.12: Model predicted variation of micrograin surface ion concentration at three different radial positions with time during CaO sulfation.
Figure 5.13: Experimental and model predictions of sulfation extent for Ca(OH)\textsubscript{2} at various temperatures.
Figure 5.14: Determination of activation energies of sulfation and solid-state product layer diffusion for Ca(OH)$_2$ sulfation.
Figure 5.15: Effect of temperature on sulfation of HRC, experimental data and model predictions. Particle size: 3.6 μm; SO₂ conc.: 3900 ppm
Figure 5.16: Determination of activation energies for HRC sulfation reaction and product layer diffusion.
CHAPTER 6

EMISSIONS OF INORGANIC TRACE SPECIES DURING COAL COMBUSTION: LITERATURE REVIEW

6.1 Introduction

The role of sulfur and nitrogen species as major air pollutants emitted during coal combustion has been well documented. In the past few years several other pollutants emitted by coal-fired combustors and utility boilers have also been identified. Some of these pollutants are emitted in trace amounts and are classified as trace heavy metals. Since 1990 the awareness regarding the toxic and hazardous effects of these pollutants has increased immensely and one of the leading candidates in this notoriety is mercury. Although mercury has received most of the attention, there are other trace elements emitted during burning of coal that are equally toxic and pose a threat to plants, animals and humans.

Although most of the inorganic matter in coal remains in the ash, pulverized coal combustion do lead to volatilization of some of the low-boiling trace elements and their subsequent transfer into the gas-phase. Some high volatility trace elements are exclusively emitted as vapor through the stack. Some of the less volatile trace elements partly deposit on the fly ash particles as the flue gas cools down and are partly emitted
into the atmosphere as vapor and particulates. These elements are known as Chalcophiles and As, Se, Pb, Sb, and Cd are some examples of elements that display such behavior.

Most of the chalcophilic elements have been identified as air toxics from coal-fired combustor and utility boilers in the 1990 Clean Air Act Amendments (CAAA). The U.S. EPA has been conducting extensive research to determine their hazardous health and environmental effects. It is soon expected to announce regulatory limits applicable to coal-fired utilities and is most likely to include some, if not all, of the chalcophiles. The control of chalcophilic emissions presents a formidable technical and economical challenge to the coal-fired utilities. This is due, in part to the lack of understanding of the behavior of these elements and also due to the trace amounts these exist in. Considerable effort has been made in last 4-5 years to determine the speciation of these elements. Most of the research has concentrated upon determining the exact chemical form(s) of these elements in a highly varied and heterogeneous flue gas environment, with very limited attention being focused on the actual methodology to be applied to their control.

Potential Hazardous Air Pollutants (HAPs) emitted from coal-fired power plants and utilities could be in vapor form or particulates (aerosols) and are generally divided into two categories:

Inorganic Elements and their compounds;

Organic Compounds.

Combustion of coal converts all the organic matter in coal into carbon dioxide and water. The nonvolatile inorganic matter constitutes the coal gas residues which includes bottom ash (or boiler slag) and fly ash. The more volatile inorganics, of which many of the chalcophiles are part of, either escape with the flue gas entirely in vapor form or
condense on the fly ash at relatively low temperature regions of the boiler. This distribution/partitioning of inorganics in the three major coal residues has been a subject of intense research. Table 6.1 gives the resulting distribution for the case where the bottom ash is 22.2% of the total ash, fly ash is 77.1% of the total ash and 0.7% of the total ash escapes with the flue gas (Valkovic, 1983a; 1983b). Trace element flow pathways in the coal fired power plant has been studied by a few researchers. Klein et al. (1975) studied the concentrations of the trace elements in T. A. Allen Steam Plant in Tennessee to determine the emission characteristics of 37 elements. They analyzed only in-plant samples for these elements and applied mass balance closure conditions and concluded that elements which do not show acceptable mass balance closure are being discharge with the flue gases. Table 6.2 summarizes the distribution of trace elements and their concentration ratios which is a measure of their partitioning. Several elements (Al, Fe, Ca, K, Mg, Ba) are distributed equally between inlet fly ash and slag and do not concentrate on the outlet fly ash. Other elements (Cr, Na, Ni) are moderately more concentrated on the inlet fly ash than on the slag and show some affinity towards outlet fly ash. Elements such as As, Se, Pb, Cd, Sb, and Zn are very poorly incorporated in slag and are subsequently more concentrated in the outlet fly ash. On the basis of mass-balance closure this study corroborated that highly volatile inorganics such as Hg, Cl, Br, and Se are being discharge into the atmosphere in vapor/gaseous forms. Studies by Kaakinen et al. (1975) at the Valmont Power Station in Colorado also reported very similar partitioning behavior.
Klien et al. (1975) divided the elements into three broad classes based to their concentration ratios:

Class I: Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti – are readily incorporated into the slag (slag/coal > 6.6). They are partitioned about equally between the inlet fly ash and slag and show no tendency to concentrate on outlet fly ash. These elements do not volatilize in the combustion zone, instead they form a melt that is incorporated in both the fly ash and slag.

Class II: As, Pb, Se, Cd, Cu, Ga, Sb, and Zn – are poorly incorporated in the slag. These elements are concentrated in the inlet fly ash compared to the slag and in the outlet fly ash compared to the inlet fly ash. These elements are volatilized on combustion and hence, depleted in the slag. But they do get adsorbed or condensed on the fly ash particles as the fly ash cools.

Class III: Hg, Cl, Br – essentially remain completely in the gas phase because of their high vapor pressure.

Most of the elements in the Class II come under the "chalocophilic" group in Goldschmidt's geo-chemical classification (Mason, 1966). Highest elemental Enrichment Factor (EF) values on in-stack particles is observed for Class II chalocophiles. EF is defined as:

\[
EF = \frac{(X/Al)_{stack}}{(X/Al)_{coal}}
\]

(7.1)

Where, \((X/Al)_{stack}\) is the ratio of the concentration of element X to aluminum (Al) in the suspended particles and \((X/Al)_{coal}\) is their ratio in coal.
6.2 Chemical state and volatility of trace elements in coal

Most of the Class I elements are known to occur mostly as oxides or form oxides upon heating in the presence of air (such as SiO$_2$, Al$_2$O$_3$, CaO, MgO, K$_2$O). They come under the category of lithophiles (aluminosilicate-associated elements) in Goldschmidt's geo-chemical classification. The Class II elements are known to occur most possibly as sulfides or oxides (Se, Pb, Zn, As, Sb, Cd). These belong to the class of elements known as chalcophiles (sulfide-associated elements) (Chigier, 1981). The chalcophiles are known to occur in coal in association with organic matter. Many studies have shown that chalcophiles such as Se and Ga have a high organic affinity (Chigier, 1981; Capes et al., 1974). During coal combustion, trace elements associated with the organic matter maybe volatilized or form aerosol particles and have a much higher probability of being transferred to the gas phase. Hence, such trace elements play an important role in particulate and gaseous emissions from coal combustion.

6.3 Concentration of trace element emissions (Se and As)

This section discusses the chalcophilic emissions with special emphasis on Se and As species. Arsenic is chosen as the candidate trace element for this study because of its presence in stack as both vapor and particulate and hence presents most difficulty from emission-control point of view. Selenium is included in the discussion to illustrate the comparison and establish that a similar approach is applicable to control of various other Class II trace elements. Furthermore, arsenic represents the typical dilemma that is pertinent to the toxicity of nearly all the trace element emissions. Despite the fact that As is an essential trace element for humans and other animals, arsenic and its
compounds have been linked to harmful toxicological impacts. Coal-fired power plants have been identified as major sources responsible for trace metal emissions including arsenic and will most likely be required to reduce these emissions by anticipated EPA regulations.

Germani and Zoeller (1988) studied the concentration of As, Se, Hg, Br, and I in the stack of the Chalk Point Electric Generation Station located in Maryland. They found that the average in-stack concentration of Se was 33 (± 5) μg/m³ (both particulates and vapor) with 59% of the total Se emitted in the vapor form. This compares well with the work of Gladney et al. (1976) also at Chalk Point facility, which reported that about 61% of Se to exit in the vapor phase. Another study by Andren et al. (1975) at the Allen Steam Plant found a very high percentage of the total emitted Se to be in the vapor phase, 93%, and they attributed that to the highly efficient ESP system compared to the one used in Chalk Power Station. Germani and Zoeller (1988) also measured the As concentration at 140 (± 80) μg/m³, with about 13% of it in the vapor phase (the % of As in the vapor phase varied from 0.7-52%). They also reported that the vapor phase concentration of As decreased linearly with increasing solids loading in the flue gas thus confirming the observations of Klien et al. (1975) that Arsenic species tend to condense on the particulate matter at low temperatures. Thurnau and Fournier (1992) reported that between 5-20% of the arsenic remains in the flue gas during incineration of arsenic laden hazardous soil matrices. Owens et al. (1993) reported that in the coal-fired cement kiln process, the vaporization of arsenic is suppressed. They cited the formation of calcium arsenate as the probable cause for the suppression.
U.S. coal is higher in As and Se content than the world average. The world average for As content in coal is 5 ppm, while the U.S. coal contains 15 ppm of As (Andren et al., 1975). Se is present at an average concentration of 3 ppm worldwide whereas in U.S. coal its content is about 4.1 ppm. Arsenic concentration in Ohio coals shows a large variation with 2 ppm being the lowest and 110 ppm being the highest recorded concentration (Botoman and Stith, 1978) whereas the Se content of Ohio coals is about 4.3 ppm (Knapp, 1977).

6.4 Chemical state of vapor emitted arsenic

Exact compound identification of As in the flue gas environment has not been confirmed in the present literature and differences exist. Probably because of the difficulty in conducting these experiments, both in vapor as well as in the particulate phases and also due to the tendency of these trace elements to form multiple chemical compounds in the variable flue gas environment (temperature and chemical composition).

The chemical state in which arsenic exists in the flue gas has been a subject of intense controversy and speculation. The elemental state As, and the oxide form, As$_2$O$_3$ have been postulated to be the two most probable species but the arguments favoring the oxide forms are gaining ground. Arsenic (along with selenium) is much more volatile as oxide than as element. The saturation concentration of arsenic occurring as As$_2$O$_3$ in flue gas is about 300 mg/m$^3$ at typical stack temperature of 150°C, while that of the elemental form is only about 0.060 mg/m$^3$. The corresponding flue gas concentration upon combustion is around 1.3 mg/m$^3$ for arsenic at 150°C and at 3% O$_2$ by volume (Dismukes, 1994). Thus, flue gas could contain all of the arsenic in the form of
oxide and not as element. Germani & Zoller (1988) have also observed that $\text{As}_2\text{O}_3$ should be the vapor-phase species instead of the elemental form because combustion would tend to produce the oxide form. They have based their observation on two main factors. Thermodynamically, the free energy of formation is most favorable for $\text{As}_2\text{O}_3$ formation under the high temperature conditions and $\text{As}_4\text{O}_6$ (a dimer of $\text{As}_2\text{O}_3$) has the higher equilibrium-saturation concentration in the vapor phase than $\text{As}_4$, as seen in Figure 6.1. Srinivasachar et al. (1992) studied the speciation of As, Cd, Cr, and Pb under simulated incineration conditions. They reported the presence of $\text{As}_2\text{O}_3$ under oxidizing conditions doped with one or both of HCl and SO$_2$. Winter et al., (1994) also observed $\text{As}_2\text{O}_3$ as the only species following injection of aqueous $\text{As}_2\text{O}_3$ into simulated combustion environment (no thermal decomposition). Woulerlood and Bowling (1979) also reported that arsenic occurs as $\text{As}_4\text{O}_6$ in the vapor state up to temperatures of 800°C. Wu and Biswas (1993) performed equilibrium analyses on the basis of Gibbs free energy minimization by the method of element chemical potentials combined with atom population constraints using a thermodynamic equilibrium computer code, STANJAN (Reynolds, 1990). They reported that in the presence of Chlorine (especially in incinerators) the formation of $\text{AsCl}_3$ was favored, with the oxide formation increasing with the temperature. Thus it can be concluded that in the absence of Chlorine (as in combustors) oxide formation of arsenic would be thermodynamically favorable.

6.5 Control of trace chalcophilic metal emissions

The available literature is replete with the elemental analysis of fly ash and the concentration of trace elements as a function of particle size and depth. Few
kinetic studies have been conducted, mostly by researchers in inhalation and toxicology fields to examine the effects of deposition of fly ash coated with toxic metals. Wouterlood and Bowling (1979) studied coal-derived fly ash as one of the materials for removal of $\text{As}_4\text{O}_6$ from flue gases at 200°C in a fixed bed. The authors found condensation of $\text{As}_4\text{O}_6$ on fly ash even though the vapor was not saturated with $\text{As}_4\text{O}_6$ at 200°C. Germani and Zoeller (1988) found that the concentration of $\text{As}_4\text{O}_6$ decreases as the total particulate loading in the flue gas increases, again at 200°C. They put forth two possible mechanisms to explain the observed As behavior. Both their mechanisms involve an irreversible reaction occurring on the particle surface, converting the vapor phase $\text{As}_4\text{O}_6$ to a nonvolatile form that remains on the surface. No further studies were conducted to validate these mechanisms. Yodnane and co-workers (1992) worked on removing arsenic and selenium from fly ash leachate, in an effort to reduce their concentration in fly ash ponds to current drinking water standards set by U.S. EPA. Results of their studies showed that arsenic can be removed effectively from fly ash leachate by both iron coprecipitation and activated alumina. Ghosh-Dastidar et al. (1996) conducted a series of experiments to determine the most efficient mineral sorbent for removal of selenium from gas phase in the temperature range of 400-1000°C. They determined that calcium-based sorbents were most effective in removing selenium and the interaction between Ca-based sorbent and selenium species involved an irreversible reaction with the formation of calcium selenite ($\text{CaSeO}_3$) as a product.

Rothenberg et al. (1991) studied the rated of adsorption of m-Xylene by fly ash. The authors found that the half-times required for mono-layer formation are similar to the residence times of fly ash in the stack. Kinetics of m-Xylene adsorption by fly
ash resembled kinetics reported for penetration of adsorbates into porous adsorbents. Rothenberg and Chang (1980a, 1980b) measured the rates of desorption of water from fly ash at different temperatures and concluded that there exists a strong chemical interaction between water and fly ash. They also reported that fly ash includes several components with can react chemically with water but did not elaborate further. Martinez-Tarazonz and Spears (1996) studied the fate of various trace elements during pulverized coal combustion. They conducted synchronized sampling of pulverized coal, bottom ash and fly ash and determined that As, Cu, Mo, Pb, and Zn were concentrated in the fly ash and as the particle sizes of the fly ash decrease, the concentration of these elements increases, which can be predicted from the volatile character of their compounds.

Uberoi and Shadman (1990, 1991a, 1991b) and Uberoi et al. (1991) tested various mineral sorbents for their efficiency in capturing cadmium, lead, and alkali metal vapors from hot flue gases. These studies were carried out in a differential bed reactor, and in the temperature range of 600-800°C. Their studies indicate that alumina, kaolinite, and bauxite are the most promising among the naturally occurring minerals for cadmium and lead removal. Leachability tests performed on the post-sorption samples of these sorbents showed that nearly 90% of the trapped metal species are not water soluble. On the basis of XRD analyses of their samples they concluded that chemical reaction, not physical reaction, in the dominant method of metal capture. Gullett and Raghunathan (1994) conducted elaborate experiments to determine the effect of sorbent injection technologies on emissions of coal-based metallic air toxics. Tested sorbents in their study included hydrated lime, limestone, kaolinite, and bauxite in the upper-furnace temperature range of 1000-1300°C. They have reported significant reductions in
sub-micrometer concentrations of antimony, arsenic, mercury, and selenium with the injection of hydrated lime and limestone (calcium-based sorbents). They also reported that the total amount of arsenic increased when using hydrated lime and limestone. Benson (1993) has also reported that injection of CaO at the furnace atmosphere leads to arsenic capture in the form of calcium arsenate.
<table>
<thead>
<tr>
<th>Element</th>
<th>Bottom Ash (22.2%)</th>
<th>Fly Ash (77.1%)</th>
<th>Flue Gas (0.7%)</th>
</tr>
</thead>
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<tr>
<td>Aluminum</td>
<td>20.5</td>
<td>78.8</td>
<td>0.7</td>
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<tr>
<td>Antimony</td>
<td>2.7</td>
<td>93.4</td>
<td>3.9</td>
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<tr>
<td><strong>Arsenic</strong></td>
<td><strong>0.8</strong></td>
<td><strong>99.1</strong></td>
<td><strong>0.1</strong></td>
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<tr>
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<td>16.9</td>
<td>81.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Boron</td>
<td>12.1</td>
<td>83.2</td>
<td>4.7</td>
</tr>
<tr>
<td>Cadmium</td>
<td>15.7</td>
<td>80.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Calcium</td>
<td>18.5</td>
<td>80.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Chlorine</td>
<td>16.0</td>
<td>3.8</td>
<td>80.2</td>
</tr>
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<td>Chromium</td>
<td>13.9</td>
<td>73.7</td>
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<tr>
<td>Lead</td>
<td>10.3</td>
<td>82.2</td>
<td>7.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>17.2</td>
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<td>0.8</td>
</tr>
<tr>
<td><strong>Mercury</strong></td>
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<td>0</td>
<td><strong>97.9</strong></td>
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<tr>
<td>Molybdenum</td>
<td>12.8</td>
<td>77.8</td>
<td>9.4</td>
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<tr>
<td>Nickel</td>
<td>13.6</td>
<td>68.2</td>
<td>18.2</td>
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<td>Selenium</td>
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<td>Zinc</td>
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Table 6.1: Distribution of trace elements among bottom ash, fly ash, and flue gas (adapted from Valkovic, 1983).
<table>
<thead>
<tr>
<th>Element</th>
<th>Element Conc., ppm</th>
<th>Slag/Coal</th>
<th>FA/Slag (Inlet)</th>
<th>FA/ Slag (Outlet)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Slag</td>
<td>I/L FA</td>
<td>O/L FA</td>
</tr>
<tr>
<td>Al</td>
<td>10,440</td>
<td>102,300</td>
<td>90,900</td>
<td>76,000</td>
</tr>
<tr>
<td>Ca</td>
<td>4,340</td>
<td>46,000</td>
<td>25,200</td>
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<tr>
<td>Fe</td>
<td>10,850</td>
<td>112,000</td>
<td>121,000</td>
<td>150,000</td>
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<td>1,540</td>
<td>15,800</td>
<td>20,000</td>
<td>24,000</td>
</tr>
<tr>
<td>Mg</td>
<td>1,210</td>
<td>12,400</td>
<td>10,600</td>
<td>-</td>
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<tr>
<td>Si</td>
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<td>229,000</td>
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<td>Ti</td>
<td>506</td>
<td>4,100</td>
<td>5,980</td>
<td>10,000</td>
</tr>
<tr>
<td>As</td>
<td>4.45</td>
<td>18</td>
<td>110</td>
<td>440</td>
</tr>
<tr>
<td>Cd</td>
<td>0.47</td>
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<tr>
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<td>&lt;200</td>
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<td>Hg</td>
<td>0.122</td>
<td>0.03</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.2: Trace elemental concentration and concentration ratios from a typical pulverized coal combustor (adapted from Klein et al., 1975).
Figure 6.1: Saturation curves for some selected metals and their compounds.
CHAPTER 7

CAPTURE OF ARSENIC SPECIES USING Ca-BASED SORBENTS

The contents of this chapter have been accepted for publication in the *Environmental Science and Technology Journal* (S. Mahuli, R. Agnihotri, S. Chauk, A. Ghosh-Dastidar, and L.-S. Fan). The article is due to appear in the journal.

7.1 Introduction

Coal combustion, waste incineration as well as metallurgical operations such as smelting of ores generate hot flue gases containing arsenic. Coal-fired power plants have been identified as major sources responsible for trace metal emissions including arsenic and will most likely be required to reduce these emissions by impending EPA regulations. The average arsenic concentration in U.S. coal is reported as 15 μg/g (Dismukes, 1994). Arsenic and its compounds have been linked to harmful toxicological impacts despite the fact that arsenic is an essential trace element for humans and other animals.

The concentration of arsenic species, its phase transformations, and its chemical state have been a subject of debate. Germani and Zoller (1988) reported between 0.7-
52% of the in-stack As to be in the form of vapor and its concentration in the vapor phase to be about 7 μg/m³. Thurnau and Fournier (1992) observed between 5-20% of the arsenic remains in the flue gas during incineration of arsenic laden hazardous soil matrices. Owens et al. (1993) found that in the coal-fired cement kiln process, the vaporization of arsenic is suppressed. They cited the formation of calcium arsenate as the probable cause for the suppression.

The elemental state As, and the oxide form, As₂O₃ have been postulated to be the two most probable species in the oxidizing flue gas environment. However, arsenic (along with selenium) is much more volatile as oxide than as element. The saturation concentration of arsenic occurring as As₂O₃ in flue gas is about 300 mg/m³ at typical stack temperature of 150°C; while that of the elemental form is only about 0.060 mg/m³. The corresponding flue gas concentration upon combustion is around 1.3 mg/m³ for arsenic at 150°C and at 3% O₂ by volume (Dismukes, 1994). Thus, flue gas could contain all of the arsenic in the form of oxide and not as element. Germani & Zoller (1988) have also observed that As₂O₃ should be the vapor-phase species instead of the elemental form because combustion would tend to produce the oxide form. Srinivasachar et al. (1992) studied the speciation of As, Cd, Cr, and Pb under simulated incineration conditions. They reported As₂O₃ under oxidizing conditions doped with one or both of HCl and SO₂. Winter et al., (1994) also observed As₂O₃ as the only species following injection of aqueous As₂O₃ into simulated combustion environment.

The high volatility and its existence in the form of vapor make arsenic emission control very difficult task. In the past few years, dry sorbent injection for in-situ
capture of the metal from hot flue gas has been studied with the aim of developing a potential control technique. The rationale behind such approach lies in its already proven performance in SO₂ removal by using calcium-based sorbents in high or medium temperature range of the flue-gas pathway.

In dry sorbent injection technique, metal sorption by the solid could take place by means of physical adsorption, chemisorption or chemical reaction or a combination of these processes. Prior investigations have involved studies on the effectiveness of different mineral sorbents in removal of cadmium, lead and alkali metal compounds from hot flue gas. Uberoi and Shadman (1990, 1991a, 1991b) have studied silica, alumina, kaolinite, bauxite, emathlite and lime for sorption of cadmium and lead in a thermogravimetric type reactor system for a reaction temperature of 700 to 800°C. Their results showed that the overall sorption process is not physical, but a complex combination of physical and chemical processes which are dependent on the temperature and the type of sorbent. Gullet and Raghunathan (1994) used several mineral sorbents, namely, hydrated lime, limestone, kaolinite and bauxite for upper-furnace injection and measured reduction in the amounts of various metallic air toxics. They reported significantly higher capture of arsenic with hydrated lime and limestone compared to the other sorbents. With Ca-based sorbent injection, there was a reduction of the submicrometer arsenic fraction. Ho et al. (1993, 1995) studied capture of lead and cadmium compounds by limestone, sand and alumina during fluidized bed combustion/incineration. Wu et al. (1995) have studied multi-functional sorbents for the simultaneous removal of sulfur oxides as well as metallic contaminants from high-
temperature gases. Gullett et al. (1992) and Jozewicz and Gullett (1995) investigated the kinetics and the reaction mechanism of dry Ca-based sorbents with gaseous HCl in a short-time differential reactor. Wouterlood and Bowling (1979) studied the removal of As\textsubscript{2}O\textsubscript{6} from flue gases at 200°C using surface-active agents as well as Ca-based sorbents. They concluded some chemical reaction or chemisorption mechanism with the sorbents.

It is known that fly ash acts as a good sink for most of the volatile trace toxics (with the possible exception of highly volatile mercury and halides). Germani and Zoeller (1988) reported that the vapor phase As concentration decreases linearly with increase in the in-stack total particulate mass loading over the entire range of their study (11-254 mg/m\textsuperscript{3}). The concentration of various elements on fly ash is highly size sensitive and has been the subject of a number of investigations. An inverse relationship has been confirmed between concentration of trace elements and the fly ash by a number of researchers (Davison et al. 1974; Natsuch et al., 1974; Lee and van Lehmden, 1973; Ondov et al., 1979; & Markowski and Filby, 1985). Davison et al. (1974) reported that the conc. of Pb, Zn, Se, As, Cd, and Sb increased markedly with decreasing particle size. Their study included both fly ash retained by the particulate collection devices as well as the airborne fly ash, covering the range from 0.65 to 74.0 \(\mu\)m. They reported that the concentration of captured As on 5-10 \(\mu\)m fly ash particles was 8 folds than that on >40 \(\mu\)m particles. Ondov et al. (1979) studied the concentration trend of 42 trace elements in fly ash particles collected in the Electrostatic Precipitator (ESP) at a western coal-fired utility and in the airborne aerosol fly ash
particles in the stack. They reported that the enrichment of fly ash particles with As was considerable and it increased with decreasing particle size. Although it is well established that fly ash particles do capture arsenic species but the nature of interaction between fly ash particles and arsenic is not well understood.

In this study, the effectiveness of some commonly used mineral sorbents is tested for removal of arsenic. Investigations are conducted with hydrated lime sorbent to identify the mechanism of As/Ca interaction and the chemical state and characteristics of captured species. In order to compare the characteristics of capture by sorbents with those of fly ash, a representative fly ash is also tested for its arsenic removal potential.

7.2 Differential bed reactor assembly

A schematic of the reactor setup is shown in Figure 7.1. The main components of this system are the microbalance-equipped toxic vapor generation assembly and the differential bed assembly housed in a furnace. The details of the reactor system are described in detail elsewhere (Ghosh-Dastidar et al., 1996).

7.2.1 Vapor generation set-up

The arsenic source is held in a Pt sample pan suspended by a Pt hangdown wire from the ATI Cahn D-200 digital microbalance. As$_2$O$_3$ is used as the arsenic source in all the experiments. The vaporization tube which houses the source pan is a 25.4 mm o.d. quartz tube with provision for carrier gas entry and thermocouple insertion for
monitoring the source temperature. Dry nitrogen, which is used as the carrier gas in all
the experiments, enters at the top of the tube and flows down over the arsenic source.
The vaporization tube is wrapped with heating tape and closely maintained at a specific
temperature using the thermocouple and a temperature controller. Solid As$_2$O$_3$ has
significant vapor pressure above 150°C (Perry and Green, 1984), as shown in Figure
7.2. The desired concentration of arsenic in the gas phase is achieved by adjusting the
temperature of the vaporization tube. A vaporization temperature of about 200°C gives
the desired uniform vaporization rate to achieve the objective of a small yet uniform
concentration of arsenic. The flow rate of the carrier gas is typically maintained at an
optimum value of 200 ml/min, since experimental observations suggest that any higher
flow rates lead to loss in accuracy of the weight reading.

7.2.2 Reactor system

The reactor assembly consists of a ceramic tube, a 1200°C Lindberg single-zone
furnace and a sorbent holder assembly. The reactor is a 2.54 cm o.d. mullite tube
cemented to custom-fabricated stainless steel end-connections at the top and bottom.
The top connection has provision for mixing the toxic vapor-laden reactant stream with
the diluent flow. A 6.4 mm o.d. flexible stainless steel tubing transports the As$_2$O$_3$-
carrying gas from the vaporization tube to the top of the reactant tube. In order to
avoid condensation of the As species in this transport line, its length is kept to a
minimum and is maintained at a higher temperature than the vaporization tube by
wrapping with heating tape. Before the carrier gas enters the reactor, it is mixed with
diluent gas. Dry air is used as the diluent stream. The diluent gas is passed through a Alltech Hydropurge II molecular sieve adsorbent. This trap serves to simultaneously remove moisture and CO₂ from the air. In order to avoid any arsenic species condensation due to lowering in temperature upon mixing, the diluent gas is preheated by passing the diluent transport line (3.2 mm o.d. stainless steel) through the reactor furnace. Mixing of the diluent gas and the carrier gas takes place in the top stainless steel end-connection just before entering the reactor. The sorbent is dispersed on a small amount of quartz wool which is supported on the quartz sorbent holder. The 9.2 mm o.d. quartz tube is cemented to a 12.7 mm o.d. stainless steel tube through which all the reactant gases are carried out after flowing through the sorbent bed. The sorbent holder assembly is inserted inside the reactor from the bottom and is positioned such that the bed lies near the center of the furnace heating section. The gas coming out from the reactor passes through a train of two aqueous impinger solutions designed to capture the remaining As₂O₃ before being vented to exhaust. 7% HNO₃ solution is used as the impinger solution.

7.2.3 Experimental procedure and analyses

The chemical composition of the different sorbents and the fly ash (NIST Certified) is given in Table 7.1. During experiments, a small amount of pre-weighed sorbent (15-20 mg) is dispersed on small quantity (3-5 mg) of quartz wool in the sample holder. The sample holder is introduced into the reactor and is allowed to reach the sorption temperature. The vaporization of As₂O₃ sample in the vaporization tube is
initiated by heating it to the required temperature and maintaining at that temperature for a near constant rate of vaporization. The vaporization rate is obtained from the weight loss curve versus time generated by the microbalance system. The arsenic concentration is calculated from the knowledge of vaporization rate and the gas flow rates. The experiments are performed with the vapor-carrier gas and diluent gas flow rates at 200 and 1000 ml/min (STP) respectively. Ca(OH)$_2$ calcination is realized in-situ by keeping the furnace at the predetermined calcination temperature for a fixed period of time under a continuous flow of N$_2$. After calcination, the furnace temperature is adjusted to the desired sorption temperature thus avoiding atmospheric exposure of the calcined sorbent.

The amount of arsenic captured is determined by measuring the arsenic content of the sorbent after the experiment. The total capture is determined by dissolving the sample in H$_2$O/H$_2$O$_2$/HNO$_3$ (5/1/1 by volume) mixture. The leaching is conducted in an ultrasonic bath for about 4 hours which is found to be adequate to leach out all the arsenic. The dispersant quartz wool itself exhibits no significant capture (<25 ppm) of arsenic. The arsenic content of the solution is determined by a Perkin-Elmer Model 3110 graphite-furnace atomic absorption spectrometer (AAS). X-ray diffraction (XRD) analysis is conducted on a Scintag PAD-V diffractometer. Quantitative analysis of arsenite and arsenate analysis is performed using a Suppressor-based Single-Column Ion Chromatograph (Alltech).

7.3 Results and discussion
The sorbent screening experiments are performed at a temperature of 600°C and the results are presented in Figure 7.3. Of the four sorbents tested, Ca(OH)$_2$ was found to exhibit the highest arsenic capture. The results of the screening experiments show good reproducibility and corroborate the findings of other researchers (Gullett and Raghunathan, 1994; Wouterlood and Bowling, 1979). Hydrated lime being the most effective in removing arsenic gaseous species is chosen to conduct thorough mechanistic studies.

7.3.1 Interaction between CaO and As$_2$O$_3$

Investigations are performed to study the mechanism of As/CaO interaction and the influence of varying experimental conditions such as temperature, concentration and time of exposure. While flue gas would typically contain CO$_2$ and H$_2$O, no attempt is made to simulate those field conditions, instead these experiments are conducted to investigate the intrinsic interaction mechanism. The effect of sorbent surface area on arsenic capture is also investigated by exposing CaO sorbents of varying surface areas (40-4.5 m$^2$/g) to As$_2$O$_3$.

The removal of CO$_2$ from the diluent air stream prevents any recarbonation of the CaO generated. Carbonation of CaO is known to be a competitive reaction in this temperature range from related work on Ca/SO$_2$ reaction at medium temperatures (Bortz & Flament, 1985). Ghosh-Dastidar et al. (1996) reported that significant portion (30-50%) of the sample CaO can be recarbonated to CaCO$_3$ during a typical 4-hour sorption run. At 600°C and higher temperatures, carbonation of CaO is not very
significant and the results are nearly identical for both N₂ and air. The actual mechanism of As sorption by CaO could involve either physisorption of As₂O₃ or some chemisorbed complex or some chemical reaction product from CaO and As₂O₃ (to yield a calcium-arsenic-oxygen compound such as Ca₃As₂O₈ or Ca₃As₂O₆) or a combination of these phenomena. Physical adsorption involves relatively weak attractive forces between the adsorbent and adsorbate, and the physisorbed amount decreases rapidly with increasing temperature (Smith, 1981; Gregg and Sing, 1982). Further, physisorption is a nonactivated process and easily reversible by either keeping the desorption temperature higher than the sorption temperature or by exposing the sample to a arsenic species free flowing gas stream at the sorption temperature. As a result, an increase in temperature or a decrease in gas phase concentration of the adsorbate species decreases the equilibrium amount of the physisorbed species.

7.3.2 Mechanism of As-CaO interaction

Figure 7.4 shows the results of arsenic sorption at both medium temperature and high temperature conditions following 1 hour of sorption at 65 ppm. The saturation vapor pressure of As₂O₃ at 400°C, the lowest temperature investigated in this study is about 240 mm of Hg which is considerably higher than the partial pressure of As₂O₃ maintained during the experiments. In order to ensure uniformity of surface area and porosity, the high temperature runs are performed after calcining and sintering the Ca(OH)₂ at 1000°C for 30 minutes, likewise, the medium temperature runs are performed following precalcination and exposure at 600°C for 30 minutes. The surface areas of the precalcined and presintered Ca(OH)₂ sorbents are measured separately.
using low temperature N₂ adsorption. The specific surface areas of 4.5 and 40 m²/g are obtained following calcination and sintering at 1000 and 600°C respectively. As can be seen from Figure 7.4, arsenic capture increases with temperature in both the temperature regions, thus indicating an activated phenomena.

The arsenic sorption in both the temperature regions is found to be irreversible. The irreversibility of capture is ascertained by desorption studies with the post-sorption sample. Arsenic-free nitrogen gas at the same flow rate is passed through the post-sorption sample at a specific temperature, after which the sample is re-analyzed. Negligible loss of arsenic is observed for both the medium temperature as well as high temperature samples following 2 hours of desorption at 800 and 1200°C respectively. This irreversible capture indicates that physical adsorption is not the dominant mechanism of capture in either temperature range.

In order to gain further insights, XRD studies are performed on the sorbent following long-time exposure. Figure 7.5 shows the XRD diffractograms of the sorbent obtained at 600°C and 1000°C following sorption for 24 hours and 12 hours respectively at 65 ppm arsenic concentration. The diffractograms for calcium arsenate and CaO are presented for comparison. At both 600 as well as at 1000°C sorption temperature the samples show the presence of calcium arsenate (Ca₃As₂O₆) and unreacted CaO. Furthermore, calcium arsenate is the only arsenic species present, no other Ca-As-O compound is identified, neither is the presence of any As₂O₃ ascertained.

Further corroboration of XRD results is obtained from the Ion Chromatography analyses of the post-sorption sample. IC results with the sample leached in deionized
water alone show all the arsenic in the sample to be present as arsenate ions and the presence of any appreciable amounts of arsenite ions could not be detected. Any physically adsorbed As$_2$O$_3$ would have lead to arsenite ions in solution. This confirms the chemical nature of interaction and also the formation of calcium arsenate as the main reaction product. The reaction scheme therefore can be postulated as:

$$3\text{CaO(s)} + \text{As}_2\text{O}_3(g) + \text{O}_2(g) = \text{Ca}_3\text{As}_2\text{O}_6(s)$$ (7.1)

This reaction is similar to the SO$_2$-CaO reaction in the presence of O$_2$ to produce CaSO$_4$. Calcium arsenate is a stable compound at temperatures up to 1400°C. It undergoes decomposition at 1400°C to yield CaO, As$_2$O$_3$ and O$_2$ (Shigematsu, 1986).

7.3.3 Kinetics of CaO/As$_2$O$_3$ interaction

Based on the reaction mechanism above, and assuming no external mass transfer resistance and chemical reaction (7.1) as the controlling mechanism, the overall rate of CaO reaction can be expressed as:

$$\frac{dx}{dt} = - k_s C^m_g A_{\text{CaO}}$$ (7.2)

where, $x$ is the conversion of the CaO to Ca$_3$As$_2$O$_6$, $C_g$ is the bulk gas phase concentration of As$_2$O$_3$, $m$ is the order of reaction with respect to the gaseous species. $k_s$ is the specific reaction rate constant, and $A_{\text{CaO}}$ is the available surface area of CaO.

The above model also assumes no internal diffusional limitations due to the small size of CaO particles. From the primary particle size analysis of Ca(OH)$_2$ using a Sedigraph, the median ($d_{50}$) size is found to be about 1.2 μm, as seen in Figure 7.6. Experiments with increased gas flow rate did not exhibit any increase in capture.
indicating negligible external mass transfer limitations. Writing the available surface area $A_{CaO}$ as:

$$A_{CaO} = S_o(1-x) \quad (7.3)$$

and integrating the rate expression assuming $n=1$ gives the following model:

$$\ln\left(\frac{1}{1-x}\right) = k_sC_s^{n}S_o t \quad (7.4)$$

Investigations are conducted to study the influence of concentration, time of exposure and surface area at a fixed temperature of 600°C. The concentration is varied from 15 ppm to 130 ppm and sorption is conducted for 1 hour at 600°C with CaO of surface area 40 m$^2$/g. The above equation (7.4) is plotted as $\ln(-\ln(1-x))$ versus $\ln C_s$. As seen in Figure 7.7, the slope, $m=1$ which indicates a first-order reaction w.r.t. $\text{As}_2\text{O}_3$.

Figure 7.8 shows the variation of capture with time of sorption at $\text{As}_2\text{O}_3$ concentration of 65 ppm. The rate of capture is seen to be high initially with nearly 100 mg/g of arsenic captured in 4 hours of sorption. The sorption rate decreases considerably at higher sorption times and is seen to reach about 200 mg/g following 24 hours of exposure.

The effect of sorbent surface area on arsenic capture is further investigated by exposing CaO sorbent of varying surface areas (40-4.5 m$^2$/g) to 15 ppm of $\text{As}_2\text{O}_3$ at a fixed sorption temperature of 600°C. Results of these experiments are presented in Figure 7.9. Arsenic capture is found to be increasing with increasing sorbent surface area.

In order to obtain the observed activation energy, the results shown in Figure 7.7 and 7.8 are used to obtain $k_s$ and $\ln k_s$ is plotted versus $1/T$. Figure 7.10 shows that
the apparent activation energy is 10.5 kcal/mol, which is also indicative of a reaction-controlling regime. The longer-time conversion data (greater than 2 hours) is not included in this calculation.

7.3.4 Fly ash-arsenic interaction

Various researchers have shown that fly ash could be a viable sorbent for capture of arsenic. Although extensive research literature is available detailing the partition/speciation of arsenic on fly ash, there is dearth of data regarding the mechanism involved in fly-ash/arsenic interaction. Experiments are conducted to determine this interaction mechanism. Figure 7.11 shows the results of fly ash sorption at 500 and 350°C for 1 hour at arsenic concentration of 65 ppm. Initial arsenic content of the fly ash is determined prior to performing the sorption experiments. As can be seen, the capture is significantly higher at the lower temperature of 350°C. The decreasing arsenic capture by the fly ash with increasing temperature is indicative of a non-activated interaction, such as physical adsorption, between fly ash and arsenic species. Desorption experiments are carried out with the post sorption sample by passing arsenic-free nitrogen gas at the same flow rate and at sorption temperature. As can be seen from the Figure 7.11, the amount of arsenic decreases drastically after desorption and reduces to the initial arsenic content of the fly-ash. This further corroborates the physical nature of interaction between the fly ash and arsenic species and indicates no chemical interaction as in the case of CaO-As$_2$O$_3$ interaction.
7.4 Conclusions

This study has shown that while fly ash retains arsenic by a physical adsorption mechanism, calcium hydroxide captures arsenic by an irreversible chemical reaction with the formation of a solid chemical product. Studies in the 400-600°C as well as higher temperatures of 800-1000°C reveal that calcium arsenate (Ca₃As₂O₈) is the dominant product of reaction which is thermodynamically stable up to temperatures of 1400°C. As a result, sorbent reinjection or recycling, typically done in the medium to low temperature regions, would not result in reintroduction of the captured arsenic. The activation energy calculations indicate a chemical reaction controlled process with first order dependence of the overall reaction rate on the gas phase arsenic species concentration.

This study is conducted at arsenic concentrations of 13-65 ppm, which are much higher than the typical arsenic concentrations in the coal-generated flue gas. In addition, presence of CO₂, SO₂, and H₂O in the flue gas will lead to a host of competing reactions with CaO which will influence the CaO/As₂O₃ interaction. The short time (1-2 s) available in this temperature range in the entrained-condition of the flue gas also may not allow complete calcination of the hydroxide, which can affect the metal capture. In order to address these issues, future studies need to be performed under typical flue gas environment. Nevertheless, this work has revealed the mechanisms involved in CaO/As₂O₃ interaction.
<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Cal. hydrate</th>
<th>Kaolinite&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Alumina&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Silica&lt;sup&gt;d&lt;/sup&gt;</th>
<th>NIST fly ash&lt;sup&gt;e&lt;/sup&gt;</th>
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<td>Ca(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>99.99</td>
<td>49.3</td>
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<td>38.5</td>
<td>99.99</td>
<td>-</td>
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<tr>
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<td>-</td>
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<td>-</td>
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<sup>a</sup> Linwood Mining & Minerals Co.  
<sup>b</sup> Albion Kaolin Co.  
<sup>c</sup> Johnson Matthey Co.  
<sup>d</sup> Fisher Scientific  
<sup>e</sup> NIST Certified fly ash (SRM 1633b)

Table 7.1: Composition of investigated mineral sorbents and NIST certified fly ash.
Figure 7.1: Schematic of differential bed reactor (DBR) system.
Figure 7.2: $\text{As}_2\text{O}_3$ vapor pressure variation with temperature.
Figure 7.3: Amount of arsenic captured by various sorbents.

$\text{As}_2\text{O}_3$ gas phase conc. : 13 ppm

Sorption temperature : $600^\circ\text{C}$; Sorption time : 1 hr.
Figure 7.4: Arsenic uptake by Ca(OH)$_2$ sorbent in 1 hr. 
$\text{As}_2\text{O}_3$ gas phase conc. : 65 ppm
Figure 7.5: X-ray diffractograms of post-sorption samples; (a) Sorption conducted at 600°C for 24 h, and (b) Sorption conducted at 1000°C for 24 h.
Figure 7.6: Primary particle size distribution of Linwood hydroxide (LH) and NIST certified fly ash.
Figure 7.7: Determination of order of reaction $m$, with respect to gas phase arsenic concentration.

Reaction temp.: 600°C; Initial specific surface area: 40 $m^2/g$
Figure 7.8: CaO conversion to $\text{Ca}_3\text{As}_2\text{O}_8$ following different exposure times.

Reaction temp.: $600^\circ\text{C}$; As$_2$O$_3$ gas phase conc.: 65 ppm
Figure 7.9: Effect of CaO sorbent surface area on extent of arsenic capture. 
\( \text{As}_2\text{O}_3 \) gas phase conc. : 15 ppm
Reaction temp. : 600°C; Reaction time : 1 hr.
Figure 7.10: Determination of activation energy, $E_a$. 

$E_a = 10.4 \text{ Kcal/mol}$
Figure 7.11: Effect of desorption on As captured by NIST fly ash at different sorption temperatures under As-free gas flow.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

This research work mainly focused on determining various interaction mechanisms between SO$_2$ and Ca-based sorbents. Investigations have been conducted to elucidate the influence of these interactions on internal pore structure. A thorough understanding of these influences could lead to development of a more effective and highly reactive sorbent for SO$_2$ abatement. Sulfur species emanating from coal-fired combustors have been known to have deleterious effects on the ecology and the biosystem and any further utilization of vast reserves of coal in the world critically depend on determining economical means of removing SO$_2$ from flue gases. Numerous studies and investigations have been conducted over the past three decades to understand the interaction between SO$_2$ and calcium based sorbents yet knowledge gaps still persist.

The overall sulfation process involves calcination and sulfation of the sorbent along with the high temperature sintering phenomena. All the three steps have their own effects on the internal pore structure which makes the overall sulfation process a complicated and challenging problem. Furthermore, the ultrafast nature and thereby the concomitant occurrence of these three steps adds to the complexity of the problem. This research has demonstrated the importance of sorbent structure in overall phenomena of
gas-solid non-catalytic reactions and applied this information in developing a high reactivity carbonate (HRC) and explaining the high reactivity exhibited by the same.

Most of the previous work in improving calcium-based sorbents have maximized the surface area of the parent sorbent in order to produce a high surface area and high reactivity CaO. However, such modifications failed to overcome the blockage and plugging of internal pores which lead to premature termination of sulfation. In order to maximize the sulfation capacity of calcium-based sorbents, it is established that the pores of their calcines have to lie predominantly in the 50-200 Å sizes.

In order to fully understand the overall sulfation behavior of calcium-based sorbents and in particular the high reactivity carbonate (HRC) at high temperatures (900-1100°C) it is imperative that short-contact time calcination behavior of these sorbents be investigated. A novel entrained flow reactor system, capable of providing time resolved reaction kinetic data, is used to conduct extensive investigations into the calcination and sintering behavior of HRC. The results thus obtained suggest that the calcination reaction is extremely fast and is accompanied by equally fast sintering (both thermal and CO$_2$ induced). More than 90% of the final calcination conversion is obtained within the first 50 ms at all the reaction temperatures.

The development of internal structural properties such as surface area, pore volume and the distributions of surface area and pore volumes is critical in determining the sorbent reactivity towards SO$_2$. Initial surface area and pore volume for HRC are significantly higher than conventionally used calcium carbonates thus providing an initial open structure. Upon calcination HRC is found to retain its open structure thereby indicating less susceptibility to sintering. Furthermore, compared to other high
surface area calcium sorbents such as modified calcium hydroxides, which have very similar initial structure, HRC still exhibits better surface area and pore retention properties. Pore structure evolution studies shed considerable light on the existence of “favorable” pore size distribution with show significant pore volume in meso pores. This advantage is manifested in providing high pore surface area for eventual sulfation with lessened pore plugging and blockage that smaller pores would suffer from. Results presented here suggest that the initial sorbent internal structure of HRC and its evolution during calcination step lead to formation of calcines, which would have high reactivity towards SO$_2$.

Calcination and sintering behavior of HRC at high temperatures is simulated fairly well by a grain-micrograin model (developed by Ghosh-Dastidar et al., 1995). Model predicted calcination extents and surface area evolution closely match the experimental results. Values of kinetic parameters, such as activation energies for calcination and sintering, obtained from the model fitting are 29.5 and 75.5 kcal/mole respectively which compare well with the values reported in the literature.

In this work, the internal pore properties (surface area and pore size distribution) of calcium carbonate sorbent are modified to improve its SO$_2$ reactivity. The modified carbonate (HRC) exhibits exceptionally high conversion of 70-75% within 0.5 s, which represents a nearly three-fold enhancement over the commercial carbonates and hydrates. The high initial surface area and the open pore structure of the modified carbonate translates into an optimum pore size distribution in its calcine, which combined with the effects of slower sintering contribute to its remarkable sulfation capacity. The surface area and the pore volume in the 50-200 Å range of its calcine are maximized which distinguishes
the modified carbonate from other sorbents. Comparative investigations with other carbonates reveal that in spite of the high surface area of the calcines' obtained from conventional carbonates, the pore size distributions of these calcines show a preferential dominance of very small pores which leads to pore plugging and premature termination of sulfation. The results of this study illustrate the impact of internal pore structure on initial reactivity and ultimate sulfation conversion of calcium-based sorbents. It also demonstrates the potential of 'tailoring' the internal pore structure of sorbents to increase their effectiveness.

The culmination of experimental studies to understand the overall sulfation behavior of calcium-based sorbents and the influence of internal pore structure at high temperatures is achieved in development of a mathematical model. The model is developed based on first order calcination kinetics (proposed by Borgwardt, 1970) and a second order sintering rate equation (proposed by Nicholson, 1965). Model also includes the sulfation reaction between \( \text{SO}_2 \) and \( \text{Ca}^{2+} / \text{O}^{2-} \) ions, diffusing outwards through the \( \text{CaSO}_4 \) product layer (Hsia et al., 1993 and 1995), and satisfactorily describes the time-resolved experimental data. The proposed mathematical model is based on a grain-micrograin concept and includes the initial particle structural properties (surface area and porosity) and structural changes due to sintering and reactions (calcination and sulfation).

The mathematical model successfully predicts the sulfation behavior of three different types of calcium-based sorbents, including laboratory generated CaO and high reactivity carbonate (HRC), at different temperatures, accurately representing the experimental observation that sulfation reaction is extremely fast with more than 75% of the final conversion occurring in the first 50 ms. The model successfully predicts
the high initial reaction rate and virtual reaction “die-off” at later stages. Versatility of
the model is demonstrated by simulating sulfation behavior of laboratory generated CaO
(obtained from pre-calcination of Ca(OH)$_2$) and data reported in the literature. Model
predictions compare well with random pore model when applied to the same
experimental data. Model predicted kinetic parameters are in significant agreement with
the values reported in the literature.

The mathematical simulations and experimental results demonstrate the severity
of sulfation and sintering on sorbent reactivity at high temperatures and influence of
initial sorbent particle structure as an important parameter for SO$_2$ capture. The results of
this study can be utilized to determine an optimum sorbent structure (as demonstrated by
HRC) for sorbent injection, with an objective of achieving superior sorbent utilization
and high sulfur capture.

This study also investigated the interaction of arsenic species, a trace pollutant
from coal-fired combustion facilities, with various mineral sorbents and specifically with
calcium-based sorbents. Arsenic is a volatile trace toxin and is emitted into the
atmosphere in vapor or particulate form with the flue gas emanating from coal-fired
combustors and boilers. This study has shown that calcium hydroxide captures arsenic
by an irreversible chemical reaction with the formation of a solid chemical product.
Studies in the 400-600°C as well as higher temperatures of 800-1000°C reveal that
calcium arsenate (Ca$_3$As$_2$O$_6$) is the dominant product of reaction which is
thermodynamically stable up to temperatures of 1400°C. Kinetic investigations
conducted to determine the activation energy calculations indicate a chemical reaction
controlled process with first order dependence of the overall reaction rate on the gas phase arsenic species concentration.

This research work, with its time resolved kinetics data and on-line measured residence time clearly demonstrated the role of internal structure on the overall desulfurization process using calcium-based sorbents. Work mentioned here showed that modifications to calcium sorbents (in particular HRC) with respect to their internal structure could greatly enhance the reactivity of the sorbent towards SO$_2$. This work has also contributed to our understanding of interaction mechanism between arsenic species and Ca-sorbent. However, it has to be acknowledged that there are certainly a number of tasks and shortcomings that would warrant further attention and research.

In this work, short-contact time calcination and sulfation reactions are studied and their influence on sorbent internal structure has been investigated. Flue gases from coal-fired utilities have a very diverse environment with multitude of gaseous species being present. These gaseous components can significantly affect the overall sulfation behavior by either taking part in gas-gas interactions or gas-sorbent interactions. One has to acknowledge that significant amounts of CO$_2$ and H$_2$O are present in flue gas and these constituents can not only interact with the calcination behavior of the sorbent but could also influence the sintering characteristics of the sorbent. Hence in order to accurately and realistically study the sulfation behavior of sorbents, experimental investigations should include the diversity of the flue gas.

A comprehensive model is developed here to predict and simulate the sulfation behavior of Ca-sorbents. One of the strong points of the model is the incorporation of
the physical mechanism of ionic diffusion, as clearly illustrated by Hsia et al. (1993, 1995), in its mathematical development and its ability to predict the solid-state diffusion coefficients. However, attempts should be made to experimentally and theoretically determine the ionic diffusion coefficient to form a basis for comparison. The proposed model can also be improved upon by including external mass transfer and heat transfer effects. In the present state, the model is ill-equipped to consider non-isothermal reaction conditions. In literature a number of models are suggested for gas-solid reaction simulations. The model presented here falls under the category of modified "grain" model. Elaborate comparisons with "pore" model can be undertaken to strength the case for the proposed models' versatility. Experimental investigation strongly suggest the influence of pore size distribution on the overall reactivity of the sorbent however, in the present formulation of the model the pore size distribution is not directly included. The model can be made more robust and comprehensive if pore sized distributions can be incorporated as one of the structural parameters. Although it has to be recognized that such improvements and additions would demand a high degree of advanced mathematical formulations. Nevertheless, it has to be acknowledged that the proposed model and its experimental validations represent an important advancement in the field of mathematical modeling of gas-solid reactions and can serve as a basis for making theoretical predictions regarding sorbent effectiveness for SO₂ removal at high temperatures.

The study regarding arsenic species interaction with calcium sorbents is the first study of its kind and it clearly indicated that calcium sorbents could serve as effect
agents for arsenic removal. This study is conducted at arsenic concentrations of 13-65 ppm, which are much higher than the typical arsenic concentrations in the coal-generated flue gas. In addition, presence of CO$_2$, SO$_2$, and H$_2$O in the flue gas would lead to a host of competing reactions with CaO which will influence the CaO/As$_2$O$_3$ interaction. Hence the next step in this important research area should involve studying the reaction in presence of other flue gas species and investigating the capture ability of calcium based sorbents at even lower arsenic concentrations. In actual entrained flow conditions of a pulverized coal combustor the contact times available for the reaction are rather short (1-2 s) and that could severely limit the arsenic capture. In order to address these issues, future studies need to be performed under typical flue gas environment in entrained flow conditions for contact times of less than 2 s. Nevertheless, this work has revealed the mechanism involved in CaO/As$_2$O$_3$ interaction and showed the multi-functional role played by calcium based sorbents in removing pollutants from flue gases.
APPENDIX A

FORTRAN PROGRAM FOR CALCINATION AND SINTERING MODEL

C
C THIS PROGRAM CALCULATES THE CALCINATION AND
C SURFACE AREA OF HIGH REACTIVITY CARBONATE
C
IMPLICIT REAL*8 (A-H,O-Z)
COMMON DELT,TEMK
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,RHOC,CSO,CONKS
COMMON /BLOCK2/ X(5000),T(5000),XN(5000),TN(5000)
COMMON /BLOCK3/
RC(5000),RG(5000),RHO(5000),SCPGM(5000),SHPGM(5000)
COMMON /BLOCK4/ SC(5000),SH(5000),STOT(5000),STOTG(5000)
COMMON /BLOCK5/ B(5000),A(5000),CBC(5000)
COMMON /BLOCK6/ RGN(5000),RCN(5000),CBCN(5000)
COMMON /BLOCK7/ BN(5000),SCN(5000),SCPGMN(5000),STOTGN(5000)
COMMON /BLOCK8/ TOTCAO

C
WRITE(6,*) 'ENTER NAME OF DATA FILE, INCLUDE DAT'
READ(5,'(A20)') FCLEINP
OPEN(UNIT=4,FILE=FCLEINP,STATUS='OLD')
READ(4,*) AKC,AKS,CONKS,SCNA,TEMK,SCA
WRITE(6,*) 'ENTER NAME OF RESULTS FILE INCLUDE OUT'
READ(5,'(A20)') FILEOUT
OPEN(UNIT=3,FILE=FILEOUT,STATUS='NEW')

C
NOMENCLATURE:
DP: Diffusivity, CO2 in air, m2/s
AKC: Reaction constant
AKS: Sintering constant
CBS: Concentration of CO2 at saturation, gmol/m3
SCA: Asymtotic S.A of CaO, m2/gmol
SCNA: Nascent S. A. of CaO, m2/gmol
SHNA: S. A. of CaCO3, m2/gmol
RHOH: True density of CaCO3, g/m3
RHOC: True density of CaO, g/m3
CSO: Solid reactant concentration, gmol/m3
DELT: DELTA TIME
NIT: Total no. of iterations

Arrays:
T,TN: Time, s
X,XN: Conversion,
B,BN: Amount of CaO formed, gmol
A,AN: Amount of CaCO3 left, gmol
A+B=1, basis: 1 gmol of CaCO3.
RC: Core radius, m
RG: Grain radius, m
RHO: 'Average-true' density of grain
SCPGM: S. A of CaO, m2 per gram basis
SC: S. A of CaO, total, m2
SHPGM: S. A of CaCO3, m2 per gram basis, remains constant
SH: S. A of CaCO3, total, m2
STOT: S. A of grain, total, m2
STOTG: S. A of grain, m2 per gram basis

Note: Any array with an "N" suffix with it is a floating variable.

DP = 13.9E-6*(TEMK/273)**1.75
RAAG1 = EXP(17.75-.0011*TEMK+2.37-22020/TEMK)
RAAG2 = 8.2E-5*TEMK
CBS = RAAG1/RAAG2
WRITE(*,*) CBS
GOTO 4

SHNA = 61.*100.
RHOH = 2.71E+6
RHOC = 3.32E+6
DELT = 0.1E-3
CSO = RHOH/100.
NIT = 299.E-3/DELT

INITIAL CONDITIONS

I = 1
T(1) = 0.0
X(1) = 0.0

C Values of all variables (which are functions of X)

B(1) = X(1)
A(1) = 1.0 - B(1)
SCPGM(1) = SCNA
SC(1) = SCPGM(1) * B(1)
SHPGM(1) = SHNA
SH(1) = SHPGM(1) * A(1)
STOT(1) = SC(1) + SH(1)
SH(1) = SHPGM(1) * A(1)
STOT(1) = SC(1) + SH(1)
TOTG = A(1) * 100. + B(1) * 56.
STOTG(1) = STOT(1) / TOTG
RHO(1) = RHOH
RG(1) = 3.0 / STOTG(1) / RHO(1)
RC(1) = RG(1) * (1.0 - X(1)) ** (1.0 / 3.0)
CBC(1) = 0.

ICTR = 1
10 CALL RK(I)

C CALCULATE VALUES OF SURFACE AREA AND RADIUS ETC AT X(I+1)

XN(I) = X(I+1)
TN(I) = T(I+1)

CALL SURFRAD(TN, XN, T, X, I)

I = I + 1
X(I) = XN(I-1)
T(I) = TN(I-1)
B(I) = BN(I-1)
RG(I) = RGN(I-1)
RC(I) = RCN(I-1)
RG(I) = RGN(I-1)
RC(I) = RCN(I-1)
SC(I) = SCN(I-1)
SCPGM(I) = SCPGMN(I-1)
CBC(I) = CBCN(I-1)
STOTG(I) = STOTGN(I-1)

ICTR = ICTR + 1
IF(ICTR.NE.21) GO TO 40

WRITE(6,21)T(I),X(I)*.97,RG(I),RC(I),CBC(I),STOTG(I)
WRITE(3,21)T(I),X(I)*.97,RG(I),RC(I),CBC(I),STOTG(I)

21 FORMAT(1X,E10.5,1X,E10.5,1X,E12.5,1X,E12.5,1X,E12.5,1X,E12.5)

ICTR=1

40 IF(I.GT.N1T) GO TO 20
GO TO 10

20 WRITE(3,* ) AKC,AKS,CONKS,SCNA,TEMK,SCA
STOP
END

SUBROUTINE RK(I)

IMPLICIT REAL*8 (A-H,O-Z)
COMMON DELT,TEMK
COMMON /BLOCK2/ X(5000),T(5000),XN(5000),TN(5000)
COMMON /BLOCKS/ B(5000),A(5000),CBC(5000)

XN(I)=X(I)
TN(I)=T(I)

CALL FUNCT(TN,XN,T,X,I,DXDT)

CAY1=DXDT
XN(I)=X(I)+DXDT*DELT/2.
TN(I)=T(I)+DELT/2.
XN(I)=X(I)+DXDT*DELT/2.
TN(I)=T(I)+DELT/2.

CALL FUNCT(TN,XN,T,X,I,DXDT)

CAY2=DXDT
XN(I)=X(I)+DXDT*DELT/2.
CALL FUNCT(TN,XN,T,X,I,DXDT)

CAY3=DXDT
XN(I)=X(I)+DXDT*DELT
TN(I)=T(I)+DELT
CALL FUNCT(TN,XN,T,X,I,DXDT)

CAY4=DXDT

X(I+1)=X(I)+DELT*(CAY1+2.*CAY2+2.*CAY3+CAY4)/6.
T(I+1)=T(I)+DELT
RETURN
END

SUBROUTINE FUNCT(TN,XN,T,X,I,DXDT)

IMPLICIT REAL*8 (A-H,O-Z)
COMMON DELT,TEMK
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,RHOC,CSO,CONKS
COMMON /BLOCK3/
RC(5000),RG(5000),RHO(5000),SCPGM(5000),SHPGM(5000)
COMMON /BLOCK4/ SC(5000),SH(5000),STOT(5000),STOTG(5000)
COMMON /BLOCK5/ B(5000),A(5000),CBC(5000)
DIMENSION X(5000),T(5000),XN(5000),TN(5000)
C DIMENSION BN(5000),AN(5000),SCN(5000),SCPGMN(5000),SHN(5000)
C DIMENSION STOTN(5000),STOTGN(5000),RHON(5000)
COMMON /BLOCK6/ RGN(5000),RCN(5000),CBCN(5000)

CALL SURFRAD(TN,XN,T,X,I)

CRITERIA=0.99*CBS
IF(CBCN(I).GE.CRITERIA) CBCN(I)=CRITERIA
DXDT=3.*RCN(I)**2*AKC*(CBS-CBCN(I))/(RGN(I)**3.*CSO)
RETURN
END

SUBROUTINE SURFRAD(TN,XN,T,X,I)

IMPLICIT REAL*8 (A-H,O-Z)
COMMON DELT,TEMK
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,RHOC,CSO,CONKS
COMMON /BLOCK3/
RC(5000),RG(5000),RHO(5000),SCPGM(5000),SHPGM(5000)

CALL FUNCT(TN,XN,T,X,I,DXDT)
Calculate incremental CaO formed over the previous:

\[ \text{BN}(I) = XN(I) - X(I) \]
\[ \text{AN}(I) = 1 - \text{BN}(I) \]

C SURFACE AREA CALCULATION

\[ \text{TERM1} = \text{SCNA} \times \text{BN}(I) \]
\[ \text{TERM11} = \text{SCNA} \]
\[ \text{SCPGMN}(I) = \text{TERM11} \]

C TERM2 CALCULATION

\[ \text{TERM2} = 0 \]
\[ \text{AKSN} = \text{AKS} \times (1 + \text{CONKS} \times (\text{CBCO}' - 100)/2.)^{0.65} \]
\[ \text{TERM2} = \text{TERM2} + (\text{SCA} + 1 / ((1 / (\text{SCPGM}(J) - \text{SCA}) + \text{AKSN} \times (\text{TN}(I) - \text{T}(J)))) \times \text{B}(J) \]

100 FORMAT(1X,E10.5,1X,E10.5,1X,1X,E12.5,1X,E12.5,1X,E12.5,1X,E12.5)

C Total CaO S. A, m²

\[ \text{SCN}(I) = \text{TERM1} + \text{TERM2} \]

C AMOUNT CAO CALCULATION

\[ \text{ANEWCAO} = \text{BN}(I) \]
\[ \text{OLDCAO} = 0 \]
\[ \text{DOB} 200 \text{ K}=1,1 \]
\[ \text{OLDCAO} = \text{OLDCAO} + \text{B}(K) \]
OLDCAO = OLDCAO + B(K)

TOTCAO = ANEWCAO + OLDCAO

C Calculate S.A per g, gmol etc.

STOTN(I) = SCN(I) + SHN(I)
TOTGN = TOTCAO * 56. + (1. - TOTCAO) * 100.

IF (TOTCAO .EQ. 0.) GOTO 36
CAOPERG = SCN(I) / (TOTCAO * 56.)
HYDPERG = SHN(I) / ((1. - TOTCAO) * 100.)
STOTGN(I) = CAOPERG * XN(I) + HYDPERG * (1. - XN(I))
GOTO 37

GOTO 37

36 STOTGN(I) = STOTN(I) / TOTGN

C "Average true" DENSITY CALCULATION

37 FRACH = (1. - TOTCAO) * 100. / TOTGN
FRACC = TOTCAO * 56. / TOTGN
RHON(I) = FRACH * RHOH + FRACC * RHOC

C ONE WAY OF CALCULATING RADIUS OF GRAIN AND CORE

RGN(I) = 3. / STOTGN(I) / RHON(I)
RCN(I) = RGN(I) * (1. - XN(I)) ** (1. / 3.)

C CALCULATE POROSITY & DIFFUSIVITY EFFECTIVE
C CALCULATING POROSITY OF PRODUCT, FROM MILNE

IF (I .GT. 2) GO TO 34
PORPRO1 = 0.5 - (0.5 / (SCPGM(I) - SCA)) * (SCPGM(I) - SCPGMN(I))
GOTO 35
PORPRO1 = 0.5 - (0.5 / (SCPGM(I) - SCA)) * (SCPGM(I) - SCPGMN(I))
GOTO 35

34 SHPRO = SCA + 1. / ((1. / (SCPGM(2) - SCA) + AKSN * (TN(I) - T(2))))
PORPRO1 = 0.5 - (0.5 / (SCPGM(1) - SCA)) * (SCPGM(1) - SHPRO)
C Calculate Knudsen diffusivity

35 PORRAD=2.*PORPRO1/(SCPGMN(I)*RHOC/56.)
DK=97.*PORRAD*(TEMK/44.)**0.5
DPEFF=1./(1./DK+1./DP)
DPN=DPEFF*PORPRO1**2
GO TO 32

C CALCULATE PRODUCT GAS CONCENTRATION AT INTERFACE.

C 32 UP=-CBS*AKC*RCN(I)**2/DPN*(I./RGN(I)-1./RCN(I))
DOWN=1.-(AKC*RCN(I)**2/DPN*(1./RGN(I)-1./RCN(I)))

CBCN(I)=UP/DOWN
RETURN
END
RETURN
END
FORTRAN PROGRAM FOR COMPREHENSIVE SULFATION MODEL

IMPLICIT REAL*8 (A-H,O-Z)
COMMON /block21/ DELT,TEMK,lmn
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOC,RHOC,CSO,CONKS
COMMON /BLOCK2/ X(5000),T(5000),XN(5000),TN(5000)
COMMON /BLOCK3/ RC(5000),RG(5000),RHO(5000),SCPMG(5000),
SHPGM(5000)
COMMON /BLOCK4/ SC(5000),SH(5000),STOT(5000),STOTG(5000)
COMMON /BLOCK5/ B(5000),A(5000),CBC(5000)
COMMON /BLOCK6/ RGN(5000),RCN(5000),CBCN(5000)
COMMON /BLOCK7/ BN(5000),SCN(5000),SCPMGN(5000),STOTGN(5000),
promg(5000),scnm(5000)
COMMON /BLOCK8/ TOTCAO
COMMON /block9/ porporl,caoperg,caoperv,proavg
COMMON /block10/ akss,dps,epsilon,beta,tau,alo
COMMON /block11/ csos(5000),xs(5000),xsold(5000),xsavg(5000),
spro
COMMON /raj1/ counter
COMMON /raj41/ mfactor,dfactor,iter
COMMON /raj6/ sccn(5000),scc(5000)
character*20 fileinp,fileout
WRITE(6,*) 'ENTER NAME OF DATA FILE, INCLUDE DAT'
READ(5,'(A20)') FILEINP
OPEN(UNIT=4,FILE=FILEINP,STATUS='OLD')
OPEN(UNIT=12,FILE='result.out',STATUS='new')
READ(4,*) AKC,AKS,CONKS,SCNA,TEMK,SCA
WRITE(*,*) 'give akss, dps, and dfactor'
READ(*,*) akss,dps,dfactor
WRITE(*,*) 'give sintering limit factor'
READ(*,*) isinter
C write(I2,*)'T=',temk
C akss=4.5E-5
C dps=8E-19
C dfactor=8E-5
mfactor=2
iter=10
lmn=50

DP=9.E-5*(TEMK/1223.)**1.5
C
cbs=1e3
IF(TEMK.EQ.1223.) CBS=1.8E+3
IF(TEMK.EQ.1323.) CBS=3.35E+3
IF(TEMK.EQ.1308.) CBS=2.95E+3
IF(TEMK.EQ.1353.) CBS=3.67E+3

SHNA= 16.9*74.
RHOH=2.4E+6
RHC=3.32E+6
DELT=0.1E-3
C CSO=(I.-.14)*RHOH/74.
CSO=RHOH/74.
NIT=299.E-3/DELT

C INITIAL CONDITIONS
C
l=1
n=10
T(1)=0.0
X(1)=0.0
do j=1,n+1
xs(j)=0.
end do

C Values of all variables (which are functions of X)
C
B(1)=X(1)
A(1)=1.-B(1)
SCPGM(1)=SCNA
SC(1)=SCPGM(1)*B(1)
SHPGM(1)=SHNA
SH(1)=SHPGM(1)*A(1)
STOT(1)=SC(1)+SH(1)
TOTG=A(1)*74.+B(1)*56.
STOTG(1)=STOT(1)/TOTG
RHO(1)=RHOH
RG(1)=3./STOTG(1)/RHO(1)
RC(1)=RG(1)*(1.-X(1))**(1./3.)
CBC(1)=0.
C
ICTR=1
10 IF(T(I).GT.0.05) DELT=0.2E-3
CALL RK(I)
C
C CALCULATE VALUES OF SURF. AREA AND RADIUS ETC AT X(I+1)
C
XN(I)=X(I+1)
TN(I)=T(I+1)
CALL SURFRAD(TN,XN,T,X,I)
I=I+1
C
X(I)=XN(I-1)
T(I)=TN(I-1)
C
B(I)=BN(I-1)
RG(I)=RGN(I-1)
RC(I)=RCN(I-1)
SC(I)=SCN(I-1)
sc(i)=scn(i-1)
SCPGM(I)=SCPGMN(I-1)
CBC(I)=CBCN(I-1)
STOTG(I)=STOTGN(I-1)
C
i=i-1
rg(i)=rg(i+1)
rc(i)=rc(i+1)
if(i.gt.isinter) then
if(i.eq.isinter+1) write(*,*) 'proavg=',proavg
go to 191
end if
spro = scc(i+1)/totcao
PROAVG = 0.49 - (0.49/(SCPGM(1) - SCA)) * (SCPGM(1) - SPRO)
C
write(*,*) i, spro, totcao
C
write(*,*) i, proavg
C
proavg = 0.49 + (0.49 - 0.05) * dlog(spro/scpgm(1))/dlog(scpgm(1)/sca)
191 continue
C
write(*,*) i, proavg
C
CALL sulfation(T, X, I)
I = i + 1
ICTR = ICTR + 1
counter = ictr
IF (ICTR .NE. 5) GO TO 40
C
21 FORMAT (1X, E10.2, 1X, E10.3, 1X, E12.3, 1X, E12.3, 1X, E12.3,
*     1X, E12.3)
ICTR = 1
40 IF (T(I).GT..3) GO TO 20
GO TO 10
C
20 continue
STOP
END

subroutine sulfation (T, X, I)
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /BLOCK1/
AKC, DP, CBS, AKS, SCA, SCNA, SHNA, RHOH, RHOC, CSO, CONKS
COMMON /BLOCK3/ RC(5000), RG(5000), RHO(5000), SCPGM(5000),
1 SHPGM(5000)
COMMON /BLOCK4/ SC(5000), SH(5000), STOT(5000), STOTG(5000)
COMMON /BLOCK7/ BN(5000), SCN(5000), SCPGMN(5000), STOTGN(5000),
1 promg(5000), scnm(5000)
COMMON /BLOCK8/ TOTCAO
common /block9/ porpro1, caoperg, caoperv, proavg
common /block10/ akss, dps, epsilon, beta, tau, alo
common /block11/ cs02(5000), xs(5000), xsold(5000), xsavg(5000),
1 spro
common /raj1/ counter
common /raj3/ rgm(5000), rcm(5000), cion(5000), gmolm(5000),
1 rgmnew
common /raj4/ m, l, km
COMMON /block21/ DELT, TEMK, I mn

204
dimension x(5000),t(5000),rad(5000),rcmn(5000),rcmm(5000)
dimension rgmm(5000)

z=2.86
caovol=totcao*56./3.32/1000000
totvol=caovol
C
totvol is in m3
cمواقv=caoperg*totcao*56./totvol
C
cمواقv is in m2/m3
C
call SO2conc(I)
if(m.lt.1) go to 30
C
lمن=50
n=m*lمن-1
ijk=1
ls=1
le=lمن
11 continue
do jk=ls,le
rcmn(jk)=rcm(ijk)
rgmm(jk)=rgm(ijk)
end do
ijk=ijk+l
ls=le+1
le=lمن*(ijk)
if(le.gt.n+1) go to 13
go to 11
13 continue
C Calculating the sulfation conversion C
do 31 k=1,n+1
rcmnfact=(rcmm(k)**3-3.*akss*cion(k)*cso2(k)*
rgmm(k)**2./rhoc*56*delt)
if(rcmnfact.lt.0.) then
C write(*,* ) 'fully reacted',k,i
   do jk=k,n+1
      xs(jk)=1.
      rcm(jk)=1e-15
   end do
km=k
go to 32
end if
if(rcmnfact.ge.0.) then
rcmm(k)=rcmnfact**(1./3.)
end if
if(rcmm(k).eq.0.) rcmm(k)=1e-15
xs(k)=1.-((rcmm(k)/rgmnew)**3.
if(i.eq.100) then
write(*,177) rcmm(k),cion(k),cso2(k),rgmm(k),xs(k),k,i
177 format(1x,5(2x,el0.4),2(1x,i4))
end if
rgm(k)=(rcm(k)**3.+xs(k)*rgmnew**3*z)**(1./3.)
C C force earlier fully reacted MG's to xs=1.
C if(km.ne.0) then
C do j=km,n
C xs(j)=1.
C end do
C end if
31 continue
32 continue
do j=700,n+1
C if(i.eq.1240) write(*) xs(j),rcmm(j),j
end do
C
ijk=1
ls=1
le=lmn
12 sum=0.
do jk=ls,le
sum=sum+xs(jk)
end do
xsf=sum/lnn
rcm(ijk)=rgmnew*(1.-xsf)**(1./3.)
if(rcm(ijk).eq.0.) rcm(ijk)=1e-15
rgm(ijk)=(rcm(ijk)**3.+xsf*rgmnew**3*z)**(1./3.)
ijk=ijk+1
ls=le+1
le=lnn*(ijk)
if(le.gt.n+1) go to 14

go to 12
14 continue

do j=1,m
xs(j)=1.-(rcm(j)/rgmnew)**3.
end do

C force earlier fully reacted MG's to xs=1.

do j=1,m
if(xsold(j).ge.0.9999) xs(j)=1.0
C if(i.gt.1200) write(*,*) xs(j),rcm(j),j,i
end do
C
calculate average conversion
C
sum=0.
do k=1,m
sum=sum+xs(k)*gmolm(k)
end do
xsavg(i)=sum
if(counter.eq.51) then
C write(12,21) t(i),xsavg(i),m,i
C write(*,*) ''
write(*,21) t(i),xsavg(i),m,i
do k=1,n+l
C write(*,*) cion(k),cso2(k),k
end do
do k=1,m
write(*,23) xs(k),k
23 format(1x,(2x,el0.4),l(lx,i4))
end do
21 format(2x,2(1x,e10.4),1x,i4,1x,i6)
22 format(2x,3(2x,e10.4),2x,i3,2x,i3)
end if
30 return
end

subroutine so2conc(I)
IMPLICIT REAL*8 (A-H,O-Z)
dimension aa(5000),bb(5000),cc(5000),dd(5000),uu(5000),
2 alfa(5000),gamma(5000),rad(5000),rgmo(5000),rcmo(5000),
2 gmolmo(5000),xsoldo(5000),xso(5000),rcmm(5000),rgmm(5000)
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,RHOC,CSO,CONKS
common /block 11/ cso2(5000),xs(5000),xsold(5000),xsavg(5000),
1 spro

207
COMON /BLOCK2/ X(5000), T(5000), XN(5000), TN(5000)
COMON /BLOCK3/ RC(5000), RG(5000), RHO(5000), SCPGM(5000),
1 SHPGM(5000)
COMON /BLOCK7/ BN(5000), SCN(5000), SCPGMN(5000), STOTGN(5000),
1 promg(5000), scnm(5000)
common /block9/ porpro1, caoperg, caoperv, proavg
common /block10/ akss, dps, epsilon, beta, tau, alo
common /raj3/ rgm(5000), rcm(5000), cion(5000), gmolm(5000),
1 rgmnew
common /raj4/ m, l, km
common /raj6/ sccn(5000)
common /raj41/ mfactor, dfactor, iter
COMMON /block21/ DELT, TEMK, lmn

C find rgmnew

rgmnew=3.*56./scna/rhoc

C Find the layers of the micrograins: m
if(m.eq.0) then
    aincrement=rg(i)-rc(i)
mnew=mfactor*aincrement/2./rgmnew
C mnew=aincrement/2./rgmnew
if(mnew.eq.0) then
    m=0
    go to 20
end if

sum=0.
do j=1,i
    sum=sum+bn(j)
end do
gmol=sum/real(mnew)
jj=i
m=mnew
do k=1,m
    rgm(k)=rgmnew
    rcm(k)=rgmnew
    gmolm(k)=gmol
    xsold(k)=0.
end do
go to 10
end if

C New micrograins formed in delta-t
if(mcount.eq.0) then
  rgold=rg(i-1)
  rcold=rc(i-1)
end if
aincrement=(rg(i)-rc(i)-(rgold-rcold))

mnew=mfactor*aincrement/./rgmnew

mnew=aincrement/./rgmnew

if(mnew.eq.0) then
  mcount=1
  go to 10
end if

if(mcount1.eq.0) then
  mnew=mnew+1
  mcount1=1
end if

sum=0.
do j=jj,i
  sum=sum+bn(j)
end do
gmol=sum/real(mnew)
jj=i

do k=1,m
  rgmo(k)=rgm(k)
  rcmo(k)=rcm(k)
  gmolmo(k)=gmolm(k)
  xsoldo(k)=xsold(k)
  xso(k)=xs(k)
end do

m=m+mnew

if(km.ne.0) km=km+mnew
do k=1,m-mnew
  rgm(k+mnew)=rgmo(k)
  rcm(k+mnew)=rcmo(k)
  gmolm(k+mnew)=gmolmo(k)
  xsold(k+mnew)=xsoldo(k)
  xs(k+mnew)=xso(k)
end do
do k=1,mnew
  rgm(k)=rgmnew
  rcm(k)=rgmnew

209
gmolm(k)=gmol
xsold(k)=0.
xs(k)=0.
end do
if(m.ge.3.and.l.ne.0) l=l+mnew
mcount=0
continue
C Boundary conditions for cso2, j=n+l is r=rg
C
cbulks=3900./22.4/1000.*298/temk
C cbulks is in gmoI/m3
C
lmn=50
n=m*lmn-1
ijk=1
ls=l
le=lmn
11 do jk=ls,le
rcmm(jk)=rcm(ijk)
rgmm(jk)=rgm(ijk)
if(rcmm(jk).eq.0.) write(*** jk,ls,m,le
if(rgmm(jk).eq.0.) write(*** jk,ls,m,le
end do
ijk=ijk+1
ls=le+1
le=lmn*(ijk)
if(le.gt.n+1) go to 13
continue
13 delr=(rg(i)-rc(i))/real(n)
do j=1,n+1
aa(j)=0.
bb(j)=0.
cc(j)=0.
dd(j)=0.
end do
z=2.86
if(epsiol.eq.0.) epsiol=proavg
if(proold.eq.0.) proold=proavg
proavg1=epsiold-(proold-proavg)
C epsi=proavg1-(z-1)*(1.-proavg1)*(xsavg(i-1)-xsavg(i-2))
    epsi=proavg-(z-1)*(1.-proavg)*xsavg(i-1)
C write(*,123) epsi,proavg,proavg1,xsavg(i-1),i
123 format(1x,4(2x,e10.4),1(1x,i4))
    if(epsi.le.dfactor.and.mdff.ne.1) then
        write('**') 'dfactor used',i
        mdff=1
    end if
C proold=proavg
    if(epsi.le.dfactor) epsi=dfactor
    proold=proavg
    epsiold=epsi
C Diffusivity at temK K
C
dso2m=2e-4*(temk/298)**1.5
    porerad=2.*epsi/(spro/56.*1000.*3.32e3)/(1.-epsi)
    if(porerad.lt.5e-10) porerad=5e-10
    dso2k=97*porerad*(temk/64)**.5
    diffusivity=(1./dso2m+1./dso2k)**(-1.)
C dso2=diffusivity*epsi
C dso2=diffusivity*epsi**2.
C write(*,*) porerad,dso2,i
C do the iterations for the cion and cso2 profiles

    do 104 ij=1,iter
    do 103 j=1,n+1
        rad(j)=rc(i)+delr*(j-1)
    103 continue
    C if(km.ne.0) then
        do k=km,m
    C cion(k)=
        0.211
211
fact1=2.*3.*(1.-epsi)*akss*delr**2*cion(j)/dso2/rgmm(j)

aa(j)=(1.-delr/rad(j))
bb(j)=-(fact1)
cc(j)=1.+delr/rad(j)

continue
bb(1)=1.
cc(1)=-1.
aa(n+1)=0.
bb(n+1)=1.
dd(n+1)=cbulks

alfa(1)=bb(1)
do k=2,n+1
alfa(k)=bb(k)-(aa(k)*cc(k-1)/alfa(k-1))
end do
gamma(1)=dd(1)/bb(1)
do k=2,n+1
gamma(k)=(dd(k)-aa(k)*gamma(k-1))/alfa(k)
end do
uu(n+1)=gamma(n+1)
do k=1,n
j=n+1-k
uu(j)=gamma(j)-(cc(j)*uu(j+1)/alfa(j))
end do

do j=1,n+1
cso2(j)=uu(j)
end do
continue
continue

do j=1,m
xsold(j)=xs(j)
end do
return
end

SUBROUTINE RK(I)

IMPLICIT REAL*8 (A-H,O-Z)
COMMON /block21/ DELT,TEMK
COMMON /BLOCK2/ X(5000),T(5000),XN(5000),TN(5000)
COMMON /BLOCK5/ B(5000), A(5000), CBC(5000)
common /block9/ porpro1, caoperg, caoperv, proavg

C

XN(I) = X(I)
TN(I) = T(I)
CALL FUNCT(TN, XN, T, X, I, DXDT)

CAY1 = DXDT
XN(I) = X(I) + DXDT * DELT/2.
TN(I) = T(I) + DELT/2.
CALL FUNCT(TN, XN, T, X, I, DXDT)

CAY2 = DXDT
XN(I) = X(I) + DXDT * DELT/2.
CALL FUNCT(TN, XN, T, X, I, DXDT)

CAY3 = DXDT
XN(I) = X(I) + DXDT * DELT
TN(I) = T(I) + DELT
CALL FUNCT(TN, XN, T, X, I, DXDT)

CAY4 = DXDT

XI(I+1) = X(I) + DELT * (CAY1 + 2 * CAY2 + 2 * CAY3 + CAY4)/6.
T(I+1) = T(I) + DELT
20 format(2x,6(lx,el0.4))
RETURN
END

SUBROUTINE FUNCT(TN, XN, T, X, I, DXDT)
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /BLOCK2/ DELT, TEMK
COMMON /BLOCK1/
AKC, DP, CBS, AKS, SCA, SCNA, SHNA, RHOH, RHOC, CSO, CONKS
COMMON /BLOCK3/ RC(5000), RG(5000), RHON(5000), SCPGM(5000),
I SHPGM(5000)
COMMON /BLOCK4/ SC(5000), SH(5000), STOT(5000), STOTG(5000)
COMMON /BLOCK5/ B(5000), A(5000), CBC(5000)
DIMENSION X(5000), T(5000), XN(5000), TN(5000)
C DIMENSION BN(5000), AN(5000), SCN(5000), SCPGMN(5000), SHN(5000)
C DIMENSION STOTN(5000), STOTGN(5000), RHON(5000)
COMMON /BLOCK6/ RGN(5000), RCN(5000), CBCN(5000)
common /block9/ porpro1, caoperg, caoperv, proavg

213
CALL SURFRAD(TN,XN,T,X,I)

CALCULATE DXDT

CRITERIA=0.99*CBS
IF(CBCN(I).GE.CRITERIA) CBCN(I)=CRITERIA
DXDT=3.*RCN(I)**2*AKC*(CBS-CBCN(I))/(RGN(I)**3.*CSO)

RETURN
END

SUBROUTINE SURFRAD(TN,XN,T,X,I)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON /block1/ DELT,TEMK
COMMON /BLOCK1/
AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,RHOC,CSO,CONKS
COMMON /BLOCK3/ RC(5000),RG(5000),RHO(5000),SCPGM(5000),
1 SHPGM(5000)
COMMON /BLOCK4/ SC(5000),SH(5000),STOT(5000),STOTG(5000)
COMMON /BLOCK5/ B(5000),A(5000),CBC(5000)
COMMON /BLOCK6/ RGN(5000),RCN(5000),CBCN(5000)
COMMON /BLOCK7/ BN(5000),SCN(5000),SCPGMN(5000),STOTGN(5000),
1 promg(5000),scnm(5000)
COMMON /BLOCK8/ TOTCAO
common /block9/ porpro1,caoperg,caoperv,proavg
common /block11/ cso2(5000),xs(5000),xsold(5000),xsavg(5000),
1 spro
common / raj4 / m,l,km
common / raj41 / diffusivity,dfactor
common / raj6 / sccn(5000),scs(5000)
DIMENSION X(5000),T(5000),XN(5000),TN(5000)
DIMENSION AN(5000),SHN(5000),proavgc(5000),proavgs(5000)
DIMENSION STOTN(5000),RHON(5000),scnmj(5000),promgj(5000)

z=2.86

Calculate incremental CaO formed over the previous

BN(I)=XN(I)-X(I)
AN(I)=1.-BN(I)
SURFACE AREA CALCULATION

Calculate modified AKS using previous CBC over 2.

AKSN = AKS * (1. + CONKS * (CBC(I-100)/2.)**0.17)

TERM1 = (SCA + 1./((1./(SCNA-SCA)) + AKSN*(TNa-T(I)))) * BN(I)
TERM11 = (SCA + 1./((1./(SCNA-SCA)) + AKSN*(T(I)-T(I))))
TERM1 = SCNA * BN(I)
TERM11 = SCNA
SCPGMN(I) = TERM11

TERM2 = 0.
DO 100 J=1,I
AKSN = AKS * (1. + CONKS * (CBC(J-100)/2.)**0.17)
scnmj(j) = SCA + 1./((1./(SCPGM(J)-SCA)) + AKSN*(T(I)-T(J)))
promgj(j) = 0.49 - (0.49/(SCPGM(1)-SCA)) * (SCPGM(1)-scnmj(j))
AKSN = AKS * (1. + CONKS * (CBC(J-100)/2.)**0.17)
100 TERM2 = TERM2 + (SCA + 1./((1./(SCPGM(J)-SCA)) + AKSN*(T(I)-T(J)))) * B(J)

SCN(I) = TERM1 + TERM2

TERM1 = SCNA * BN(I)
TERM11 = SCNA
SCPGMN(I) = TERM11

TERM21 = 0.
DO 211 J=1,I
if(i.lt.75) go to 212
AKSN = AKS * (1. + CONKS * (CBC(J-100)/2.)**0.17)
aksnn = aksn
if(i.gt.50.) go to 213
if((i-j-75).le.0.) aksnn = 0.
211 TERM21 = TERM21 + (SCA + 1./((1./(SCna-SCA)) + AKSNn*(T(I)-T(J)))) * B(J)
215
C go to 213
C 212 continue
C sum=0.
C do j=1,i-1
C sum=sum+bn(j)
C end do
C term2=scpgm(1)*sum
213 SCcN(I)=TERM1+TERM2

C AMOUNT CaO CALCULATION
C
ANEWCAO=BN(I)
OLDCAO=0.
DO 200 K=1,I
200 OLDCAO=OLDCAO+B(K)
C
TOTCAO=ANEWCAO+OLDCAO

C Calculate S.A per g, gmol etc.
C
IF(TOTCAO.EQ.0.) GO TO 210
SCPGMN(I)=SCN(I)/TOTCAO
210 SHN(I)=SHNA*(1.-TOTCAO)
TOTN(I)=SCN(I)+SHN(I)
TOTGN=TOTCAO*56.+(1.-TOTCAO)*74.
C
IF(TOTCAO.EQ.0.) GO TO 36
CAOPERG=SCN(I)/(TOTCAO*56.)
HYDPERG=SHN(I)/((1.-TOTCAO)*74.)
STOTGN(I)=CAOPERG*XN(I)+HYDPERG*(1.-XN(I))
GOTO 37
36 STOTGN(I)=STOTN(I)/TOTGN
C
"Average true" DENSITY CALCULATION
C
37 FRACH=(1.-TOTCAO)*74./TOTGN
FRACC=TOTCAO*56./TOTGN
RHON(I)=FRACH*RHOH+FRACC*RHOC
C
ONE WAY OF CALCULATING RADIUS OF GRAIN AND CORE
C
rg(1)=3./stotg(1)/rho(1)
C write(*,*) 'rg=',rg(1)
RGN(I)=3./STOTGN(I)/RHON(I)
C RGN(I)=rg(1)

if(xn(i).gt.1.) write(*,*) xn(i),i
RCN(I)=RGN(I)*(1.-XN(I))*((I./3.)
C RCN(I)=Rg(1)*(1.-XN(I))*((I./3.)
C
IF(I.GT.2) GO TO 34
C epsi0=.4529
proavgc(i)=0.49-(0.49/(SCPGM(I)-SCA))*(SCPGM(I)-SCPGMN(I))
GOTO 35
34 SHPRO=SCA+1./((1./SCPGM(2)-SCA)+AKSN*(TN(I)-T(2))))
proavgc(i)=0.49-(0.49/(SCPGM(1)-SCA))*(SCPGM(1)-SHPRO)
C
35 continue
if(totcao.eq.0.) proavgc(i)=0.49
if(m.le.2) then
proavgs(i)=proavgc(i)
C proavg=proavgc(i)
go to 10
end if
C proavg=proavgc(i-1)-(proavgc(i-1)-proavgc(i))
if(proavg.le.0) proavg=proavgc(i)
proavgs(i)=proavg-(z-1)*(1-0.49)*(xsavg(i-1)-xsavg(i-2))
10 continue
if(proavgs(i).le.dfactor) proavgs(i)=proavg
C PORRAD=2.*PORPRO1/(SCPGMN(I)*RHOC/56.)
C PORRAD=2.*proavgs(i)/(SCPGMN(I)*RHOC/56.)
PORRAD=2.*proavgc(i)/(SCPGMN(I)*RHOC/56.)
DK=97.*PORRAD*(TEMK/18.)**0.5
DPEFF=1./(1./DK+1./DP)
DPN=DPEFF*PORPRO1**2
C DPN=DPEFF*proavgs(i)**2
C DPN=DPEFF*proavgc(i)**2
C GO TO 32
C
CALCULATE PRODUCT GAS CONCENTRATION AT INTERFACE.
C32 UP=-CBS*AKC*RCN(I)**2/DPN*(1./RGN(I)-1./RCN(I))
UP=-CBS*AKC*RCN(I)**2/DPN*(1./RGN(I)-1./RCN(I))
DOWN=1.-AKC*RCN(I)**2/DPN*(1./RGN(I)-1./RCN(I))
CBCN(I)=UP/DOWN
C
RETURN
END
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