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MECHANISTIC STUDIES OF ULTRAFAST SO$_2$ AND SELENIUM REMOVAL BY CALCIUM-BASED SORBENTS

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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To My Parents
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NOMENCLATURE

A Surface area of the pore used in calculation of pore volume distribution, $m^2/g$.

$A_t$ Total surface area of calcine calculated from the pore volume distribution, $m^2/g$.

B Constant to incorporate effect of H$_2$O partial pressure on sintering.

Bi Biot modulus, dimensionless.

$C_p$ Specific heat capacity of particle, cal/gmol K.

$C_a$ Ca(OH)$_2$ solid concentration, g mol/cc.

C Concentration of SO$_2$ inside the grain, g mol/cc.

$D_{AB}$ Molecular diffusivity of H$_2$O in N$_2$, cm$^2$/s.

$D_{eff}$ Overall effective diffusivity of H$_2$O through the porous CaO micrograins, cm$^2$/s.

Overall effective diffusivity of SO$_2$ through the porous media, cm$^2$/s.

$D_p$ Product layer diffusivity of SO$_2$ through the solid CaSO$_4$ layer, cm$^2$/s.

$D_k$ Knudsen diffusivity, cm$^2$/s.

$d$ Width of parallel plate pore, Å.

$d_p$ Diameter of particle, μm.

$\Delta H_c$ Heat of Ca(OH)$_2$ calcination reaction, K cal/gmol.

$h$ Convective heat transfer coefficient, cal/m$^2$ s K.

$k$ Thermal conductivity of bulk gas surrounding particle, cal/m s K.
\(k_p\)  Thermal conductivity of particle, cal/m s K.

\(k_c\)  Specific reaction rate constant for Ca(OH)\textsubscript{2} calcination, m/s.

\(k_s\)  Specific rate constant for CaO sintering, g/m\textsuperscript{2} s.

\(k_{sa}\)  Modified specific rate constant for CaO sintering, g/m\textsuperscript{2} s.

\(k_s\)  Specific reaction rate constant for CaO sulfation, m\textsuperscript{4}/kmol s.

\(M_s\)  Molecular weight of sorbent, g/gmol.

\(M_{CaO}\)  Molecular weight of CaO, g/gmol.

\(M_p\)  Molecular weight of product CaSO\textsubscript{4}, g/gmol.

\(m\)  Constant to incorporate effect of H\textsubscript{2}O partial pressure on sintering.

\(\text{Nu}\)  Nusselt number, dimensionless.

\(P\)  Partial pressure of H\textsubscript{2}O in the CaO product layer, atm.

\(P_e\)  Partial pressure of H\textsubscript{2}O at the CaO/Ca(OH)\textsubscript{2} interface, atm.

\(p^\circ\)  Saturation vapor pressure of adsorbate nitrogen, atm.

\(P_e\)  Equilibrium H\textsubscript{2}O dissociation pressure for Ca(OH)\textsubscript{2} calcination, atm.

\(P_t\)  Total pressure, atm.

\(R\)  Universal gas constant, cal/gmol K.

\(R_p\)  Particle radius, A°.

\(r_c\)  Instantaneous unreacted core radius, A°.

\(r_g\)  Instantaneous grain radius, A°.

\(r_{go}\)  Initial grain radius, A°.

\(r_p\)  Actual radius of cylindrical pore or width of parallel plate, A°.
\( r_m \) mean radius of cylindrical pore in which condensation occurs at relative pressure \( p/p^0 \), Å.

\( S \) Specific surface area of product CaO layer, m\(^2\)/g.

\( S_a \) Asymptotic specific surface area of CaO at a particular temperature, m\(^2\)/g.

\( S_{CaO} \) Specific surface area of CaO product shell, m\(^2\)/g.

\( S_{Ca(OH)_2} \) instantaneous specific surface area of Ca(OH)_2, m\(^2\)/g.

\( S_o \) Specific surface area of nascent CaO, m\(^2\)/g.

\( S_{j,i} \) Specific surface area of CaO formed in the \( j \)-th time interval at the end of \( i \)-th interval, m\(^2\)/g.

\( S_s \) Overall specific surface area of the particle, m\(^2\)/g.

\( T \) Reaction temperature, K.

\( T_b \) Bulk gas temperature, K.

\( T_p \) Particle temperature, K.

\( t \) time, sec.

\( \theta \) thickness of adsorbed film, Å.

\( V_p \) Particle volume, cc.

\( V_e \) Experimental pore volume of sorbent following calcination, cc/g of partially calcined sorbent.

\( V_{\text{calc}} \) Calculated pore volume following sulfation, cc/g of partially sulfated sorbent.

\( V_t \) Total sorption of nitrogen in a pore including the contribution of the film thickness, cc/g.

\( V_p \) Volume of pore completely filled with liquid nitrogen, cc/g.

\( V_L \) Molar volume of liquid adsorbate nitrogen, cc/gmol.

\( v_o(\theta) \) Pore volume distribution obtained from the BET analysis.
$w_{\text{CaO}}$ 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 CaSO$_4$ per unit weight of partially calcined sorbent.

$W_{\text{CaO}}$ Weight of unsulfated CaO per unit weight of partially calcined sorbent.

$X_\gamma$ Extent of calcination of sorbent.

$X_s$ Extent of sulfation reaction.

$x$ Fractional conversion of Ca(OH)$_2$ to CaO.

$x_s$ Fractional conversion of CaO to CaSO$_4$.

$z_j$ Fraction of total CaO formed in the j-th time interval.

$Z$ Molar volume ratio of CaSO$_4$ to CaO.

**Greek Symbols**

$\gamma_{\text{Ca(OH)\textsubscript{2}}}$ Rate of Ca(OH)$_2$ calcination reaction.

$\epsilon$ Product layer porosity.

$\epsilon_0$ Initial product layer porosity.

$\epsilon_{\text{theo}}$ Theoretical porosity of CaO produced from Ca(OH)$_2$.

$\epsilon_{\text{exp}}$ Experimentally measured porosity of CaO produced from Ca(OH)$_2$.

$\epsilon_p$ Emissivity factor of the particle.

$\rho_p$ Density of the particle, g/cc.

$\rho$ Overall solid density of the grain, g/cc.

$\rho_{\text{CaO}}$ Density of CaO, g/cc.

$\rho_{\text{Ca(OH)\textsubscript{2}}}$ Density of Ca(OH)$_2$, g/cc.

$\sigma$ Stefan-Boltzmann constant.
$v_p$  Molar volume of product CaSO$_4$, cc/gmol.

$\nu_{CaO}$  Molar volume of CaO, cc/gmol.

$\gamma$  Surface tension of liquid nitrogen, ergs/cm$^2$.

$\Psi$  Structural parameter used in random pore model.

$\beta$  Biot Modulus used in random pore model.
CHAPTER I

INTRODUCTION

This research deals with the mechanism of interaction and kinetics of various phenomena involved in the capture of SO₂ and selenium from flue gas by using dry calcium-based powders. The deleterious effect and environmental impact of SO₂ emissions can hardly be over emphasized. SO₂ and NOₓ emissions from fossil-fuel burning power plants and industrial utilities are the major contributors to the acid rain problem. In the case of coal-fired boilers, sulfur in the coal reacts with O₂ in the air to form SO₂. Coal itself, according to its sulfur content, may be classified as low (about 1% S), medium (1-2% S) and high (> 2% S). The utilization of the vast reserves of coal containing high-sulfur with minimum environmental impact hinges upon our ability to improve the efficiency of existing flue gas desulfurization (FGD) technologies.

Many FGD technologies have been under development for a number of years. Wet scrubbing, dry scrubbing, and dry sorbent injection (DSI) are some of the dominant technologies at the present time. Wet scrubbing though an effective technique to removing majority of the SO₂ requires very high capital cost and involves operational problems. Spray drying, considered the second generation of SO₂ control
technology, is a lower capital cost alternative. Even though it eliminates the need for liquid waste treatment systems, it still involves the preparation and injection of a wet slurry for injection. Some other techniques that have emerged in the recent years include duct injection, dry injection with recycling (R-SO₂), retrofit of electrostatic precipitator (ESP) or baghouse (E-SO₂), SO₂ NOₓ Rocks in a Box (SNRB), etc., are also either under development or have been proven at the pilot-scale or demonstration-scale.

Dry sorbent injection on the other hand is a simple process which doesn’t involve high capital costs and can be easily retrofitted to existing power plants. DSI development was initiated by the U. S. EPA under the Limestone Injection Multistage Burner (LIMB) program in the early 1980’s. It involves the injection of dry sorbent powders into the above-the-flame region or the upper-furnace region of the boiler, hence it is also referred to as Furnace Sorbent Injection (FSI). The temperature window in this upper furnace region is 1150-800°C and the residence time of the flue gas is about 1-2 seconds. Figure 1.1 gives a schematic of the typical pulverized coal combustor (PCC) facility and the various regions and their temperature ranges.

Limestone (calcium carbonate, CaCO₃) or hydrated lime (calcium hydroxide, Ca(OH)₂) upon injection undergo calcination or decomposition.

\[ CaCO_3 \rightarrow CaO \ + \ CO_2 \]  

(1.1)
The calcination yields a highly reactive and porous CaO which then reacts with SO\textsubscript{2} in the presence of O\textsubscript{2} to form CaSO\textsubscript{4}.

\[ CaO + \frac{1}{2}O_2 + SO_2 \rightarrow CaSO_4 \]  

The formation of CaSO\textsubscript{4} is restricted to the temperature range of 800 to 1200°C. Below 800°C, the rate of formation of CaSO\textsubscript{4} is too slow and above 1195°C, it decomposes to CaO and SO\textsubscript{2}.

One of the main drawbacks of this technology is the partial reaction of the sorbent leading to its incomplete utilization. As a result, the process has not been shown to remove more than 70-75% of the total sulfur even when the sorbent is used in twice the stoichiometric requirement. The new EPA regulations for the Title IV hazardous air pollutants (which covers SO\textsubscript{2} and NO\textsubscript{x} emissions) cannot be met with the current state-of-the-art in dry sorbent injection and would necessitate the usage of additional sulfur removal with some other downstream process.

The continued usage and development of dry sorbent technology is predicated on the improvements in the utilization of the sorbent through increase in reactivity. Loss in surface area due to the phenomena of sintering and the plugging of pores due to the formation of the higher molar volume product are the two important factors in influencing the loss of reactivity and causing the cessation of reaction.
In spite of numerous studies by researchers, a thorough understanding of these phenomena and their interaction has not been accomplished. The main reasons are the ultrafast and overlapping nature of all the three phenomena involved, calcination, sintering and sulfation; and the development and influence of the pore structure on the short time reactivity and the ultimate conversion. Calcination is an extremely fast reaction and it is completed within 200 milliseconds under the high temperature conditions. Sulfation is also very rapid and a major portion of the reaction is completed in the same time scale of few hundred milliseconds. As a result, even though the sulfation reaction is preceded by calcination, under actual conditions, both these reactions occur simultaneously inside a sorbent particle. Surface area, which plays a crucial role in kinetics of gas-solid reactions is simultaneously consumed by sintering. The key to improving the dry sorbent injection technology lies in developing our understanding of these ultrafast phenomena at very short time scales.

Ghosh-Dastidar (1993) has discussed the development of a high-temperature, entrained-flow reactor system for these studies with capabilities of on-line residence time measurement, in-situ particle sizing and instantaneous heat-up and quenching of the reaction. In addition, he obtained time-resolved kinetic data in less than 100 milliseconds time-scale. Ghosh-Dastidar (1993) studied the kinetics of independent sulfation (by using precalcined and presintered CaO) and obtained data for Ca(OH)$_2$ sulfation. He explored the effects of various parameters such as particle size and concentration on the sulfation kinetics.

The original objectives of this study can be classified into three parts:
(a) investigate the influence of the internal pore structure of the sorbent, its evolution, and its interaction with the kinetics of various phenomena; study and characterize calcination and sintering independently; and investigate the overall sulfation of sorbent for role of pore structure.

(b) investigate the high reactivity of modified (ligno-additive) Ca(OH)$_2$ and develop a fundamental mechanistic understanding for its enhanced utilization.

(c) develop a reactor system and a methodology for selenium removal at high temperatures; investigate the various phenomena involved in its interaction with calcium-based sorbents.

In part (b), the high surface area Ca(OH)$_2$ was the initial focus of the study. As the research progressed, findings of very high reactivity exhibited by a particular high surface area CaCO$_3$ inspired the inclusion of carbonates in this research. The organization of the subject matter into different chapters and their significance is delineated in the following.

Chapter II describes the design and operational features of the reactor system. The interplay of calcination and sintering, their opposing effects on the surface area evolution and influence of temperature and particle size on the net or overall surface area development is the main focus of studies described in Chapter II. The development of a comprehensive theoretical calcination and sintering model to simulate the kinetics and surface area development is also discussed in detail. The model visualizes the Ca(OH)$_2$ as being composed of discrete grains and the product CaO formed is visualized as micrograins surrounding the unreacted core. Further, the
model incorporates the sintering of the CaO micrograins and takes into account the age distribution of those CaO in modeling the surface area development. The model assumptions, equation development, the model fit of the experimental kinetic and surface area data and its short-comings are discussed.

Chapter III is devoted to the studies of the pore volume and pore size distribution changes occurring with calcination and sulfation. The distribution of pore sizes plays a crucial role since the filling and plugging of the smaller pores leads to tremendous transport resistance to SO$_2$ and subsequent termination of reaction. These studies are conducted at a isothermal temperature with emphasis on the pore structure in the first 100 milliseconds. Previous studies have shown that the pore shape characteristics of Ca(OH)$_2$ and CaCO$_3$ are different and thereby lead to differences in their reactivities. The chapter discusses some of the basic aspects of analyzing and studying pore shape, pore sizes and their distribution in mesoporous solids. The adsorption-desorption isotherm characteristics, the Kelvin equation which forms the basis of these pore size distribution calculations, its capabilities and drawbacks are reviewed. Both the calcination and sulfation experiments are carried out at the same temperature and with the same particle size for comparative analyses. The detrimental effect of sintering on porosity and the transformations of the pore volume distribution are discussed. The influence of sulfation in further lowering the porosity and the possible particle expansion is theoretically analyzed.

Chapters II and III deal with Ca(OH)$_2$ and its calcination and sintering. Chapter IV delves into development and analysis of a improved reactivity Ca(OH)$_2$
through modification of the parent hydrate (using a surfactant additive). The modified hydrate possesses a high surface area and porosity and its higher reactivity and the influence of additive concentration have been studied previously. It has been shown that the lignosulfonate additive leads to, at best, a 20% improvement in reactivity. However, the reasons for the promotion and more importantly, a lack of promotion beyond 20% are not well understood. The above two questions were the main driving force behind this work. Chapter IV describes these studies on the pore structural evolution of the modified sorbent and the identifying factors that lead to a initial steep increase in reactivity but a equally sudden loss of it due to very fast changes in pore structure. The chapter also identifies a high-surface area carbonate (Forbsy limestone) which from previous studies has shown exceptionally high conversions. The results of the studies conducted to identify the factors leading to the phenomenally high reaction rate on part of the Forsby carbonate are discussed in detail. The results are compared with a commonly used low surface area limestone and the differences are analyzed.

Chapter V discusses the modeling of the overall sulfation of Ca(OH)$_2$ sorbent. The model is built upon the calcination and sintering model discussed in chapter II by incorporating an additional phenomena of sulfation. The model visualizes the sintering CaO product layer as a porous medium and makes use of the pore model to predict the sulfation kinetics. The model assumptions, the equations development and the model solution scheme are discussed. The model predictions are compared with the previous experimental data (Ghosh-Dastidar, 1993) and its short-comings are
analyzed.

The problems and characteristics of heavy metal toxic emissions and the investigations of selenium and its removal are the subject of chapters VI and VII. Selenium is a heavy metal pollutant found in coal in trace quantities and due to its volatile nature, is emitted to atmosphere in the form of vapor. Chapter VI is a literature review of the various trace pollutants emitted from fossil-fuel fired power plants. The chapter discusses the various volatile trace toxics, their concentration in the flue gas, their interaction with the other flue gas components and their fate upon emission to atmosphere. This review has particularly focussed on one representative heavy metal element, selenium, due to its volatile nature which makes its emission control a difficult and challenging task.

Chapter VII describes the design and development of a high-temperature differential bed reactor system for conducting tests of selenium removal using dry sorbents. The unique features of the reactor system include a microbalance-equipped toxic vapor generation assembly. The selenium removal tests are conducted with various alumino-silicate sorbents as well as calcium-based sorbents in the medium and high-temperature ranges. The thorough studies with Ca(OH)$_2$ are discussed and the various investigations conducted in order to identify of the mechanism of interaction form the main core of the Chapter VII.

The main contributions and conclusions of this research work are highlighted again in chapter VIII. Recommendations for future research work are also discussed in this chapter.
Figure 1.1: Schematic of a typical Pulverized Coal Combustion (PCC) facility.
CHAPTER II

Calcination and sintering of Ca(OH)$_2$:
Experimental and Modeling

The contents of this chapter have been published as a paper in the Chemical Engineering Science Journal (A. Ghosh-Dastidar, S. Mahuli, R. Agnihotri, and L.-S. Fan; Vol. 50, No. 13, 1995).

2.1 Introduction and Literature Survey
Calcination of Ca(OH)$_2$ is the endothermic, reversible decomposition which starts at a temperature of about 450°C and leads to the formation of a solid product (CaO) with much lower molar volume.

$$\text{Ca(OH)}_2(s) \rightleftharpoons \text{CaO}(s) + \text{H}_2\text{O}(g) \quad (2.1)$$

The difference in molar volume between CaO (16.87 cm$^3$/gmol) and Ca(OH)$_2$ (33.64 cm$^3$/gmol) results in the product CaO being highly porous and possesses a high surface area. The theoretical porosity of CaO generated from Ca(OH)$_2$ can be calculated to be about 0.49 neglecting the initial porosity and assuming no change in particle size. However, under actual conditions of flue gas temperatures and gas
compositions, deactivating phenomenon of sintering takes place as discussed below.

Sintering of a porous particle is the mechanism by which the micrograins comprising the particle coalesce together when heated at temperatures below the melting point. As coalescence proceeds, the surface area and porosity of the particle decrease and larger but fewer grains are ultimately formed. Sintering has been extensively studied in the field of metallurgy and known to be a solid-state phenomenon brought about by the force of surface tension such that the variations in curvature give rise to fluxes of matter (Borgwardt, 1989). In the case of CaO (mp. 2500°C), sintering becomes appreciable at temperatures above 800°C. German and Munir (1976) discuss sintering induced by high temperatures and the various transport mechanisms leading to grain fusion; surface diffusion, grain boundary diffusion, lattice diffusion and plastic flow. Each of these mechanisms is significant and dominates the sintering process over a certain temperature range. In addition to thermal effect, sintering of CaO is also significantly accelerated by the presence of CO$_2$ and H$_2$O (Borgwardt et al., 1986). These gaseous species promote sintering by forming short-lived solid bridges between adjacent CaO grains (Newton et al., 1989). Sintering kinetics plays an important role in determining the rate of loss of surface area and porosity of the CaO formed and its subsequent reactivity with SO$_2$.

2.1.1 Kinetic studies

Early kinetic studies of calcination involved studies with either large particles (greater than 50 μm) or under non-dispersed conditions in a thermogravimetric
apparatus. Those studies did not minimize the external or interparticle diffusional resistances (Gallaghar and Johnson, 1976; Coutant et al., 1971; Beruto and Searcy, 1974). As a result, most of the early reported kinetic data and the apparent activation energies were limited by interparticle heat and mass transfer effects. Borgwardt (1985) represents the first exhaustive study of calcination kinetics and surface area evolution with both fixed bed as well as dispersed flow systems under differential conditions.

Entrained-flow reactor systems are typically used to obtain time-resolved kinetic data for short reaction time scale of interest. Milne et al., 1990 and Gullett et al., 1988 have discussed the advantages of using entrained-flow reactor systems as compared to thermogravimetric techniques. 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.

Both calcination and sintering phenomena together determine the effectiveness of Ca(OH)$_2$ sorbent in removing SO$_2$ from combustion gases, and occur very rapidly under upper-furnace temperatures of 850-1200°C. Bortz and Flament (1985) reported 70% calcination of Ca(OH)$_2$ particles within first 25 milliseconds (ms) of the reaction at 700°C. Mai and Edgar (1989) reported a comparatively slower decomposition rate, 35% calcination in 100 ms at 1150°C for reagent grade hydroxide powder (mass
median diameter = 12.5 µm). They suggested inadequate sorbent/gas mixing and slow particle heat-up to be the possible reason for the low calcination rate in their studies. Studies on thermal sintering at such short time scales are however, quite scarce. Nonetheless, those which are available, report a very fast sintering rate leading to rapid reduction in surface area within 100 to 200 ms (Roman et al., 1985; Cole et al., 1986) of the reaction. Borgwardt (1989) reported that the CaO derived from Ca(OH)2 sintered faster than carbonate derivatives. Although the apparent activation energy for sintering is similar in both cases, the rate constant is an order of magnitude greater at a given temperature.

For small sizes (less than 10 µm) of sorbent particles, intraparticle heat and mass transfer do not offer any significant resistance to calcination (Powell and Searcy, 1980). In Powell and Searcy's (1980) work, chemical reaction was suggested to be the rate controlling mechanism. They also showed that the calcination rate was proportional to the available surface area of the unreacted particle, which was later confirmed by Borgwardt (1985). Borgwardt (1989) found the maximum attainable surface area of CaO from the calcination of limestone and hydrated limes. At a temperature of 700°C, when the effect of sintering is minimal, surface area of the Ca(OH)2-derived nascent CaO was measured to be in the range of 70-80 m²/g for 2-10 µm particles. However, at higher temperatures, such a high surface area of the nascent CaO is readily lost, and studies with pre-calcines suggest that the rate of surface area reduction is proportional to the square of the instantaneous surface area (Milne et al., 1990; Cole et al., 1986; Silcox et al., 1989). In addition to observing
a strong effect of temperature, Mai and Edgar (1989) also noticed a substantial enhancement of sintering in presence of H₂O and CO₂ in the combustion gas.

### 2.1.2 Modeling efforts

Most early modeling efforts were directed towards predicting the overall sulfation rate of Ca(OH)₂ or CaCO₃. They assumed Ca(OH)₂ calcination to be instantaneous (Bortz et al., 1986, Simon and Garman, 1986). Silcox et al. (1989) represent the first serious effort at modeling the simultaneous calcination and sintering of CaCO₃ sorbent. They developed a mathematical model for the flash calcination of dispersed CaCO₃ sorbent and compared their results with experimental data. They suggested that sintering of the product CaO surrounding the undecomposed sorbent core causes diffusional resistance on the outgoing CO₂ gas which may limit the calcination rate at a later stage. They indicated that similar resistance to H₂O diffusion may be rate-limiting for Ca(OH)₂ decomposition. Mai and Edgar (1989) developed a simple one-dimensional mathematical model to explain the rate of decomposition and surface area evolution resulting from concomitant calcination and sintering of Ca(OH)₂ particles. They used entrained flow reactor data to validate their model. However, they used a very simplistic, empirical first-order Arrhenius type expression for calcination rate. They took into account the age distribution of the CaO grains in their overall surface area formulation. Hartman et al. (1994) proposed an empirical kinetic model to correlate the experimental data on the calcination rate and surface area of magnesium and calcium hydroxides. They essentially fitted an n-
th order Arrhenius type rate equation to their experimental data. Milne et al. (1990) developed an overlapping grain model based on the empirical modification of the shrinking-core model (Levenspiel, 1962) to simulate the staged availability of transient high surface area CaO. The time dependent decrease in CaO reactivity due to sintering is simulated by reducing the grain-center spacing for the matrix of overlapping CaO grains.

Sintering has been studied extensively by researchers in the field of powder metallurgy. The basic mechanisms of transport of matter during thermal sintering and the influence of impurities have been explored in detail (Bemiere and Catlow, 1983). However, the effect of sintering on surface area and pore structure is not very well understood and correlated. Modeling the surface area reduction of CaO simultaneously with its generation by calcination is even more complex. The kinetic relations developed by German and Munir (1974) and by Nicholson (1965) have been used by previous researchers in modeling the CaO sintering kinetics. German and Munir (1974) developed a rate equation based on the theory that sintering is driven by the curvature gradients at the necks of the contacting grains. According to the model, the rate of sintering is a function of the initial surface area before sintering commenced. Further, the rate of sintering is infinite at time zero. The following generalized expression was derived for this process.

\[
\frac{S_o - S}{S_o} = k_s t
\] (2.2)
Nicholson (1965) proposed that the rate of surface area loss is proportional to the difference between the actual surface area and the equilibrium surface area that the particle reaches after long sintering times. This is based on the theory that sintering is a physical transformation to lower surface energy.

In this work, calcination of Ca(OH)$_2$ sorbent is carried out in a specially designed high-temperature, entrained flow reactor. The system has special design features capable of measuring the particle residence time on-line and also ensure rapid heating and quenching of the particles at injection and sampling points respectively. The details of the reactor system are described in the following.

2.2 Entrained flow reactor system

The high-temperature, entrained-flow reactor system used for carrying out the kinetic experiments is shown in Figure 2.1, and described in detail elsewhere (Raghunathan et al., 1993; Ghosh-Dastidar, 1993).

The reactor system consists of a reactor tube assembly within a high-temperature furnace, a powder feeder, water-cooled injection and collection probes with microcomputer interfaced data acquisition systems, and a particle separator/classifier. The reaction temperature is maintained by a Lindberg 3-zone, 1500°C vertical furnace, temperature of each zone being controlled independently. The reactor consists of an outer mullite tube (7.62 cm OD) and an inner concentric tube assembly (5.08 cm OD), which holds an entrance block made of alumina between two mullite tubes. The entrance block is designed for gas entry into the inner tube
from outer annular region and also for instantaneous mixing of injected sorbent and reactant gas stream. The reactant gas is heated to the reaction temperature as it travels up the annular region before it enters into the reaction zone through the entrance block. Sorbent powder is injected into the reactor in a low, steady flow through the injection probe. Reaction zone lies below the entrance block. After passing through the reaction zone, the sorbent/gas mixture is sampled by the water-cooled collection probe. The collection and injection probes are discussed in section 2.2.1. Positioning the collection probes at different axial locations inside the inner tube makes it possible to sample sorbents at various residence times. The residence time measurement and the powder feeding system are highlighted in section 2.2.2.

After traversing the entire length of the collection probe, the gas/solid mixture passes through the cascade cyclone sampler which provides \textit{in situ} classifications of the samples in various size ranges. Solid samples from all the stages of the cyclone sampler are analyzed for determining the reaction kinetics and particle size effects. Section 2.2.3 discusses the particulars of the particle classification and size measurement.

### 2.2.1 Collection and Injection Probes

Schematic of the collection probe is shown in Figure 2.2. It is made of stainless steel and has an OD of 2.54 cm. The gas-particle mixture flows through a 4.8 mm central hole along the probe axis. Two other identical holes of 3.8 mm diameter are oriented parallel to the central axis and are used for housing the optical
guides. These two holes are connected radially near the probe tip by an 1.6 mm opening for passage of light. Inserted into each 3.8 mm hole is a 3.2 mm OD stainless steel tube, which serves as a light guide. As shown in Figure 2.2, a miniature 2-mm prism is placed inside this tube and below the prism is a fiber optic cable which runs through the entire length of the optical guide and extends outside the probe. The 1.6 mm opening is located at the side of the each optical guide, toward the prism face. Dry nitrogen is purged through the annular space surrounding the optical guides, which comes in contact with the incoming hot gas-particle mixture causing rapid cooling. The collection probe design is recently modified by the addition of a ceramic sheath for the upper 46 cm of the probe and a ceramic cap which covers the top. This reduces the cooling effect of the water-cooled collection probe on the reactor. As a result, a more uniform temperature is attained over the entire reaction zone. Figure 2.3 shows that a near-isothermal temperature profile is maintained over most of the reaction zone when the nominal reactor temperature is 1050°C, and the collection probe is located at 10.16 and 20.32 cm. from the bottom of the entrance block.

The injection probe, located above the entrance block, injects sorbent powder into the incoming hot gas stream. A schematic of the injection probe is shown in Figure 2.4. The hot impinging gas stream ensures rapid heating of the solid to the reaction temperature. An R-type thermocouple is inserted through a 3.8 mm hole parallel to the central axis for monitoring temperature at various axial locations in the reaction zone. Both the injection and collection probes house an assembly of two
optical guides, which in association with photomultiplier and microcomputer-interfaced data acquisition system detect any particle flow through the probe tips.

2.2.2 Powder feeding and residence time measurement

In order to perform experiments under differential conditions, the powder feeding rate needs to be very low and the amount of transport nitrogen gas needs to be accurately estimated. As seen in Figure 2.5, an off-take tube (1.6 mm ID) carries particles out of the fluidized bed to the injection probe. A fan attached to the feeder set-up acts as a vibrator and assists in smooth flow of the particles. The powder is fed continuously at a rate of 300-600 mg/hr, ensuring good dispersion of powder. During residence time measurements (performed after the experimental run is completed), the fluidizing flow is diverted through the by-pass line, and pulse injection of solid is done manually by a syringe in the feeder line. All the reactor and process variables are maintained at the conditions of the experimental run. During residence time measurement, the powder is injected as a train of pulses, as the particles cross the optical path at the tip of the injection probe, a corresponding spike is produced in the injection probe signal. After a certain residence time inside the reaction zone, the pulse enters the collection probe and produces another spike in this probe signal. The time delay between the two signals is the residence time of the solids in the reactor. The residence time of the sorbent is thus determined on-line from a cross-correlation of these two signals (Raghunathan et al., 1992, 1993). The

cross-correlation, $r_{xy}(\tau)$, is given by
where \( x(t) \) and \( y(t) \) are the injection and collection probe signals, respectively, \( \tau \) the time delay variable, and \( T \) is the duration of the signal. For a given set of conditions, good reproducibility of the measured residence time is obtained over a large number of pulse injections. Figure 2.6 shows a schematic of the powder residence time measurement.

\[
\rho_{xy}(\tau) = \frac{1}{2T} \int_{-T}^{T} x(t) y(t+\tau) \, dt
\]  

(2.3)

2.2.3 In-situ particle separation and classification

The particles are separated and classified using a Model 283-2 Graseby Anderson Cyclade which is a 4-stage cascade cyclone sampler. Cyclones along with Cascade Impactors are the two most commonly used in-stack particulate size-fractionating samplers. The cyclade is a series of cyclones of specific sizes followed by a Model 274 2.5 inch diameter back-up filter. Figure 2.7 shows the schematic of the 4-stage cyclone set used in these studies. The cyclones fractionate and collect the particles according to their aerodynamic characteristics. The gas-particle mixture enters the cyclone body tangentially and causes a vortex flow pattern. Centrifugal forces cause particles larger than the cut-point of the cyclone to migrate radially outward to the wall and get deposited in the collection cup. Particles smaller than the cut-point pass through the cyclone to the second cyclone with smaller dimensions. This creates a stronger vortex and smaller particles are collected. The back-up filter collects all the particles smaller than the cut-point of the last cyclone in the series.
More detailed information about the data analysis and particle size distribution calculations are given in the instruction manual (Anderson Bulletin No. 280-482-IM). The cyclade gives complete size distributions from 10 to 0.3 μm and has been calibrated for flow rates from 5 to 35 lpm. The cut-off diameter, the equivalent aerodynamic diameter of particles with unity mass density in air, for a given cyclone is a function of the flow rate and the gas temperature (viscosity). For example, at a typical flow rate of 28 lpm at a gas temperature of 150°C, the cut-points of the four cyclones (Model 280-1, 280-2, 280-3, and 280-5) are 7.5, 3.5, 2.7 and 0.57 μm respectively.

2.2.4 Calcination run conditions and analysis

Calcination runs are performed using commercial calcium hydroxide powder (Linwood Mining & Minerals Company, Davenport, Iowa; 94% Ca(OH)$_2$ from TGA analysis) under nitrogen environment. Extent of calcination in the reactor is measured in a Perkin-Elmer TGA (Thermogravimetric Analyzer). Surface area measurements are conducted by low-temperature nitrogen adsorption in a Quantachrome BET apparatus. For all the calcination experiments, 10 lpm (STP) of reactant gas is preheated by passing through the annular section, 1 lpm (STP) of N$_2$ gas flow is used for each of the feeder fluidizing flow and the injection probe purge. 3 lpm (STP) of N$_2$ is used as quench gas purge through the collection probe. 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. Figure 2.8 shows a schematic of the gas flows during
calcination and sulfation experiments. The details of the sulfation experiments are described in chapter III.

In order to verify that no significant rehydration of the collected sorbent occurs in the cascade cyclone sampler, samples of high-surface area CaO are placed in all stages of the sampler. H$_2$O-laden N$_2$ gas is passed over the CaO samples for about 30 minutes, which is the typical duration time for calcination experiment. The H$_2$O 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.

2.2.5 Estimation of heating and quenching time of the particles

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:

$$\frac{\rho_p V_p C_p}{4\pi R_p^2} \frac{dT_p}{dt} = h (T_b - T_p) + \sigma \epsilon_p (T_b^4 - T_p^4) - \gamma_{Ca(OH)_2} \Delta H_c$$  (2.4)

The Ca(OH)$_2$ particle is assumed to be initially at room temperature as it is transported by nitrogen gas through the water-cooled injection probe. The hot bulk gas impinges upon the Ca(OH)$_2$ particle and due to the high bulk/transport gas ratio, the resulting gas is assumed to reach the final temperature instantaneously, implying
a step increase in the surrounding temperature to $T_0$. The surrounding gas is assumed to be stagnant and the internal temperature gradients in the particle are assumed to be insignificant. Thus, the Nusselt number defined in equation (2.5) is equal to 2 and the Biot number defined in equation (2.6) for the small particles of interest is less than 0.1 (Holman, 1972).

$$\textit{Nu} = \frac{h d_p}{k} = 2 \quad (2.5)$$

$$\textit{Bi} = \frac{h d_p}{k_p} \leq 0.1 \quad (2.6)$$

Alvfors and Svedberg (1992) also justify the assumption of a flat temperature profile for small diameter particles. A simple calcination rate equation obtained from Mai and Edgar (1989) is used to estimate the rate of calcination:

$$\ln (1-x) = -k_c S_{\text{Calc}} t \quad (2.7)$$

Equations (2.4) and (2.7) 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 $\mu$m in diameter are heated to the final temperature 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.

Gullett et al. (1988) and 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 2.3. Upon entering the collection probe, the hot stream is mixed with two cold N₂ 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 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.
2.3 Combined Calcination and Sintering Model

The mathematical model developed here describes the kinetics and surface area evolution during simultaneous calcination and sintering of very small \((d_p < 5 \, \mu m)\) Ca(OH)_2 particles. The overall concept of the model is illustrated in Figure 2.8. A single Ca(OH)_2 particle is assumed to be composed of identical, spherical, non-overlapping grains. Calcination takes place on a single grain of Ca(OH)_2 according to the sharp interface model. As hydroxide decomposes, smaller grains of CaO are formed surrounding the unreacted Ca(OH)_2 core, and the product gas, H_2O diffuses out through the CaO product layer. The CaO micrograins sinter rapidly, reducing the internal surface area and porosity of the product layer.

The overall reaction progresses according to the following steps: decomposition of Ca(OH)_2 at the CaO/Ca(OH)_2 interface, diffusion of the product gas H_2O through the product shell to the grain surface, and diffusion of H_2O through the inter-grain voids to the bulk gas phase. For small diameter Ca(OH)_2 particles, intraparticle mass and heat transport are not considered to be rate limiting (Beruto and Searcy, 1974). All the grains can be considered to be at the same conditions of temperature and gas concentration, and H_2O diffusion from the grain surface to the bulk gas is assumed to experience negligible resistance. On the other hand, the product CaO layer offers resistance to the H_2O transport. The product shell is composed of CaO micrograins of varying ages with varying degrees of sintering, and hence, it can be described as a multilayered CaO shell, each layer corresponding to CaO of certain age. The most recently formed CaO layer possesses the highest surface area and porosity.
2.3.1 Calcination Modeling

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

\[ \gamma_{\text{Ca(OH)}_2} = \frac{k_c (P_e - P_c)}{RT} \]  

(2.8)

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

\[ \frac{dx}{dt} = \frac{3r^2 k_c (P_e - P_c)}{R T \rho_0^3 C_s} \]  

(2.9)

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

\[ P_e = \exp \left( -0.023 \ln T - 0.001771 T - 46300 T^{-2} - 12997.48 T^{-1} + 18.20 \right) \]  

(2.10)

The species continuity equation for product gas H$_2$O diffusing through the product CaO assuming the pseudo-steady state approximation can be written as:

\[ \frac{\delta^2 P}{\delta r^2} + \frac{2 \delta P}{r \delta r} = 0 \]  

(2.11)
with the following boundary conditions.

$$-D_{eff} \frac{\delta P}{\delta r} \bigg|_{r=r_e} = k_e (P_e - P_c)$$  \hspace{1cm} (2.12)

$$P \bigg|_{r=r_e} = 0$$  \hspace{1cm} (2.13)

The latter boundary condition assumes negligible bulk H$_2$O concentration and no resistance to intraparticle gaseous diffusion.

Although several researchers have investigated the effect of CO$_2$ pressure on CaCO$_3$ decomposition kinetics (Darroudi and Searcy, 1981; Silcox et al., 1989) and the diffusion of gaseous CO$_2$ through the porous lime, similar studies on the effects of H$_2$O partial pressure and H$_2$O diffusion are non-existent. Both Knudsen and ordinary diffusion may be important at different stages of reaction. Hence, Knudsen and ordinary diffusion coefficients are estimated and the effective diffusivity is derived from the following equations:

$$D_{AB} = 8.938 \times 10^{-6} \left(\frac{T}{273}\right)^{1.5} P_t^{-1}$$  \hspace{1cm} (2.14)

$$D_k = 0.013 \epsilon T^{0.5} S^{-1}$$  \hspace{1cm} (2.15)

and,

$$D_{eff} = (D_k^{-1} + D_{AB}^{-1}) \epsilon^2$$  \hspace{1cm} (2.16)

S and $\epsilon$ 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 (2.16) approximates the value of calcine’s tortuosity as $e^1$, (Smith, 1981).

2.3.2 Sintering Modeling

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

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

(2.17)

where $S_a$ is the asymptotic surface area of CaO at the specific sintering temperature, and $k_s$ is the sintering rate constant (in g/m$^2$ s).

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

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

(2.18)

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

According to the model, the CaO product shell is divided into multiple layers depending on the time interval in which they are formed. At the end of the i-th time interval, the CaO formed during j-th time interval will have a surface area,
where $S_o$ is the surface area of the nascent CaO formed during j-th time interval. The surface area of the entire product shell and the overall specific surface area of the partially calcined particle are calculated as:

$$S_{CaO} = \sum_{i=1}^{j} S_{j,i} z_j$$

(2.20)

where $z_j$ is the fraction of CaO formed during j-th time interval.

A host of previous studies have indicated a linear relationship between surface area and porosity in the low surface area-porosity range (Gullett and Bruce, 1987; Gullett and Blom, 1987; Bruce et al., 1987, Milne et al., 1990). In this work, it is assumed that $\Delta \varepsilon$ is proportional to $\Delta S$ and $\varepsilon$ approaches zero as CaO surface area approaches the asymptotic value. In such a case, the particle porosity results from intergrain voids alone. With such an assumption, the porosity of an individual layer of CaO can be written as a function of its surface area as:

$$\varepsilon = \varepsilon_0 \left( \frac{S-S_0}{S_o-S_0} \right)$$

(2.22)

where $\varepsilon_0$ is the theoretical porosity of the nascent CaO.

The calcination rate equation (2.9) is coupled with the product H$_2$O continuity equation (2.11). The core radius $r_c$ is related to the solid conversion as:
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.

\[
r_s = \frac{3}{S_g(x,t) \rho(x,t)}
\]  

(2.24)

The \( \text{H}_2\text{O} \) partial pressure profile in the product layer can be obtained analytically by solving the continuity equation (2.11) with the given boundary conditions. The \( \text{H}_2\text{O} \) partial pressure at the interface of the unreacted \( \text{Ca(OH)}_2/\text{CaO} \) can be expressed in terms of \( r_c \), \( r_g \) and \( D_{\text{eff}} \):

\[
P_c = -P_e \frac{k_c r_c^2 (1 - \frac{1}{r_c})}{D_{\text{eff}} \frac{r_c}{r_g}}
\]

(2.25)

The calcination rate equation (2.9) 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 \( S_c \) value obtained from the model represents the predicted surface area of the partially calcined particle. The reaction
constant, $k_c$ and the sintering constant, $k_s$ represent the two specific rate parameters of the model. The FORTRAN program of the calcination and sintering model is given in Appendix A.

2.4 Results and Discussion

2.4.1 Calcination of Linwood Ca(OH)$_2$

Figure 2.10 shows the experimental data and model prediction for calcination of 3.6 $\mu$m Ca(OH)$_2$ 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. Nearly 75% of the final extent of calcination (at about 250 ms) is achieved within the first 50 ms at all the temperatures studied.

The sharp attenuation of reaction rate at higher residence times is seen clearly from the 1050°C data which exhibits virtual ceasing of calcination at about 90%. This near 'die-off' of the reaction at higher residence times is also observed at lower temperatures of 900 and 950°C. The characteristic behavior of high initial rate followed by attenuation with virtual die-off is closely linked with the structural effects accompanying the reaction. For these high temperature studies, sintering of product CaO holds the key to explaining and modeling these observed features.

The model discussed earlier assumes that the reaction proceeds on a single Ca(OH)$_2$ grain according to the shrinking core model. The strong influence of
temperature during the initial stage of reaction and the high porosity of the nascent product layer suggest that chemical reaction at the CaO/Ca(OH)$_2$ interface may be the rate limiting step. The product CaO layer rapidly sinters losing surface area and porosity. This offers increasing resistance for the gaseous product H$_2$O to diffuse through the product shell. This leads to increasing H$_2$O concentration in the product layer and at the interface which not only enhances the rate of CaO sintering but also retards the calcination rate. All these phenomena eventually result in the overall calcination reaction being dominated by outward H$_2$O diffusion through the CaO.

2.4.2 Activation energies of calcination and sintering

Experimental data is used to establish values of the two parameters, the calcination rate constant, $k_c$, and the sintering rate constant, $k_s$. The initial surface area of the nascent CaO produced in the dispersed environment is taken to be 100 m$^2$/g (Milne et al., 1990). The asymptotic CaO surface area is a function of the temperature of study, and its value is obtained by utilizing the experimental data. $S_s$ is estimated to be 15.5 m$^2$/g at 900°C and 12.5 m$^2$/g at 1050°C. The rate constants are determined by trial and error procedure to obtain the best fit of the experimental data. A statistical sum of squares of error minimization is not attempted. The activation energies and the pre-exponential factors are obtained from the Arrhenius-type plots shown in Figure 2.11. Figures 2.10 and 2.12 show the values of $k_c$ and $k_s$ respectively, that give the best fit of the experimental data. The activation energy value for calcination reaction is calculated to be 22.5 Kcal/mole, while that for
sintering is 57 Kcal/mol. The calcination activation energy obtained in this study compares with 16.4 Kcal/mol estimated by Mai and Edgar (1989) from calcination data of larger particles (12.5 μm) of Ca(OH)$_2$ in an entrained flow reactor. The sintering activation energy of 57 kcal/mol compares to a value of 77 Kcal/mol obtained by Mai and Edgar (1989) and 58 Kcal/mole reported by Bortz 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 calcination temperature of 900°C, the model underestimates the initial slope while at higher residence times, its prediction lies above the experimental data. The model fits the higher temperature data of 1050°C very well at both short time scales as well as at higher residence times.

2.4.3 Surface area evolution

The overall surface area evolution of the partially calcined Ca(OH)$_2$ shown in Figure 2.12 represents the net effect of the two opposing phenomena of calcination and sintering. For the two lower temperatures of 900 and 950°C, calcination kinetics dominates over the sintering kinetics at short time scales, hence surface area of the partially decomposed Ca(OH)$_2$ initially rises above the parent hydroxide surface area. The surface area goes through a maxima, then rapidly decreases due to sintering and tends to level off to an asymptotic value at higher residence times. On the other hand, at the higher temperature of 1050°C, the effect of sintering is more pronounced and the observed surface area decreases continuously toward the asymptotic value from
the very beginning of the decomposition process. For 1050°C, the surface area attains a value of about 13 m²/g beyond 250 ms.

The model predictions agree well with the observed trends. At the two lower temperatures, the model predicts the initial rise in surface area and the maxima; the predicted maxima are lower than the observed values for both the temperatures. The rapid reduction and the asymptotic leveling also match with the observed trends. At 1050°C however, the model predicts a sharp spike in surface area at very low residence time of about 8 ms before the rapid downward trend toward the asymptotic value. This predicted sharp spike is not observed experimentally, probably due to lack of data at the low residence time of 8 ms.

The model also simulates the build-up of H₂O partial pressure at the CaO-Ca(OH)₂ interface with increasing reaction time as shown in Figure 2.13. With increasing decomposition temperature, the H₂O 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 2.10, where attenuation in reaction rate is exhibited earlier at higher temperatures.

Further, the changes in the simulated grain and core radius are shown in Figure 2.14. Initially, due to domination of calcination, the decreased molar volume product leads to a reduction in the grain and core radius. As time proceeds, sintering causes the formation of fewer and larger grains which is seen from the increasing radii. Moreover, the highest temperature shows the largest grain size and the smallest core size indicating the highest conversion and the smallest surface area.
SEM analyses are conducted to complement the studies of structural changes accompanying the simultaneous calcination and sintering. Figure 2.15(a) shows the structure of 42% calcined 1.5 μm particles after 24 ms at 950°C, which possesses a surface area of 24 m²/g. The granular nature of the surface and the presence of uneven cracks are easily observable. Figure 2.15(b) shows the SEM photomicrograph of the 90% calcined powder of the same size after 235 ms at 1050°C, possessing a much reduced surface area of about 13 m²/g. From this picture, the surface appears much less granular and considerably glazed with reduced apparent porosity. The grain size appears to be larger than the 24 ms grains, due to the sintering process.

2.4.4 Effect of particle size

Studies on the effect of particle size on hydrate calcination are conducted to verify some of the model assumptions and to check the range of validity of the model predictions. The calcination behavior at 1050°C is shown in Figure 2.16 for three different sizes of 1.5, 3.6, and greater than 7.8 μm. There appears to be no effect of particle size on calcination for the two smaller particle sizes, suggesting negligible intraparticle heat and mass transfer limitations. However, for the largest size group, the effect of particle size is quite pronounced from the very onset of the reaction. For this size group, intra-particle transport effects play an important role over the entire calcination time scale. This size group may contain large agglomerates, which are big enough to experience internal heat transfer resistance.

A comparison of surface area evolution for different particle sizes shows a
distinct particle size effect on the extent of sintering. Figure 2.17 shows the surface area evolution curves for 3.6 \( \mu m \) and greater than 7.8 \( \mu m \) particles at 950\(^\circ\)C. The larger particles exhibit a higher maxima in surface area than the smaller particles. The peak surface area is about 24 m\(^2\)/g for the 3.6 \( \mu m \) particles while it is nearly 29 m\(^2\)/g for the > 7.8 \( \mu m \) particles. Such higher peak surface area observed for the larger particles compares with the data of Mai & Edgar (1989) who observed a peak surface area of about 32 m\(^2\)/g for 12.5 \( \mu m \) particles at 1012\(^\circ\)C. This strongly suggests a heat-transfer limited sintering for the bigger particles. The larger particles probably experience internal temperature gradients with the inner core requiring longer time to reach the reaction temperature and sintering to a lower degree. Calcination on the other hand progresses at reasonably high rate, though slower than for the smaller particles.

2.5 Conclusions

Experimental data for simultaneous calcination and sintering of small calcium hydroxide particles are obtained for high temperatures and short reaction times. A mathematical model is developed based on first order decomposition kinetics and second order sintering rate equation, which satisfactorily describes the time-resolved experimental data. At 1050\(^\circ\)C, high extent of calcination of about 90\% is observed, whereas for the lower temperatures of 900 and 950\(^\circ\)C, the calcination rate exhibits considerable attenuation after about 50 and 70\% conversion respectively.

The mathematical model also matches the surface area evolution data for the
three temperatures, accurately representing the experimental observation that the highest peak surface area is achieved at the intermediate temperature of 950°C. The model predicts an initial increase and then a drop in the surface area to an asymptotic value for all the three temperatures. No sharp spike is however, observed experimentally for the highest temperature of 1050°C, possibly due to unavailability of surface area data at residence times lower than 13 ms.

This research has importance in the on-going effort to develop a comprehensive model for the furnace sorbent injection technology. The results demonstrate the severity of sintering at high temperatures, which drastically reduces the CaO surface area, an important parameter for SO₂ capture. Opting for a lower temperature apparently helps in producing a higher surface area and preserving it for a longer time, but on the other hand fails to achieve substantial decomposition of the hydroxide, which leads to a lower sorbent utilization. Furthermore, a decrease in the reaction temperature also should reduce the rate of sulfation reaction. In view of this, the results of this study can be utilized to determine an optimum condition for sorbent injection, with an objective to achieve superior sorbent utilization and high sulfur capture.
Figure 2.1: Schematic of the high-temperature entrained-flow reactor system.
Figure 2.2: Schematic of the collection probe.
Figure 2.3: Typical axial temperature profile inside the reactor with a nominal reactor temperature of 1323 K.
Figure 2.4: Schematic of the injection probe
Figure 2.5: Schematic of the continuous powder feed system.
Figure 2.6: Schematic of the cross-correlation analysis for on-line estimation of particle residence time.
Figure 2.7: Schematic of the Cascade cyclone sampler system.
Figure 2.8: Schematic of the gas flows during calcination and sulfation experiments.
Figure 2.9: Schematic illustration of the calcination and sintering model
(a) single, spherical Ca(OH)$_2$ grain;
(b) partially calcined grain with inner Ca(OH)$_2$ core and
sintered CaO micrograins.
Figure 2.10: Effect of temperature on calcination of 3.6 μm Linwood Ca(OH)$_2$; experimental data and model predictions.
Figure 2.11: Arrhenius plots to estimate activation energies of calcination and sintering.
Figure 2.12: Effect of temperature on surface area evolution during calcination of 3.6 μm Linwood Ca(OH)$_2$; experimental data and model predictions.
Figure 2.13: Ratio of interface H$_2$O partial pressure to the dissociation pressure with time; model simulation.
Figure 2.14: Variation of the grain and core radius with time; model simulation.
Figure 2.15: SEM photomicrographs of partially calcined Ca(OH)$_2$ particles:
(a) 42% calcined, 1.5 μm particles after 24 ms at 950°C, surface area 24 m$^2$/g; (b) 90% calcined, 1.5 μm particles after 235 ms at 1050°C, surface area 13 m$^2$/g.
Figure 2.16: Influence of particle size on calcination of Linwood Ca(OH)$_2$ at 1050°C.
Figure 2.17: Effect of particle size on surface area evolution during calcination of Linwood Ca(OH)$_2$ at 950°C.
CHAPTER III

STRUCTURAL EVOLUTION STUDIES:

Ca(OH)$_2$ CALCINATION & SULFATION

3.1 Pore structure and analysis

The internal surface area for Ca(OH)$_2$ as well as h-CaO (CaO derived from hydrate) lies predominantly in pores of size 20 to 500 Å. Such pores are classified as mesopores by the International Union of Pure and Applied Chemistry (IUPAC) classification according to which, pores less than 20 Å in width are considered micropores; between 20 and 500 Å are mesopores; and more than 500 Å are macropores. The physical adsorption isotherm exhibited by such mesoporous solids is generally classified as Type IV isotherm according to the Brunauer, Deming, Deming and Teller (BDDT) classification. Figure 3.1(a) shows the various types of adsorption isotherms. The exact shape of the pores of mesoporous solids can be cylindrical (tubular), parallel plate-shaped or spherical with narrow opening. Another characteristic feature of the mesoporous solids is the hysteresis loop obtained in the adsorption-desorption isotherm. The exact shape of the hysteresis loop varies from one adsorption system to another and is determined by the shape of the associated pores. The hysteresis loops, as originally classified by de Boer in 1958 into Types
A, B and E (Gregg and Sing, 1982) are shown in slightly revised form in Figure 3.1(b). These are exhibited by cylindrical, parallel-plate and spherical with narrow opening type of pores respectively. Previous researchers have shown that h-CaO possesses a parallel plate pore structure, i.e., it exhibits a Type B hysteresis loop (Gullett and Bruce, 1987). A similar hysteresis diagram for calcium hydroxide is not available in the literature. The adsorption-desorption isotherm constructed for Ca(OH)$_2$ using the BET apparatus is easily identifiable as a Type B hysteresis loop, indicating a parallel plate pore structure for Ca(OH)$_2$. All the pore size distribution calculations for Ca(OH)$_2$ as well as h-CaO are done using the parallel plate model.

Figure 3.2(a) shows the adsorption-desorption isotherm for Ca(OH)$_2$ and Figure 3.2(b) shows a classical Type IV isotherm which will be used to briefly outline the fundamentals of pore size distribution. Figure 3.2(b) shows the low pressure region path ABC followed by a upward deviation in the isotherm at a certain point D (CDE). The slope decreases (EFG) at higher pressures, however, as the saturation vapor pressure approaches, the amount adsorbed may either follow along FGH or it may show a final upward turn (GH'). In an attempt to provide an interpretation of these isotherms, Zsigmondy (Gregg & Sing, 1982) proposed his capillary condensation model. Zsigmondy made use of the principle established earlier by Lord Kelvin on thermodynamic grounds, that the equilibrium vapor pressure, $p$, over a concave meniscus of liquid, must be less than the saturation vapor pressure, $p^*$, at the same temperature. Hence, a vapor will be able to condense to a liquid in the pores of a solid, even when its relative pressure is much less than unity. It is assumed that along
the initial part of the isotherm (ABC), adsorption is restricted to the thin layers on the walls, however, starting at point D (inception of the hysteresis loop) capillary condensation commences in the smallest pores. As the pressure is increased, bigger and bigger pores are filled until at the saturation pressure the entire system is full of condensate. The Kelvin equation is given as:

\[
\ln\left(\frac{P}{p^0}\right) = \frac{-2\gamma V_L}{RT} \frac{1}{r_m}
\]

(3.1)

\(p/p^0\) is the relative pressure of vapor in equilibrium with a meniscus having a radius of curvature \(r_m\), and \(\gamma\) and \(V_L\) are the surface tension and molar volume respectively, of the liquid adsorbate. Using nitrogen as the adsorbate, the angle of contact is zero. Further for cylindrical pores, the mean radius of curvature \(r_m\) becomes equal to the radius of pore \((r_p)\) less the thickness of the adsorbed film on the walls \((t)\). By application of Kelvin equation, it is thus possible to calculate the radius of pores in which capillary condensation takes place, starting from the relative pressure at D, the lower limit of the hysteresis loop. However, the Kelvin equation leads to values of core size rather than the actual pore size. The desorption branch of the hysteresis loop is conventionally used for the calculations (Gregg and Sing, 1982) even though mathematically, the procedure is equally valid for either branch of the loop. In using the Kelvin equation for calculations of pore size distribution, the value chosen for the upper limit of the range (point corresponding to point G in Figure 3.2(b)) is inevitably somewhat arbitrary. For cylindrical pores, \(p/p^0 = 0.95\) (corresponding to \(r_p = 200\))
A®) is common. For parallel-plate pores which show the upward swing as at GH
(Figure 3.2(b)), the Kelvin equation is somewhat inaccurate. In these studies, 0.98
has been used as the upper limit. Gregg and Sing (1982) have provided an excellent
discussion of the importance of the role played by the adsorbed film and the various
models for correcting for the film thickness.

The Kelvin equation as originally proposed involves the assumption of
cylindrical pore shape. It is necessary to modify the Kelvin equation in order to
assess the size distribution of pores of other shapes. In this work, the Kelvin equation
for a parallel plate model is developed based on Innes (1957). The Kelvin equation
is the same as for cylindrical pores, except the pore radius is replaced by the pore
wall separation, d. The original equation (3.1) can be written as:

\[
d - 2t = - \frac{2\gamma V_L}{RT} \ln\left(\frac{P}{P^0}\right) \tag{3.2}
\]

By substituting the values for liquid nitrogen; T = 77 K (-195.8 °C); \(\gamma = 8.85\)
ergs/cm²; \(\theta = 0^\circ\); \(V_L = 34.7\) cm³/gmol for liquid nitrogen:

\[
d - 2t = - 4.14 \log_{10}\left(\frac{P}{P^0}\right) \tag{3.3}
\]

The values of t are calculated using the Schull equation for parallel plate model
(Innes, 1957) and from the Halsey equation for the cylindrical pore model
The equation development for pore size distribution is shown below in the case of parallel plate pores:

\[ V_t = V_p + A \Delta t \]  

(3.4)

where \( V_t \) is the total sorption, \( V_p \) is the volume of pore completely filled with liquid nitrogen, and \( A \) is surface area of pore. For small increments,

\[ \Delta V_t = \Delta V_p + A \Delta t + \Delta A \Delta t \]  

(3.5)

also,

\[ \Delta A = \frac{2 \Delta V_p}{d} \]  

(3.6)

Substituting equation (3.6) in (3.5)

\[ \Delta V_p = \frac{d}{d-2t} (\Delta V_t - A \Delta t) \]  

(3.7)

The QuickBasic program used in this work for performing pore size distribution analyses for parallel plate pore structure is given in Appendix B.

For cylindrical pores, the equation (3.7) can be derived as

\[ \Delta V_p = \left(\frac{r_p}{r_p - t}\right)^2 (\Delta V_t - A \Delta t) \]  

(3.8)
Studies of pore structure and its influence on calcination and sulfation are very scarce in the existing literature. Gullett and Bruce (1987) have studied influence of sulfation reaction on pore size distribution of precalcined h-CaO and c-CaO. Newton et al. (1989) have examined the role of porosity in rate of sulfur capture and its evolution with calcination and sulfation. They did not include pore size distribution in their studies, however, they analyzed the variation of average pore diameter with calcination and sulfation.

In this work, rapid changes in sorbent surface area, porosity, and pore size distribution were investigated for both Ca(OH)$_2$ calcination and sulfation experiments in the reaction time of 0 to 200 ms.

3.2 Ca(OH)$_2$ Calcination & Sintering

The surface area evolution during calcination has been discussed in detail in chapter II, this section discusses the porosity and pore size distribution changes at two temperatures, 1000 and 1050°C.

3.2.1 Pore volume and porosity evolution

The theoretical porosity of CaO generated upon complete calcination of Ca(OH)$_2$ can be calculated from their molar volumes; 16.87 cc/gmol for CaO and 30.84 cc/gmol for Ca(OH)$_2$. This gives rise to a theoretical h-CaO porosity of 45.3% not including the pore volume of the original Ca(OH)$_2$. Assuming a basis of 1 gmol of Ca(OH)$_2$ and including the initial Ca(OH)$_2$ pore volume (0.05 cc/g or 3.7 cc/gmol)
it can be shown that the theoretical porosity of the partially calcined sorbent (in the absence of sintering) will vary according to:

$$\varepsilon_{\text{theo}} = 0.39 \times 0.107$$ (3.9)

The experimental porosity is calculated from the pore volume based on the nitrogen uptake (in terms of cc of liquid nitrogen per gram of sorbent) obtained from the BET at relative pressure of 0.98. Assuming a basis of 1 gram of partially calcined sorbent, the porosity is calculated as:

$$\varepsilon_{\text{expt}} = \frac{V_c}{(w_{\text{CaO}}) \left( \frac{1}{\rho_{\text{CaO}}} \right) + (w_{\text{H}_2O}) \left( \frac{1}{\rho_{\text{Ca(OH)\_2}}} \right) + V_c}$$ (3.10)

The $w_{\text{CaO}}$ (g CaO/g sorbent) and $w_{\text{H}_2O}$ (g Ca(OH)$_2$/g sorbent) are calculated from the extent of calcination obtained from the thermogravimetric analysis.

Figure 3.3 shows the sorbent porosity evolution with calcination data for the two temperatures 1000 and 1050°C. The experimental porosity is seen to be much less than the theoretical porosity upon calcination alone, indicating the influence of sintering. The overall porosity of the sorbent initially increases with the increasing sorbent conversion to CaO. At higher temperature, the porosity rises faster and higher, but also reduces faster at longer residence times. Sintering affects both the surface area as well as the pore volume. From surface area studies, the detrimental effect of sintering wherein the overall surface area decreased with increasing
conversion has been discussed in chapter II. Thus, this result is indicative that effect of sintering is less severe on overall porosity than overall surface area. Gullett and Bruce (1987) have also noted this behavior in their studies. Thermal sintering causes grain coalescence or coalescence of smaller pores into larger pores. As most of the surface area resides in smaller pores, it is readily lost due to sintering. On the other hand, larger pores primarily contribute to the total sorbent porosity, and consequently, the effect of sintering on this sorbent property is less pronounced. In fact, any loss of porosity due to sintering is more than compensated by the evolving porosity due to further calcination, and the overall porosity increases with increasing sorbent decomposition. For comparative analysis, the raw pore volume evolution data is shown in Figure 3.4.

3.2.2 Pore size distribution changes

The pore size distribution data shown in Figure 3.5 provides some further insight into the pore structure evolution phenomenon. The parent Ca(OH)$_2$ powder exhibits a peak in the pore size distribution at a pore size (plate separation) of about 90 Å, and the median pore size ($d_{50}$) defined as the plate separation below which 50% of the volume exists lies at 115 Å. The formation of the nascent CaO is evidenced by the small peaks in the size range of 20-60 Å for these partially calcined sorbents. However, the pore size distribution clearly shifts to the right due to rapid sintering and a comparison of 79.5% and 82% calcined sorbent (not much difference in conversion) would indicate a shift to the larger pores with time, induced by sintering.
This shifting of the entire distribution to the right is even clearly elucidated in Figure 3.6 for 1050°C. As an example of the pore size shift, the \(d_{20}\) increases from about 115 Å for parent \(\text{Ca(OH)}_2\) to about 240 Å as can be seen from the cumulative pore volume distribution plot in Figure 3.7. The peak pore size shifts appreciably from about 90 Å for parent to about 225 Å for the 91% calcined sorbent. The decreased contribution of the less than 100 Å pore sizes is also clearly apparent from comparison of the p.s.d curves.

3.3 \(\text{Ca(OH)}_2\) Sulfation

The mechanism of \(\text{SO}_2\) capture at high temperatures involves the calcination of \(\text{Ca(OH)}_2\) or \(\text{CaCO}_3\) followed by the sulfation reaction of the \(\text{CaO}\) in the presence of \(\text{O}_2\) as follows.

\[
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4
\]  

Sulfation is a exothermic reversible reaction. The favorable window for formation of \(\text{CaSO}_4\) is between 800 - 1200°C. Below 800°C, the rate of formation of \(\text{CaSO}_4\) is very low and at temperatures higher than about 1195°C, the \(\text{CaSO}_4\) decomposes back to \(\text{CaO}\) and \(\text{SO}_2\). Thus \(\text{Ca(OH)}_2\) interaction with \(\text{SO}_2\) represents the concomitant occurrence of calcination, sintering and sulfation reaction, all three of which together influence the surface area, porosity and pore size distribution changes. Sulfation reaction leads to formation of the higher molar volume product \(\text{CaSO}_4\) and plays a crucial role in the filling up of the pores.
3.3.1 Literature review

The sulfation reaction occurs sequentially or consecutively with calcination and sintering. Apart from temperature and particle size, the molar ratio of calcium fed to sulfur in the gas is an important factor influencing \( \text{SO}_2 \) capture. The sulfation of \( \text{Ca(OH)}_2 \) has been studied extensively but mainly for kinetic investigations and is shown to be comparably rapid by several investigators. Milne and Pershing (1987) observed 30\% sulfur capture within 40 milliseconds for hydrates at a temperature of 1094°C. They conducted their investigations at a Ca/S ratio of 2:1. A sorbent conversion of 16\% was observed within 50 ms by Gullett et al. (1988) for \( \text{Ca(OH)}_2 \) at 1000°C. Milne et al. (1990b) reported sulfation data for Linwood hydrates, they observed 15\% conversion in first 40 ms at 1095°C. Their results compared well with 18\% conversion observed by Ghosh-Dastidar (1993) in 14 ms at 1115°C. The rate controlling mechanism is a strong function of the initial particle properties and the extent of sulfation and has been a subject of considerable debate. Simons et al. (1987) suggested that the chemical reaction step is rate limiting for very small particles. On the other hand, diffusion through the product \( \text{CaSO}_4 \) layer has been proposed to be the rate limiting step by a number of researchers (Borgwardt et al., 1987; Milne et al., 1990b). The actual mechanism of diffusion through the product layer also has been extensively explored by researchers. In the study by Borgwardt et al. (1987), it was proposed that \( \text{SO}_4^- \) ions are formed at the \( \text{CaSO}_4/gas \) interface which migrate through the product layer to the \( \text{CaO/CaSO}_4 \) interface. Later, thorough marker and isotopic labeling experiments by Hsia et al. (1993) conclusively showed that \( \text{Ca}^{++} \) and \( \text{O}^- \) ions
diffuse through the product layer and the reaction proceeds at a rate limited by such ionic transport. However, at the later stages of the reaction, the phenomena of pore filling and pore mouth plugging by CaSO$_4$ significantly retards the rate of sulfation (Simons and Garman, 1986; Milne and Pershing, 1987).

Effect of Ca(OH)$_2$ particle size on its reactivity has also been investigated by a number of researchers. This effect has been studied by both pre- and post-reaction sizing methods (Gullett and Blom, 1987; Snow et al., 1986). An increase in sorbent reactivity was observed with smaller size, most probably due to higher surface area to volume ratio for smaller particles and also because of reduced diffusional resistance for reactant SO$_2$. Milne and Pershing (1987) reported a strong particle size effect on conversion for only first 200 ms of the reaction time, and also noticed no effect of size for less than 2.5 $\mu$m. Similar observations were made by Cole et al. (1986), who claimed that below 2-5 $\mu$m, particle size no longer influences reactivity. Elimination of pore diffusional resistance was cited as the possible reason for such vanishing size effect. However, both the above studies worked with pre-sized sorbent particles and did not take into account the possible sorbent agglomeration during transport. Gullett and Blom (1987) employed post-reactor in-situ sizing method in their studies and contrary to previous work, observed constant effect of size over the range of 0.72 to 12.1 $\mu$m.

Borgwardt and Bruce (1986) showed that sulfation rate exhibited a greater sensitivity to specific surface area than expected for chemical reaction control. They proposed the product layer diffusion to be the rate limiting mechanism to explain such
behavior. Other studies also reported similar strong dependence of sorbent reactivity on CaO surface area (Milne et al., 1990b; Borgwardt et al., 1987; Ghosh-Dastidar, 1993). Kinetic studies of Ca(OH)$_2$ sulfation at three different temperatures, the influence of particle size has been conducted by Ghosh-Dastidar (1993). Ghosh-Dastidar (1993) represented the first study of its kind which reported exhaustive kinetic data in the time scale of less than 100 ms. His studies with particle size influence proved that the effect of sorbent size vanishes below a particle size of about 5 $\mu$m. Sadakata et al. (1994) produced ultrafine CaO particles using laser ablation method and examined their reaction rate with SO$_2$. They reported that the reaction rate of ultrafine CaO particles with SO$_2$ was about 100% higher than that for the other CaO particles larger than 1 $\mu$m.

3.3.2 Experimental Conditions

Evolution of sorbent structural properties during Ca(OH)$_2$ sulfation was investigated for a reaction temperature of 1050°C in the entrained flow reactor system described in Chapter II. The bulk gas composition for the sulfation experiments were maintained at 5.45% O$_2$, 3900 ppm SO$_2$ and balance N$_2$. Conversion is obtained using the Alltech Ion Chromatography (IC) system. A Universal Anion Column, 50 mm in length and 4 mm in diameter is used for the separation, and a 4 mM Lithium hydrogen phthalate in methanol buffer is used as the eluant. An Alltech 320 Conductivity detector is used for measuring the sulfate concentration. For the sulfation experiments, the cascade cyclone sampler is maintained at a temperature of
about 250°C in order to avoid any acid-mist condensation on the collected solid samples. Verification was performed for sulfation reaction by placing high-surface area CaO inside the sampler (maintained at 250°C) and passing SO$_2$ laden gas. Analysis showed negligible conversion of CaO sample to CaSO$_4$.

3.3.3 Surface area and porosity analysis

Figure 3.8 shows the plot of sorbent surface area during sulfation along with the extent of solid conversion. The surface area evolution during calcination & sintering alone is also plotted versus time for the same temperature. As can be expected, the overall surface area lies below the calcination surface area curve because of the additional loss of surface area due to the formation of the non-porous CaSO$_4$ product.

The porosity evolution with sulfation is shown in Figure 3.9 along with its evolution during calcination for comparison. Unlike calcination, the porosity decreases continuously from the beginning of sulfation. In addition to sintering, deposition of higher volume reaction product (CaSO$_4$) fills up the CaO pores and reduces the overall porosity. A rigorous quantitative analysis of the loss of pore volume due to calcination and sulfation is discussed in chapter IV.

3.3.4 Transformation of pore size distribution with sulfation

The change in the cumulative volume distribution is seen in Figure 3.10. Most notable are the much faster decrease in the total pore volume with sulfation and the
much higher loss of the smaller pores than 100 Å. As sulfation conversion increases from 14 to 21%, contribution of the pores smaller than 100 Å to the overall pore volume decreases drastically, and maximum volume contribution slowly shifts towards the mesopore size range between 300-400 Å.

3.4 Conclusions

Sintering does not have as much of a detrimental effect on porosity during calcination, compared to its effect on surface area. Even though the observed porosities are much lower than the theoretically predicted porosity upon calcination alone, the porosity does exhibit an increasing trend at both the temperatures studied, 1000°C and 1050°C. The generation of pores due to formation of lower volume product is manifested at 1000°C in the form of increased contribution of the very small (less than 50 Å) pores. However, with increasing time, those small pores are again lost due to sintering. The increasing median pore size is most clearly observed at the higher temperature of 1050°C, wherein the pore distribution is shifted towards macropores size.

With sulfation, the porosity as well as surface area reduction is enhanced over calcination alone as expected, due to the formation of the non-porous higher volume product. The preferential filling of the smallest pores is also demonstrated in the intensified loss of the smallest pores of less than 50 Å, compared to calcination.
Figure 3.1: (a) BDDT classification of the adsorption isotherms, and (b) de Boer classification of the hysteresis loops of Type IV isotherms.
Figure 3.2: (a) Ca(OH)$_2$ adsorption-desorption isotherm, and (b) the classical Type IV isotherm.
Figure 3.3: Influence of temperature on evolution of porosity during calcination of 3.9 µm Linwood hydrate.
Figure 3.4: Influence of temperature on evolution of pore volume during calcination of 3.9 μm Linwood hydrate.
Figure 3.5: Pore size distribution changes during Ca(OH)$_2$ calcination at 1000°C.
Figure 3.6: Pore size distribution changes during Ca(OH)$_2$ calcination at 1080$^\circ$C.
Figure 3.7: Cumulative pore volume distribution changes during Ca(OH)$_2$ calcination at 1080°C.
Figure 3.8: Development of surface area during sulfation and during calcination only of Ca(OH)$_2$ at $1080^\circ$C.
Figure 3.9: Porosity evolution during sulfation and during calcination only of Ca(OH)$_2$ at 1080°C.
Figure 3.10: Pore size distribution changes for pure Linwood hydrate at different extents of sulfation at 1080°C.
CHAPTER IV
HIGH SURFACE AREA Ca(OH)$_2$ & CaCO$_3$: SULFATION STUDIES

Most of the contents of this chapter (except the discussion in section 4.3.6) have been submitted as a paper to the *Industrial and Engineering Chemistry Journal* (Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R. and Fan, L.-S.). This paper has been accepted for publication.

4.1 Introduction and Literature Review

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 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.

4.1.1 Modified/promoted sorbents

The most difficult problem in the use of lime as a sorbent is the difficulty in achieving high conversions. Incomplete utilization with non-regenerable (throw-away) sorbents leads to reduced process efficiency and increased operating costs. Earlier researchers who worked on this problem identified the particle size as the parameter and worked on reducing the size of the sorbent particles. Ca(OH)$_2$ sorbent which is generated from CaCO$_3$ has a smaller particle size and is much more porous than the parent limestone. Hydrated lime can be considered the first attempt at generating better lime-based sorbents with improved capacity.
Subsequently, the use of inert additives to enhance the Ca(OH)$_2$ reactivity were explored by a number of investigators. Promoters, additives, modifiers are the various terms used to identify a component which, when added to the parent lime in a small quantity leads to an increase in its reactivity. The various types of additives investigated can be classified either according to their chemical nature or according to their proposed mechanism of promoting reactivity in the parent lime. According to one classification, the types of additives have been categorized as (Prudich and Venkataramakrishnan, 1994)

* inorganic salts
* sodium-containing basic compounds
* organic compounds
* oxidation catalysts

Promoters can also be classified according to their mechanism: structural modifiers which reduce agglomeration/ sintering characteristics; and ionic modifiers which induce ionic defects in the crystal structure to enhance rate of diffusion through the ionic lattice. For Ca(OH)$_2$ sorbent, the additives could be added as a physical mixture or incorporated into the sorbent during the hydration process. Snow et al. (1986) investigated NaHCO$_3$ as an additive for capture of SO$_2$ at about 1150°C from flue gas. They observed an increase of about 17% in sulfur capture compared to the unpromoted sorbent, when the additive was physically mixed with the sorbent at a Ca/Na molar ratio of 15. Muzio et al. (1986) performed thorough studies with various alkali metal based additives, and studied their relative effectiveness, the
method of incorporating the additive, the amount of additive, and the effect of coal ash. They found that the additives were less effective when incorporated as physical mixtures compared to their addition to the water of hydration. From thermochemical considerations, they proposed a volatilization mechanism of the alkali compounds in the combustion zone which they speculated, leads to opening of the pore structure at reaction conditions. Gooch et al. (1986) evaluated alcohol and sucrose as the organic additives. Hydrates produced using aqueous solutions of ethanol had surface areas of up to 80 m²/g. Sulfation experiments with a 40 m²/g aqueous ethanol produced hydrate showed as much as 20% increase in relative utilization. However, with increasing temperature of injection, the high surface area hydrate loses its surface area faster and leads to less than 10% increase in final conversion. Gooch et al. (1986) speculated that alcohols act to improve sorbent surface area by abstracting the heat of hydration from the sorbent surfaces by evaporation. Sucrose on the other hand acts by increasing the solubility of CaO in water. No experimental evidence was reported to support either of these proposed mechanisms.

Most of the earlier studies however lacked a mechanistic understanding of how the promoter leads to increase in reactivity. Borgwardt et al. (1987) revealed that the diffusion through the CaSO₄ product layer occurs via a solid-state ionic diffusion mechanism. Their finding also lead to a more fundamental approach to understanding the role of additives or impurities in the sorbent structure. Borgwardt et al. (1987) pointed out that solid state diffusion of ions is enhanced by lattice defects. These lattice defects may involve point defects through individual atoms. Hence, the
presence of foreign ions in the product layer (due to impurities in the original CaO) can be expected to lead to higher diffusivities, when a solid-state mechanism is involved. Impurities in the form of aliovalent ions are known to generate defects in the crystal structure in order to compensate for local charge imbalance (Berniere and Catlow, 1983). Borgwardt et al. (1987) observed significant increase in sulfation with addition of single-valent cations. They observed this behavior upon physically mixing and grinding the CaO with sulfates of alkali metal ions. However, upon "doping" the foreign ions along with the hydration process to make Ca(OH)$_2$ lead to reduction in reactivity. This result is explained by their finding that the doped Ca(OH)$_2$ or CaCO$_3$ loses surface area very rapidly as a result of fast sintering. Sintering also being solid-state diffusion controlled, is thus accelerated by the lattice defects. Thus, the effect of doping which leads to increased product layer diffusion and sulfation rate also leads to increased rate of sintering which more than compensates the former effect leading to reduced conversion. The observed effect on sintering also served as an indirect support of their ionic diffusion hypothesis.

Shadman and Dombek (1988) viewed the role of additives as structure modifiers. They studied bauxite, silica and kaolinite as the additives to Ca(OH)$_2$ during the hydration process and observed a significant increase in reaction rate as well as in the ultimate conversion. They hypothesized that the effect was purely physical in nature with the pore structure being opened to lead to increased macro-porosity and the diffusivity. Between those additives, when their concentration and particle size were the same, there was little difference in their performance.
4.1.2 Lignosulfonate modified Ca(OH)$_2$.

Kirchgessner and Lorrain (1987) modified the Ca(OH)$_2$ sorbent with calcium lignosulfonate, a surfactant they added to the water of hydration at various concentrations. They observed that the utilization of sorbent increases with increasing additive concentration, reaches a maximum and then decreases. The maximum occurred at a lignosulfonate concentration of 1.5 weight % (w.r.t. dry Ca(OH)$_2$), where the sorbent utilization was about 20% higher than the unmodified hydroxide. They performed size analysis of the sorbents using cascade impacter and sedigraph and observed a reduction in particle size for the modified hydroxide. They concluded that the additive was effective in desegregating the agglomerates. They hypothesized that the additive could reduce the particle size of Ca(OH)$_2$ in either or both ways: (1) by reducing the primary crystal size of the material as it is being formed in the hydration process; (2) by preventing agglomeration of the hydrate particles after they had formed. The agglomeration of hydrate can be caused by hydrogen bonding in the adsorbed water layers around the individual hydrate crystals. The lignosulfonate molecule can be incorporated into the adsorbed water layer thus preventing the bonds from forming particularly due to the presence of the organic, hydrophobic portion of the molecule. They also suggested that above the optimal level of 1.5%, the large lignosulfonate molecule or its residue may block access of the SO$_2$ molecule to reactive CaO sites.

Subsequently, Kirchgessner and Jozewicz (1989) and Jozewicz and Kirchgessner (1989) performed extensive studies of the changes in pore structure
during sintering of CaO produced from 1.5% lignohydrate. They observed that the lignohydrate calcined faster, and retained more of its original surface area and porosity than the unmodified hydrate. Moreover, with increasing time and temperature the difference between the ligno and pure hydrate became more pronounced. In order to explain the reduced sintering, they proposed that due to the large size of the lignosulfonate molecule, it locates at the grain boundaries rather than within the crystal structure. In this structure, it reduces grain mobility, thus reducing the sintering effects.

Lee et al. (1995) studied lignosulfonate modified hydrates for their crystal growth, surface area and reactivity using SEM and carbonation rate. They concluded that lignosulfonate modifies the crystallization process and growth habit of Ca(OH)$_2$. In order to explain the larger hexagonal crystals of modified hydrate compared with the ill-defined cubic crystal structure of pure hydrate, they proposed that the lignosulfonate molecules adsorb on the basal planes of the hydrate crystals and hinder growth in the c-axes directions. In addition, the lignosulfonate molecules retard the nucleation process, resulting in larger crystal size. They also observed that the BET surface area of Ca(OH)$_2$ increases with increasing wt% lignosulfonate up to 1.5 and then decreases. This, they proposed was due to the competing factors of dispersive action, interference with nucleation, and alteration of growth habit.

Calcium lignosulfonate is an anionic surfactant whose general formula can be written as RSO$_3$-Ca$^{++}$ with the SO$_3$- being the surface-active portion (hence anionic). Its molecular weight and exact chemical formula is unknown, it is soluble in water.
It belongs to the chemical family of lignin, it is considered a sulfonated polymer with molecular weight ranging from $10^3$ to $10^4$. It is a byproduct of the paper industry, it is fermented spent sulfite liquor (Kirk and Othmer, 1995). The lignosulfonate is obtained from Georgia-Pacific Corporation, Bellingham, WA which markets it under the trade name, lignosite 100. The lignosite decomposes above a temperature of 600°C.

4.1.3 High surface area carbonates

In recent years, findings by a number of researchers have confirmed that sulfur capture with known pure and modified sorbents falls short of the 90 to 95% sulfur removal goal. Promoting hydroxide or carbonate 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 (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) 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.
Table 4.1 shows the maximum utilization reported for calcium hydroxide and carbonate by various previous researchers and the conditions of their study. Ye (1994) investigated four Swedish limestones, Forsby, Ignaberga, Limhamn, and Malmo Chalk. Of these, the first three possessed high surface areas between 10 to 12 m²/g. Also, the first three were similar in their particle size distribution, with between 87 to 96 wt% being smaller than 3 μm in size. Forsby was about 95% carbonate while Ignaberga was only about 83% CaCO₃. In Ye’s work (1994), Forsby was found to exhibit the highest SO₂ capture at 1000°C and 1000 ppm SO₂ concentration for a residence time of 2 seconds. Moreover, the difference in capture increased with increasing Ca/S ratio from 0.4 to 1.4, and at a Ca/S = 1, Forsby showed nearly 30% conversion in 2 sec. Also, they observed a initial rapid period of sulfation in the first 100-200 milliseconds followed by considerable slowing of the reaction rate at higher residence times. In Ye’s (1994) comparative studies of pore size distribution changes on sulfation, he observed that Forsby upon calcination produces CaO with highest % of its total pore volume in pores larger than 100 Å. Malmo Chalk on the other hand, has negligible pore volume in pores > 100 Å. Limhamn lies in between Malmo Chalk and Forsby. Upon sulfation and sintering, the loss of smaller pores due to formation of CaSO₄ and the generation of larger pores due to sintering of smaller grains yields almost constant pore volume in the large pores for Forsby. Malmo Chalk on the other hand, just shows an increase in large pores due to sintering and therefore a very slow sulfation rate. However, the ultimate capacity of Malmo Chalk was observed to be nearly the same as Forsby. In
comparing the pore size distributions of Forsby and Ignaberga, Ye et al. (1995) revealed that while nearly 80% of the pore volume lies in $< 100 \text{Å}$ pores for Forsby, less than 45% of Ignaberga’s pore volume lies in the same size range. From their studies with the influence of grinding the powders, they concluded that in addition to particle size, the surface area and the pore volume located in the larger pores ($> 50 \text{Å}$ in radius) contribute to the overall SO$_2$ removal.

The reasons for such superior reactivity exhibited by this particular carbonate powder, Forsby, are still not completely understood. One property which distinguishes this sorbent from most other carbonate powders is its high initial surface area measuring to be around $12 \text{m}^2/\text{g}$, compared to only $1-3 \text{m}^2/\text{g}$ for most other calcium carbonates. However, a number of calcium hydroxide powders possess initial surface areas equal to 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 $1-3 \mu\text{m}$ particles, failed to produce high conversion for various hydroxide, carbonate, and dolomitic sorbents, suggesting that small particle size alone probably can not explain such high utilization of the carbonate powder.

In this work, short-time calcination and sulfation studies are carried out in a high-temperature, entrained-flow reactor for the high surface area limestone along with a commonly used low surface area carbonate powder and pure and modified calcium hydroxide powders. Modification of the calcium hydrate sample is achieved
by addition of pre-determined amount of calcium lignosulfonate additive in the water of hydration during its preparation. The hydroxides and low surface area carbonate are studied to perform a critical comparison between these sorbents and the high surface area limestone. 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 of the Forsby carbonate.

4.2 Experimental Section

4.2.1 Sorbents and preparation

The sorbent comparison studies are performed for two calcium hydroxide and two limestone samples. In order to prepare the modified hydroxide sorbent (MH), the as-received calcium hydroxide (LH) powder from Linwood Mining and Minerals Company is calcined at 600°C, and then rehydrated in excess water containing dissolved calcium lignosulfonate powder. The calcination is carried out with a batch of about 25 grams of Ca(OH)$_2$ powder in a horizontal furnace under dry nitrogen atmosphere. A schematic of the batch calcination set-up is shown in Figure 4.1. The calcined product is then quickly transferred to a large vessel placed in a water bath. The water of hydration with the dissolved lignosulfonate is added to the CaO. The volume of water used gives about 10 times the stoichiometric amount needed for complete hydration. This is comparable with that used by Lee et al. (1995). The modifier is added in such a quantity that the final hydroxide product has about 1.5%
mass concentration of the lignosulfonate, reported to be optimum by previous investigators (Kirchgessner and Lorrain, 1987). The slurry is manually stirred for a few minutes and the water bath is used to carry away the exothermic heat of the hydration reaction. After most of the excess water has evaporated, the sorbent slurry is dried in a vacuum oven at about 70-80°C overnight. Finally, the dried cake is crushed and ground in a ball mill facility (in the Materials Science and Engineering Department) to produce fine powders.

Forsby carbonate (FC), is a naturally occurring limestone in Sweden and is marketed there by Carbital Company. Dr. Bjerle’s research group at the Lund University in Sweden has provided the FC sample powder. Forsby is received as a thick slurry and is similarly dried and ground. Dr. Bjerle’s group used a surfactant in making the slurry in order to assist in their wet grinding process. The additive used is an anionic surfactant available in the market under the trade name, Dispex from Allied Colloids Inc. Suffolk, VA. The Dispex surfactant range consists of sodium or ammonium salt of a polycarboxylic acid. Dispex is a low molecular weight, water soluble surfactant that is principally used as non-foaming pigment dispersant for aqueous systems. Dispex produces the stabilizing and dispersing action by ionizing in water to produce either a sodium or ammonium cation together with a polyanion. This polyanion adsorbs irreversibly onto the particle surface causing the particle to become negatively charged. Adjacent particles then repel one another to maintain a state of dispersion. The dispex is obtained as a mobile liquid with 40% solids content.
Linwood calcium carbonate (LC) and Linwood calcium hydroxide (LH) are used in their as-received forms. From the manufacturer’s sieve analysis report, the LH has a size of 100% passing through 50 mesh and 85% passing through 200 mesh standard sieves. The LC powder is slightly finer with 100% passing through 50 mesh, 87% through 200 mesh and 75% through 325 mesh.

4.2.3 Sorbents chemical and structural properties

The chemical and physical properties of all the sorbents are shown in Table 4.2. The LC limestone has the lowest surface and pore volume, it can be considered nearly non-porous. Most limestones reported in the literature possess about 1-2 m$^2$/g surface area and negligible pore volume. However the Forsby powder exhibits exceptionally high surface area (12 m$^2$/g) and pore volume for a carbonate. The MH hydrate shows a tremendous improvement in surface area and porosity over the LH pure hydrate. Previous researchers who worked on the lignomodified hydrate have studied the surface area and porosity evolution of the CaO obtained from the pure and modified hydrate but haven’t reported on the surface area and other physical properties of the original modified hydrate (Kirchgessner and Jozewicz, 1989).

Figure 4.2 shows the primary particle size distribution of these sorbents as obtained by a Micromeritics Sedigraph 5100. It can be seen that the LC is the coarsest with the mass median (d$_{50}$) diameter of about 8 µm, however, the LH, MH and FC are similar in size with the d$_{50}$ between 1 to 2 µm.

Figure 4.3 shows the initial cumulative pore volume distribution of the sorbents
investigated. As discussed in detail in chapter III, the hydrate powders are analyzed using the parallel plate model (hence the Kelvin equation gives the plate width) while the carbonate powders are analyzed using cylindrical pore model (Kelvin equation gives the radius of pore). Further, the volumes shown in figure have been corrected for the volume taken up at a relative pressure $p/p^*$ of 0.35. This is because the uptake is considered to be in the form of a monolayer surface coverage up to a relative pressure of about 0.35 and hence doesn’t contribute to the volume of the pores. In order to include the largest intraparticle pores in the measurement of pore volume, it is necessary to achieve $N_2$ condensation at a relative pressure close to its saturation pressure. The pore volume measurement is therefore made at a relative pressure of 0.98, at which the Kelvin equation predicts that pores up to 500 Å will be filled. This ensures inclusion of most of the intraparticle pores while omitting the interparticle voids. As expected, the MH curve lies much above both the LH and the FC curve due to its high porosity.

4.2.2 Experimental conditions and analysis

Calcination and sulfation studies are performed at a fixed reaction temperature of 1080°C. Calcination is carried out under inert $N_2$ environment, whereas the bulk gas composition for the sulfation runs is maintained at 5.45% $O_2$, 3900 ppm $SO_2$ and balance $N_2$. Partially reacted sorbents are classified into various size fractions in the cascade cyclone sampler, and also for different reaction times, ranging from 20 ms to 550 ms. The sorbents of a particular size group, having mean aerodynamic
diameter of 3.9 μm, are analyzed for determining reaction conversion and performing structural development studies. Obtaining these information from particles of same size fraction eliminates particle size as a variable parameter between the sorbents and makes it possible to perform a comparative study based solely on the internal structural properties. For selected sulfation runs with the Forsby carbonate and modified hydroxide powder, reacted samples from all the stages of the cyclone assembly are collected and analyzed for conversion, which provides the information on size effect of the sorbent.

4.3 Results and Discussion

4.3.1 Kinetic studies

Figure 4.4 plots the extent of sorbent conversion with reaction time for sulfation of 3.9 μm sorbent particles at a temperature of 1080°C. As previously observed by Ye (1994) and Wang et al. (1995), the FC powder exhibits a remarkably high sorbent conversion, reaching 50% in 500 ms. Conversion data for MH also corroborate the findings by Kirchgessner and Jozewicz (1989) that addition of lignosulfonate additive results in about 20% improvement over pure hydroxide in terms of final sorbent utilization. The most significant difference between Forsby carbonate and the other powders is the former’s high initial reactivity, evident clearly from the data of first 50 ms. The higher reactivity of MH compared to LH is also observed only at very short contact times of under 50 ms. At higher residence times, except for the Linwood carbonate, conversion curves for all the sorbents lie almost
parallel to one another, indicating similar reaction rate. Linwood carbonate shows a much stronger attenuation in reaction rate beyond 100 ms. The long residence time conversion values for LH and LC match well with the results reported by previous researchers for comparable reaction temperature and SO$_2$ concentration (Milne et al., 1990; Gullett et al., 1988). An interesting point is that in the initial 50 ms, LC shows higher conversion than LH, even though it reaches a lower final utilization value than that for the hydrate powder. Due to the small particle size of sorbents, diffusional limitations are expected to be insignificant, as a result of which, the parameters influencing the sulfation rates 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 reaction rate is determined.

4.3.2 Investigation of calcine pore structure

The CaO pore structure resulting from calcination reaction alone is investigated by studying the cumulative pore volume distribution changes in the calcines with reaction time. Figure 4.5 corresponds to the sorbent structure after 20 ms of calcination, when all the sorbents exhibit between 80 to 85% decomposition. Bruce et al. (1989) have suggested that calcination of calcium hydroxide can be considered almost instantaneously complete after sorbent injection into the high temperature of the furnace, however, carbonates have much slower decomposition characteristics.
They cited two possible reasons: first, the hydroxides start calcining at much lower temperatures than the carbonates (550°C compared to 700°C), and second, the less porous carbonate structure offers significant diffusional resistance to the escaping CO₂, rendering the decomposition process diffusional rate-limited for the solid in the inner core. However, the calcination results of this study for 3.9 μm particles show that carbonate samples calcine equally fast as the hydroxide samples at a reaction temperature of 1080°C, suggesting that the particle size considered is small enough to eliminate diffusional limitations during decomposition.

The pore volume distributions of Figure 4.5 provide information about the structural differences between the calcines, which may be used to gain insights into their sulfur capture behaviors. CaO generated by FC powder shows the highest pore volume (0.19 cc/g) among all the sorbents. The respective porosity values for FC-CaO, LC-CaO, MH-CaO, and LH-CaO are calculated to be 37, 19, 25, and 17% at this stage of calcination. Further, LC shows a pore volume higher than the LH, but a large % of its volume lies in pores less than 50 Å. The MH does not compare well with the FC even though it is higher than the LH at this stage of calcination. Figure 4.6 shows the transformation in pore volume distribution after 40 ms of calcination. The trends are similar except the total or cumulative pore volumes are smaller due to additional sintering without significant further increase in calcination.

Since the total surface area of the calcine is more closely related to CaO sulfation rate, the contribution of each pore size range to the total surface area is calculated from pore size distribution for each of the sorbents (Innes, 1957; Gregg and
From the equations developed in chapter III for a parallel plate pore structure, when $V_p \to 0$, $A$ is equal to the total surface area, also at the highest $p/p^*$ all the pores are filled, so at $V_p = V_s$, the area $A$ should equal zero. The incremental change in area can be calculated from the incremental change in pore volume $V_p$ using equation (3.6). The total surface area of the calcine ($A_t$) in Figure 4.7 is calculated by summation over all size intervals as shown in equation (4.1). This total area at $V_p \to 0$ agrees within ±10% with that obtained from the BET method which is another independent test of the validity of the pore volume distribution analysis.

$$A_t = \sum_{V_p = 0}^{V_s} \frac{2 \Delta V_p}{d}$$  \hspace{1cm} (4.1)

This distribution of area is shown in Figure 4.7 after 20 milliseconds of calcination. The cumulative surface area of the FC-CaO powder is much greater than that of the other three sorbents. Interestingly, LC-CaO also possesses a higher surface area than the hydroxide-calcines. Moreover, both the carbonate derived CaO are able to retain a considerable fraction of pores of diameter less than 70 Å, for which the effect of sintering is expected to be most severe in nature leading to their disappearance into larger pores. The capability to retain higher surface area indicates that the sintering process proceeds at a slower rate for both the carbonate derived CaO samples. One possible explanation for the lower sintering rate as proposed by Borgwardt (1989), suggests that due to differences in molar volumes between CaCO$_3$
and Ca(OH)_2, packing of CaO grains produced from carbonates is relatively less dense, which offers fewer contact points between these grains. 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. Figure 4.8 shows the cumulative area distribution after 40 ms of calcination.

Figures 4.5 & 4.7 elucidate two contributing factors which lead to the higher reactivity of Forsby carbonate in the initial phase of the sulfation reaction. Firstly, its calcine provides a higher surface area and pore volume due to lower sintering rate. Secondly, FC-CaO also possesses a favorable pore size distribution, which distinguishes this sorbent from other carbonates. Most of the pore volume for less reactive LC-CaO originates from pores which are smaller than 50 Å in diameter. As pore surface area preferentially concentrates in the smaller pores, more than 90% of its surface area resides in these pores. In spite of the relatively high surface area to volume ratio this pore structure offers, pore-filling and more damagingly pore-mouth-plugging occur predominantly in these small pores due to the formation of higher-volume sulfation product. In the event of pore-mouth-plugging, further SO_2 access into the inner pore region is severely limited, and the sulfation rate rapidly dies off (Simons and Garman, 1986; Milne and Pershing, 1987). Another point to note is that the initial high surface area of LC-CaO leads to a steeper rise in the conversion curve in the first 50 ms reaction time, exceeding the sulfation rate of LH-CaO. However, a more favorable pore size distribution of the LH-calcine results in its higher final
utilization as seen in Figure 4.4, and also reported by previous researchers (Milne et al., 1990).

SEM analyses are conducted to complement the studies of structural changes accompanying the simultaneous calcination and sintering. Figure 4.9(a) shows the structure of 85% calcined 1.2 μm FC particles after 20 ms at 1080°C, which possess a BET surface area of about 60 m²/g. The small grain size and the granular nature of the surface are easily observable. Figure 4.9(b) shows the SEM photomicrograph of the 80% calcined LH powder of the same size after 20 ms at 1080°C, possessing a much lower surface area of 17 m²/g. From this picture, the surface appears much less granular with reduced apparent porosity. In addition, the grains are larger in size and appear more agglomerated in the case of LH-CaO, an effect of faster sintering.

4.3.3 Effect of sulfation on pore structure

Sorbent physical properties such as particle size and internal pore structure are closely linked with the rate controlling mechanism during CaO sulfation process. For small particles, chemical reaction is most likely the rate controlling step in the initial stages of sulfation (Simons et al., 1987). However, with CaSO₄ build-up, ionic diffusion through the product layer becomes the limiting step (Borgwardt et al., 1987; Hsia et al., 1993). As the FC-CaO offers a more open internal structure with higher surface area, the initial rate of sulfation is faster in its pores, considering sulfation rate being directly proportional to the available surface area, when reaction proceeds under chemical reaction control regime. Dependence on surface area is further enhanced in
the succeeding product-layer-diffusion control regime, under which the rate is proportional to the square of the CaO surface area (Bruce et al., 1989). Such rapid sulfation in FC-CaO, however, quickly fills up the pore volume, which is elucidated in Figure 4.10, where the resulting cumulative pore volume distributions are compared for 20 ms of calcination and sulfation reactions. The largest reduction in total porosity occurs for FC-CaO, which corresponds to its highest sulfur capture, while the MH-CaO shows an intermediate drop which accounts for about 19% conversion. Conversions of LC-CaO and LH-CaO in the same time are only 17 and 14% respectively. Almost complete loss of pores in the very small pore sizes (less than 50 Å radius or plate separation) for all the sorbents indicates rapid pore filling or pore-mouth plugging by higher molar-volume CaSO₄ product. Figure 4.11 plots pore volume distribution curves for sulfation reaction which allows expansion of the ordinate scale to perform a comparative analysis between different sorbents. Sulfation conversion curves in Figure 4.4 indicate that beyond initial 25 ms of reaction, while FC, MH, and LH samples show 16 to 18% of additional conversions in the maximum allowed reaction time of about 550 ms, only about 6 to 8% of further utilization is observed in case of Linwood carbonate (LC). This agrees quite well with Figure 4.10, which 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 100 Å pores. Figure 4.12 shows the pore volume distribution after 40 ms of sulfation. Figure 4.13 shows the cumulative surface area distribution after 20 and 40 ms of sulfation for FC, MH and LH. It shows that after even after 20 ms (that is 32% of sulfation), FC
4.3.4 Porosity reduction during simultaneous sulfation and sintering

In case of only calcination reaction, the nascent CaO looses its surface area and porosity due to rapid sintering which immediately follows its formation. However, when the reactant gas contains SO₂, the nascent surface area is consumed by an equally competitive sulfation reaction. The net effect of this phenomenon is an apparently reduced sintering process which is demonstrated by a comparison between residual pore volumes remaining after 20 ms of calcination and sulfation reactions. The theoretical pore volume after 20 ms of sulfation is calculated by assuming that the extent of CaO pore reduction due to sintering is identical for both sulfation (with SO₂) and calcination (without SO₂) reactions. Furthermore, it is assumed that the extent of hydroxide or carbonate decomposition to CaO is not affected by the presence of SO₂, i.e., for both the cases, calcination extent can be represented by Xᵣ. The fraction of CaO (w_{CaO}) in a unit weight of partially calcined product can be expressed as:

$$w_{CaO} = \frac{X_r}{M_{SO_2}} \frac{M_{CaO}}{M_{CaO} + X_r}$$  \hspace{1cm} (4.2)
where $M_s$ and $M_{CaO}$ are molecular weights of the unreacted sorbent (Ca(OH)$_2$ or CaCO$_3$) and CaO respectively. During sulfation reaction, a fraction of this $w_{CaO}$ converts to CaSO$_4$. If the overall sulfation conversion is expressed as $X_s$, the amount of CaSO$_4$ can be obtained as:

$$W_p = X_s \left( \frac{w_{CaO}}{M_{CaO}} + \frac{w_s}{M_s} \right) M_p \tag{4.3}$$

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

$$W_{CaO} = \left[ \frac{w_{CaO}}{M_{CaO}} - X_s \left( \frac{w_{CaO}}{M_{CaO}} + \frac{w_s}{M_s} \right) \right] M_{CaO} \tag{4.4}$$

So the theoretical reduction in pore volume can be obtained by calculating the additional volume occupied by the product CaSO$_4$ due to its higher molar volume ($v_p$) compared to that of CaO ($v_{CaO}$). If $V_c$ is the specific pore volume after 20 ms of calcination, then theoretical pore volume after equal duration of sulfation on a unit weight of sulfated sample can be expressed as:

$$V_{theo} = \frac{[V_c - X_s (v_p-v_{CaO}) \left( \frac{w_{CaO}}{M_{CaO}} + \frac{w_s}{M_s} \right)]}{(w_s+W_{CaO}+W_p)} \tag{4.5}$$

These theoretical pore volume values for each sorbent are calculated and plotted in
Figure 4.14 with the experimentally obtained values. The theoretically calculated data lie much below the experimentally obtained values for all the sorbents, suggesting that the effect of sintering on pore volume loss is diminished in presence of SO$_2$.

Newton et al. (1989) performed calcination and sulfation experiments in presence of CO$_2$ and observed a similar reduction in sintering effect during sulfation. They concluded that during sulfation, the influence of CO$_2$ in accelerating the rate of sintering is inhibited due to the product layer surrounding the CaO grains. Figure 4.15 shows the comparison of experimental pore volumes after 20 ms of calcination with that predicted from sulfation results.

4.3.5 Influence of particle size

In order to assess the validity of the earlier assumption that particle size used in this study is small enough not to pose any significant intraparticle diffusional limitations, sulfation conversions of various particle sizes were studied. These are plotted for the Forsby and the modified hydrate powder in Figure 4.16. No appreciable difference in the extent of sulfation is noticed when particle size ranges from 0.7 $\mu$m to 3.9 $\mu$m. This suggests that the advantage of using smaller particle size vanishes below a minimum value. However, the particles larger than 20 $\mu$m show appreciably lower conversions at 40 ms as well as at longer exposure time of 235 ms. Similar observation was made by prior investigators (Milne and Pershing, 1987; Cole et al., 1986) studying particle size effect on sulfation.
4.3.6 Comparison of LH and MH

The MH modified hydrate has much higher surface area and pore volume than the LH pure hydroxide. Also, the modified hydrate possesses a overall porosity of 32% as compared to the 14% porosity for parent hydrate. In addition to internal structural characteristics, the median primary particle size (at 50% mass finer) of the modified hydrate is about 1.2 μm as compared to almost 2 μm for the parent hydrate from the Sedigraph analysis.

However, from the kinetic results shown in Figure 4.4 with lignohydrate and pure hydrate, the LH shows superior performance only in the initial 50 milliseconds, at higher residence times however, the rate of sulfur capture attenuates considerably. The conversion profiles of both the hydrates become parallel to each other at higher times, with the lignohydrate maintaining the initial edge achieved in the first 30 milliseconds. In order to understand and explain this characteristic behavior, the internal structure evolution of the partially sulfated lignohydrate was also conducted. Figure 4.17 shows the comparison of porosity development and extent of sulfation between the two hydrates. The lignohydrate initially possesses about 32% porosity which is rapidly lost within the first 50 milliseconds to approach very close to that of the unmodified hydrate. Thus, the lignohydrate does not seem to hold any advantage over the unmodified hydrate (with respect to internal porosity) beyond about 50 ms. The pore size distribution behavior with sulfation is shown in Figure 4.18. As seen, the p.s.d. curves of the partially sulfated samples lie much below the initial lignohydrate and moreover, the closure of smaller pores below 100 Å is also obvious.
4.4 Conclusions

The extraordinary sulfur capture ability shown by Forsby carbonate makes it a viable sorbent for Furnace Sorbent Injection (FSI) process. The entrained-flow reactor results suggest that its use can reduce sulfur dioxide emissions from utility plants by as much as 95%. It is evident that Forsby carbonate's initial high surface area and associated pore structure translate into optimum pore size distribution in its calcine, which combined with the effect of slower sintering contribute to its remarkable sulfation capacity. It has been observed in prior studies that not all the limestone samples with initial high surface area exhibit very high sulfation conversion. The pore size distribution of their calcines show a preferential dominance of very small pores, and much like Linwood carbonate sample, such high concentration of small pores leads to premature pore plugging. Therefore, there must exist an optimum pore structure affiliated with the uncalcined carbonate, which on calcination, makes the nascent pore size distribution of CaO favorable for the sulfation reaction. Identifying the optimum pore distribution of original carbonate powder has not been attempted in this study and presents an area for future work.

The results of this investigation bring up an interesting comparison between limestone and hydrated lime sorbents. Some of the earlier studies employed very low surface area (non-porous) carbonates and also of average size larger than the hydrates. So, the higher conversion shown by the hydrate sorbents most probably has been a result of smaller particle size. When particle size is equally small for both these powders, the advantage of hydroxides may have resulted from a more favorable pore
size distribution of its calcine. This can be explained if we consider the initial structure of the hydroxide sorbents, which is more porous with an inherent distribution of pore sizes. As a result, the size distribution of its nascent calcine is shifted to the larger sizes, preventing rapid reaction termination caused by pore-mouth-plugging. In case of carbonates, the small CaO pores experience severe pore-mouth-plugging which restricts its final utilization. However, when the parent carbonate powder is porous and possesses a favorable pore size distribution, the calcine pore structure can make the carbonate powder a more attractive furnace-injection sorbent than typical Ca(OH)$_2$ powders.
Table 4.1: Maximum utilization reported for calcium hydrate and carbonate by various previous researchers and the conditions of their studies.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>T (°C) &amp; SO₂ Conc. (ppm)</th>
<th>Sorbent type</th>
<th>Ca/S</th>
<th>Rxn. time (ms)</th>
<th>Conv. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milne et al. (1990)</td>
<td>1094, 1460</td>
<td>Linwood hydrate, 2.4 μm</td>
<td>2</td>
<td>500</td>
<td>27</td>
</tr>
<tr>
<td>Milne et al. (1990)</td>
<td>1094, 1460</td>
<td>Linwood carbonate 4.4 μm</td>
<td>2</td>
<td>500</td>
<td>18</td>
</tr>
<tr>
<td>Bortz &amp; Flament (1985)</td>
<td>1000-1100, 2000</td>
<td>Hydrate carbonate</td>
<td>2</td>
<td>500-600</td>
<td>30-35 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;0. 1</td>
<td>250</td>
<td>25</td>
</tr>
<tr>
<td>Gullett et al. (1988)</td>
<td>1000, 3000</td>
<td>Linwood hydrate</td>
<td>&lt;0. 1</td>
<td>1250</td>
<td>35-38</td>
</tr>
<tr>
<td>Kirchgessner &amp; Jozewicz (1989)</td>
<td>1000, 3000</td>
<td>1% ligno-hydroxide, 3 μm</td>
<td>&lt;0. 1</td>
<td>1250</td>
<td>35-38</td>
</tr>
<tr>
<td>Bjerle et al. (1993)</td>
<td>1000, 1000</td>
<td>Forsby CaCO₃, 3-4 μm</td>
<td>2</td>
<td>2000</td>
<td>49-50</td>
</tr>
</tbody>
</table>
Table 4.2. Composition and initial structural properties of sorbents investigated.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>LH*</th>
<th>LC</th>
<th>FC*</th>
<th>1.5%-ligno hydrate (MH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>94.0</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>1.0</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>
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<td>0.5</td>
<td>0.30</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
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<td></td>
<td>0.88</td>
<td>1.0</td>
</tr>
<tr>
<td>CaO</td>
<td>1.0</td>
<td></td>
<td></td>
<td>1.0</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>Calcium lignosulfonate*</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Composition (wt%)

<table>
<thead>
<tr>
<th></th>
<th>LH*</th>
<th>LC</th>
<th>FC*</th>
<th>1.5%-ligno hydrate (MH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>94.0</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>1.0</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>1.0</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>Calcium lignosulfonate*</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BET surface area (m$^2$/g)

<table>
<thead>
<tr>
<th></th>
<th>LH*</th>
<th>LC</th>
<th>FC*</th>
<th>1.5%-ligno hydrate (MH)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16.9</td>
<td>1.9</td>
<td>12.0</td>
<td>62.0</td>
</tr>
</tbody>
</table>

Pore Volume (cc/g)

<table>
<thead>
<tr>
<th></th>
<th>LH*</th>
<th>LC</th>
<th>FC*</th>
<th>1.5%-ligno hydrate (MH)</th>
</tr>
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<tr>
<td></td>
<td>0.06</td>
<td>0.02</td>
<td>0.044</td>
<td>0.13</td>
</tr>
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</table>

* Linwood Mining & Minerals Co.
* Carbital Company, Sweden
* Georgia-Pacific Corp.
Figure 4.1: Schematic of the tubular batch reactor used for calcination.
Figure 4.2: Primary particle size distribution from Sedigraph analysis.
Figure 4.3: Initial pore size distribution plots for Linwood hydrate (LH), 1.5% lignohydrate (MH), and Forsby carbonate (FC).
Figure 4.4: Sulfation of 3.9 μm Linwood hydrate (LH), 1.5% lignohydrate (MH), Forsby carbonate (FC) and Linwood carbonate (LC) at 1080°C.
Calcination, 20 ms
- LH, 80%
- MH, 82%
- FC, 85%
- LC, 80%

Figure 4.5: Pore volume distribution after 20 ms of calcination at 1080°C; particle size: 3.9 μm.
Fig. 4.6: Pore volume distribution after 40 ms of calcination at 1080°C; particle size: 3.9 μm.
Calcination, 20 ms
- LH, 80%
- MH, 82%
- FC, 85%
- LC, 80%

Figure 4.7: Surface area distribution after 20 ms of calcination at 1080°C; particle size: 3.9 μm.
Figure 4.8: Surface area distribution after 40 ms of calcination at 1080°C; particle size: 3.9 μm.
Figure 4.9: SEM photomicrographs after 20 ms of calcination at 1080°C; mean particle size: 1.2 μm.

(a) FC, 85% calcined, BET surface area of 60 m²/g.
(b) LH, 80% calcined, BET surface area of 17 m²/g.
Figure 4.10: Comparison of cumulative pore volume distribution after 20 ms of calcination and sulfation at 1080°C.
Figure 4.11: Pore volume distribution after 20 ms of sulfation at 1080°C; particle size: 3.9 μm
Figure 4.12: Pore volume distribution after 40 ms of sulfation at 1080°C; particle size: 3.9 μm
Figure 4.13: Comparison of cumulative surface area distribution after 20 ms and 40 ms of sulfation for FC, MH and LH.
Figure 4.14: Comparison of experimental pore volumes after 20 ms of sulfation at $1080^\circ$C with that predicted from calcination results.
Figure 4.15: Comparison of experimental and predicted pore volumes after 20 ms of sulfation at 1080°C.
Figure 4.16: Effect of particle size on sulfation of FC and MH at 1080°C.
Figure 4.17: Comparison of porosity development during sulfation of Ca(OH)$_2$ and 1.5\% ligno-Ca(OH)$_2$ at 1080$^\circ$C.
Figure 4.18: Cumulative pore volume distribution changes with sulfation for 1.5% lignohydrate at 1080°C; particle size: 3.9 μm.
5.1 Grain versus Pore Models

Sharp interface models and volume reaction models represent two of the earliest classes of non-catalytic gas-solid reaction models. The various later models can be classified into two broad categories: models based on representation of the solid phase as an assemblage of dense objects (grain models), and models based on the representation of the porous media by a collection of hollow objects (pore models) (Ramachandran and Doraiswamy, 1982). The grain model, proposed by Szekely and Evans (1971) represents the solid particle as an assemblage of small grains, each of which react according to the sharp interface model and the gas has to diffuse through the pores surrounding the grains in order to react with the solid. The product layer also offers additional resistance to diffusion. The grain shape itself could be assumed to be spherical, slab, or long cylindrical, and the detailed formulation and solution procedure are detailed by Sohn and Szekely (1974) and Szekely et al. (1976). However, gas-solid reactions are accompanied by complex structural and other changes which need to be incorporated for the model to be realistic. The earlier models (the sharp interface, volume reaction models as well as the original grain
model) cannot predict certain special patterns that are observed experimentally, such as (a) levelling-off of the conversion-time data far below complete conversion, (b) existence of maxima in the rate-time data, and (c) strong dependence of rate on the pore size distribution. The calcination and sulfation reactions exhibit characteristics (a) and (c) very strongly. Chemical reaction and sintering are the two main influencing factors for these structural changes. The original grain model assumed the structural properties such as porosity and surface area to be invariant. It has been modified by a number of researchers in order to account for one or more of the above patterns, either empirically or through theoretical considerations. Hartman and Coughlin (1976) proposed a empirical relationship between particle porosity and conversion. Georgakis et al. (1979) proposed a changing grain size model to account for density changes during reaction. Ramachandran and Smith’s work (1977a) represents the first attempt to incorporate sintering as well as density changes into the grain model. Ranade and Harrison (1979; 1981) also modified the constant property grain model to take into account both the sintering and reaction. The calcination and sintering model described in chapter III was inspired by Ranade and Harrison’s (1981) work. All the above models assumed that there is no overlapping of the grains which leads to monotonically decreasing reaction surface area with progress of reaction. Lindner and Simonsson (1981) and Alvfors and Svedberg (1988) developed what they called the partially sintered spheres model (PSSM) which represented the solid phase as an aggregate of spherical grains in an initial state of sintering. Their work was the first attempt at developing the partially overlapping class of grain models. Sotirchos
(1987) and Sotirchos and Yu (1988) also developed the overlapping grain model. Milne et al. (1990a) further extended the overlapping grain model to calcination and sintering of CaCO$_3$ particles.

The single-pore model proposed by Ramachandran and Smith (1977b) represents the earliest pore model for reactions with solid product and sintering effects. The model represents the entire pore structure of the solid as a single equivalent pore of the same volume and models the reaction occurring at the internal surface. The changes due to reaction are manifested in the form of changes in the radius and/or length of the single pore. Since a real solid consists of a network of pores of various sizes and lengths, a logical extension of the single pore model to the actual solids should account for the pore network. Peterson (1957), Hashimoto and Silveston (1973), and Simons and Finson (1979) developed reaction models which take the entire solid pore network into account with conversion. However, these models were either developed for reactions with no solid product (such as coal gasification) or did not consider the effect of solid product. Bhatia and Perlmutter (1980; 1981a) extended the pore models to include the effects of solid product and also considered the random overlapping of the reaction surfaces. They called their model as the random pore model. Their model could predict the reaction surface area at any given conversion as a function of the initial pore structure parameter. This made possible explanation of the strong influence of pore structure on reaction rate. Bhatia and Perlmutter (1981b, 1983a) also applied their model to SO$_2$-lime and CO$_2$-lime reactions. They compared their predictions with those of the grain model and showed
that their model performed better for both the above case studies. Bhatia and Perlmutter (1980) did not consider the distribution of size in their pore network structure. The evolution of a network with same sized pores is not perfectly representative of the actual case which is the evolution of a distribution of pores. Christman and Edgar (1983) proposed a distributed pore-size model which represented a refinement over the previous pore models. Their model followed the reaction and changes inside the pores of all sizes in predicting the overall conversion, global rate and other transformations. They illustrated the significance of pore size distribution by a comparison of three experiments conducted on CaO with different pore size distributions. Their model showed that the differences in the kinetic behavior can be attributed to the different pore structures. However, their model neglected the intersection of the pores as reaction proceeds, which is taken into consideration by Bhatia and Perlmutter (1980). Bhatia and Perlmutter (1983b) and Bhatia (1985) later extended and improved upon their earlier work by incorporating the distributed pore reaction and pore closure. A number of other variations of the pore network model have been proposed in the literature (Simons and Garman, 1986; Simons et al., 1987).

5.2 Sulfation and Comprehensive Modeling: Previous work

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

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

Most of the early efforts to model Ca(OH)$_2$ sulfation assumed the calcination reaction to be instantaneous and neglected the effect of sintering altogether. Most modeled the experimental data of independent CaO-SO$_2$ reaction. Borgwardt and Bruce (1986), as well as Bruce et al. (1989) applied the limiting case of product layer control with the grain model to fit their CaO-SO$_2$ reaction data. They derived the specific rate constants for product layer control from their best fit of the data. Ramachandran and Smith (1977b) applied the single-pore model to the sulfation reaction data of Hartman and Coughlin (1976). Bhatia and Perlmutter (1981b) tested their model predictions with experimental CaO-SO$_2$ data from Borgwardt (1970). They found that a combination of kinetic and diffusional resistances is needed to explain the experimental data. The specific reaction rate constant and the product layer diffusivity were the two model parameters varied to fit the model. Their values of the rate constants compared with those of previous researchers (Ramachandran and Smith, 1977b). Christman and Edgar (1983) also used the surface reaction rate constant and the product layer diffusivity as the two variable model parameters which they estimated from the kinetic data. They estimated the reaction rate constant from the initial rate data and found their value to be in reasonable agreement with Bhatia and Perlmutter (1981b). However, they noted that the values of both the parameters
varied over a large range in the literature. Simons and Garman (1986) modeled the plugging of the smallest pores as the rate-controlling step in levelling-off of the conversion-time data. Milne et al. (1990b; 1990c), and Alvfors and Svedberg (1988) modeled the sulfation of CaO using the overlapping grain concept.

Comprehensive Ca(OH)$_2$ sulfation modeling has been attempted by very few researchers due to the complex nature of the various phenomena and the lack of a thorough understanding of their interaction. In Ca(OH)$_2$ sulfation, there exist consecutive reactions where in the product of the first reaction (CaO) becomes the reactant for the second, as well as concomitantly undergoes structural changes due to sintering. Mai’s (1987) work used a pore model for the sulfation and second-order kinetics for sintering. Milne and Pershing (1987) presented a combined model using the grain model for sulfation, second-order kinetics for sintering and an empirically modified shrinking-core model for the calcination. Alvfors and Svedberg (1992) attempted to model the total process occurring when a sorbent particle is injected into the flue gas atmosphere. The calcination is described by first-order kinetics at the reaction surface, similar to the empirically verified model of Borgwardt (1985). The sintering is based on the German and Munir’s (1976) formula. The calcination and sintering models together are used to predict the available surface area as a function of time. The predicted area is then used to calculate calcium sulfation. The sulfation itself considers pore diffusion, product layer diffusion and chemical reaction. Alvfors and Svedberg (1992) used their PSSM model for predicting the sulfation behavior by adjusting the model parameters. They concluded that qualitative predictions of
conversion of limestone to calcium sulfate were possible but quantitative predictions proved to be difficult.

5.3 Comprehensive Model Development

The calcination and sintering model described in chapter II used the grain model as the basis but was largely modified to take into account the sintering of the product CaO layer and the diffusion resistance the porous sintering CaO layer offers to the outward diffusion of H$_2$O (in case of Ca(OH)$_2$ calcination). The model thus incorporated a number of unique features and was able to fit both the experimental kinetics and the surface area evolution data extremely well. Hence, it was decided to take advantage of the already existing work in order to develop the comprehensive sulfation model. This also meant taking into consideration some of the already existing features of the calcination model, namely, the conceptualization of the CaO formed as a multilayered sintering porous product shell on each grain. In order to the develop the sulfation model, both the grain model formulation as well as the pore model formulation were studied for a number of factors such as ease of adaptability with the existing work, the solution scheme, and the reliability, robustness etc. The random pore model (Bhatia and Perlmutter, 1980) and the distributed pore model (Christman and Edgar, 1983) have well-refined formulation and a number of capabilities. Further more, the random pore model has been applied to the sulfation reaction and has been shown to model the experimental data well. After careful consideration of the various existing models, it was decided to use the random pore
model formulation for developing the comprehensive model.

Since the sulfation is restricted to the sintering CaO only, the region of interest is the product CaO shell with its micrograins and associated porosity and surface area. In order to develop the pore model formulation, the reacting solid CaO is now visualized not as grains but rather it is represented as a network of random pores. For the random pore model formulation, the pores are considered to be of the same size and their intersections are taken into account. A schematic illustration of the product CaO layer building during calcination of a Ca(OH)$_2$ grain is shown in Figure 5.1. The various diffusion and reaction steps are:

(a) SO$_2$ diffusion through the intergrain voids,
(b) diffusion through the intragrain voids of the sintering and sulfating CaO,
(c) diffusion through the product layer (after its formation), and finally,
(d) reaction with CaO.

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

A differential mass balance for diffusion and reaction of SO$_2$ through the porous CaO product shell of the grain can be written as:
Here, $r$ is the radial distance along the grain and $D_{\text{eff}}$ represents the effective diffusivity of $SO_2$ through the pores of CaO product. $C$ is the concentration of $SO_2$ inside the porous structure of CaO. $dx/dt$ is the local rate of conversion of CaO to CaSO$_4$. The boundary conditions are based on radial symmetry and on no mass transfer resistance at the grain boundary.

$$\frac{\partial C}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad (5.2)$$

$$C = C_{\text{bulk}} \quad \text{at} \quad r = r_g \quad (5.3)$$

The local reaction rate, $dx/dt$ at the internal surface of the pores (actually the interface of the CaO and CaSO$_4$), is obtained from the random pore model which takes into account the growing product layer and the diffusion of the reactant gas through the layer. The pores are considered to be cylindrical in shape and their random overlapping nature is taken into consideration. For the detailed equation development, the reader is referred to Bhatia and Perlmutter (1980; 1981a).

$$\frac{dx_s}{dt} = \frac{k_r S_o C (1-x_s) \sqrt{1-V} \ln(1-x_s)}{(1-\epsilon_o) [1 + \frac{V}{W} (\sqrt{1-V} \ln(1-x_s)-1)]} \quad (5.4)$$
Ψ is a structural parameter defined as

$$\psi = \frac{4 \pi L_0 (1 - \epsilon_o)}{S_o^2} \quad (5.5)$$

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

$$\beta = \frac{2 k_r \rho_{CaO} (1 - \epsilon_o)}{M_{CaO} D_p S_o} \quad (5.6)$$

Z is the molar volume ratio of the product CaSO₄ to reactant CaO. \( k_r \) is the specific reaction rate constant and \( D_p \) is the diffusivity through the product layer.

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

$$\epsilon_o = \int_0^r v_o (r) \, dr \quad (5.7)$$

$$S_o = 2 \int_0^r \frac{v_o (r)}{r} \, dr \quad (5.8)$$
\[ L_0 = \frac{1}{\pi} \int_0^\infty \frac{v_r}{r^2} \, dr \quad (5.9) \]

The conversion-time behavior can be obtained by the simultaneous solution of equations (5.1) and (5.4) with boundary conditions (5.2) and (5.3). The solution scheme requires the simultaneous solution of two highly non-linear ordinary differential equations. Further, some of the existing models (Bhatia and Perlmutter, 1981b) have made a number of simplifying assumptions and have shown reasonable agreement with the experimental data. In this work, the intragrain mass transfer resistance is neglected, then chemical kinetics and product layer diffusion control the overall reaction rate. Equation (5.4) can be integrated to give the local reaction rate which is also representative of the global reaction rate for the particle due to insignificant intragrain transport resistances. The solution procedure requires the predictions of \( \varepsilon_o, S_o \) and \( L_o \), which are the structural properties of the porous CaO reactant. The calcination and sintering model calculates the porosity and surface area of the individual layers of the CaO and also the average values of the above by integration over the entire layer structure. In the original random pore model formulation, the properties \( \varepsilon_o, S_o \) and \( L_o \) are calculated from experimental data and are invariant since the reactant is not undergoing any sintering induced structural changes. However, in this case, sintering largely affects the values of the above three parameters and their variation cannot be neglected. \( \varepsilon_o \) and \( S_o \) are calculated from the calcination and sintering model. \( L_o \) itself is not available from the model or any
experimental data, an average representative non-variant value is assumed for this parameter. $k_c$ and $D_p$ are the two variable model parameters. The FORTRAN program for the integrated calcination, sintering and sulfation model is shown in Appendix D.

5.4 Results and Discussion

In order to test the model, the entrained flow reactor kinetic data for Ca(OH)$_2$ sulfation at 1080°C (discussed in chapter IV) and at other temperatures obtained by Ghosh-Dastidar (1993) is utilized. The predictions of the model for three temperatures of 950, 1035 and 1080°C are shown in Figure 5.2. For comparison, experimental data at 1035 and 1080°C is also shown in the figure. The model predictions agree qualitatively with the data, however, the initial high reaction rate is not predicted well by the model. Moreover, the experimental conversion can be seen to be leveling-off even as early as 200 ms, which is not represented well by the model. The variation of the reactant CaO surface area and porosity are shown in Figures 5.3 and 5.4 respectively. As can be seen, the steep changes in both these structural characteristics lead to very drastic changes in the non-dimensional parameters, $\Psi$ and $\beta$ which influence the sulfation rate. The changes in $\Psi$ and $\beta$ are shown in Figure 5.5 and Figure 5.7 respectively. As can be seen, both $\Psi$ and $\beta$ level-off asymptotically after the first 50 ms of reaction and sintering. The value of $k_c$ can be computed from the initial rate data (Bhatia and Perlmutter, 1981b) or can be obtained together with $D_p$ by fitting the experimental data at specific temperatures.
The values of $k$, obtained in this work varied from $1.0 \times 10^6$ at 950°C to $2.6 \times 10^6$ (in m$^2$/kmol s) at 1080°C. These values compare with those reported in the literature. Bhatia and Perlmutter (1981b) obtained $k_r$ to be $0.834 \times 10^6$ at 980°C in fitting Borgwardt’s (1970) limestone data. Ramachandran and Smith (1977b) calculated $k_r$ to be $1.72 \times 10^6$ at 850°C. The variation in these values can also be partly attributed to the different reactivities of CaCO$_3$ and Ca(OH)$_2$ as well as compositional variations.

The values of $D_p$ were $0.06 \times 10^{-12}$ at 950°C and $0.22 \times 10^{-12}$ at 1080°C. Bhatia and Perlmutter (1981b) calculated $D_p$ as $0.86 \times 10^{-12}$ at 980°C, while Hartman and Coughlin (1976) obtained $0.6 \times 10^{-12}$, both of which were for limestone derived CaO. Figure 5.7 shows the Arrhenius type plots for $k_r$ and $D_p$ used to obtain the activation energies for reaction and product layer diffusion. The activation energy for reaction is obtained as 24 Kcal/gmol and for product layer diffusion as 38 Kcal/gmol. Borgwardt and Bruce (1986) obtained 36.6 Kcal/gmol, Bruce et al. (1989) obtained 39 Kcal/gmol by using the product layer controlled expression of the grain model to fit their CaO sulfation data. Bhatia and Perlmutter (1981b) obtained 29 Kcal/gmol and proposed the highly activated solid-state diffusion as the mechanism for product layer diffusion. In fitting the model to the experimental data, it was observed that the $\beta$ has a strong influence on the predictions as well as the stability of the solution scheme. The value of $\beta$ is seen to level off to about 40 for all the three temperatures studied. The asymptotic value of $\beta$ was observed to give a better and more robust performance, and the model predictions shown in Figure 5.2 are using the asymptotic $\beta$ values. Bhatia and Perlmutter (1981b) found the best fit value of $\beta$ to be 200 in
order to model Hartman and Coughlin's (1976) data. Their fitted their model such that the reaction ceased beyond a specific time due to surface pore closure. Moreover, the conversion-time curves were found to be not as sensitive to value of $k_r$. Considering the large value of $\beta$, it can be said that this model represents the entire sulfation data using the limiting case of product layer diffusion control. The initial rapid reaction rate occurs during the period in which the extent of sulfation is quite small (less than 5%) and so is the product layer build-up. During this period, both kinetic and diffusion limitations will need to be considered. However, this period lasts for a very short time (less than 25 ms) and therefore, the overall behavior is better explained by the diffusion-control mechanism. The main drawback of this scheme is the inability to predict the initial prompt capture.

5.4 Conclusions

This modeling work represents an initial effort to develop a comprehensive framework for predicting the total process. The model incorporates the pore model (for sulfation) into the framework of the grain model (used for calcination and sintering) and therefore represents a unique approach. However, it involves some simplifying assumptions and some inherent limitations. Neglect of intraparticle diffusion resistance and consideration of $SO_2$ and $H_2O$ (from calcination) diffusivities, use of the limiting product layer control to model the initial rate data could be the two important drawbacks. The model parameter values as well as the activation energies for reaction and product layer diffusion match very well with the literature. The high
activation energy obtained for product layer diffusion serves to corroborate the solid-state diffusion mechanism proposed earlier.
Figure 5.1: Schematic of the overlapping pore structure of the random pore model. The blackened area represents the unreacted solid, the dotted area the product layer. (a) early stage, showing product layer around each pore, and (b) intermediate stage, showing some overlapping reaction surfaces (from Bhatia and Perlmutter, 1981a).
Figure 5.2: Comparison of comprehensive model predictions with experimental sulfation data for 3.9 μm Linwood Ca(OH)$_2$. 
Figure 5.3: Variation of CaO porosity as predicted by the calcination and sintering model and used in the sulfation modeling.
Figure 5.4: Variation of CaO surface area as predicted by the calcination and sintering model and used in the sulfation modeling.
Figure 5.5: Variation of the structural parameter $\Psi$ with time; model simulation.
Figure 5.6: Variation of the parameter $\beta$ with time; model simulation.
Figure 5.7: Arrhenius plot to estimate activation energies of surface reaction and product layer diffusion.
6.1 Introduction

Coal contains a large number of trace elements in wide concentration ranges. During the process of coal burning, vaporization of these elements take place. The vaporization temperatures of the volatile elements vary according to whether the element is in elemental or oxidized state. Consequently, the temperature and oxidation potential of the furnace become important factors in determining trace element concentration in the various types of residues produced during coal combustion. The relative order of volatility for the elements in the elemental state is:

$$Hg > Se > As > Cd > Zn > Sb > Bi > Tl > Mn > Ag = Sn = Cu > Ga = Ge$$

The list of species boiling or subliming below or at $1550^\circ C$ during coal combustion include $As, As_2O_3, As_2S_3; Ba; Bi; Ca; Cd, CdO, CdS; Cr(CO)_6, CrCl_3, CrO; Hg, HgS; K; Mg; Ni(CO)_4; PbCl_2, PbO; Rb; Se, SeO_2, SeO_3; Sb, Sb_2S_3, Sb_2O_3; SnS; Sr; Tl, Tl_2O, Tl_2O_3; Zn, ZnS$ (Valkovic, 1983b).

Depending on the volatility, the trace elements are distributed or partitioned unevenly between three major coal residues, i.e., bottom ash, fly ash, and flue gas.
Table 6.1 shows the distribution of elements between the residues when bottom ash is 22.2% of total, fly ash 77.1% of total, and flue gas contains 0.7% fly ash of total ash (Valkovic, 1983b). Klien et al. (1975) studied the concentrations of trace elements at the T. A. Allen Steam Plant in Tennessee to determine emission characteristics of 37 elements. They analyzed only in-plant samples for these elements and applied mass balance closure conditions (weight of element entering with the coal should equal the total weight leaving with slag, ash and flue gas). Elements which did not show acceptable mass balance closure, they concluded, were being discharged with the flue gases. Table 6.2 summarizes the distribution of trace elements and their concentration ratios which is a measure of their partitioning. Klien et al. (1975) divided the elements into three classes based on their concentration ratios:

Class I: 25 elements - Al, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Mg, Mn, Na, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti, U, and V - are readily incorporated in the bottom ash or slag. These elements are partitioned about equally between the inlet fly ash and slag. There is no apparent tendency to concentrate in the outlet fly ash.

Class II: 8 elements - As, Cd, Cu, Ga, Pb, Sb, Se, and Zn - are poorly incorporated into slag. These elements concentrate preferentially in the inlet fly ash compared to the slag and in the outlet fly ash compared to the inlet fly ash.
Class III: Hg, Cl, and Br essentially remain completely in the gas phase. Two elements are unclassified: Mo should probably be included in Class II, and Ni probably in Class I. Class I elements are not volatilized in the combustion zone, instead they form a melt of somewhat uniform composition which generates both slag and fly ash. Since these elements essentially remain in the condensed state, they show minimal partitioning between slag, inlet fly ash, and outlet fly ash.

Class II elements are volatilized on combustion. Since the slag is removed from the combustion zone, they have very little opportunity to condense on the slag. These elements are thus preferentially depleted from the slag and concentrate more on fly ash as the flue gas cools downstream.

6.2 Concentration-Size Effects

A relationship between particle size and chemical composition of the fly ash has been confirmed by a number of researchers (Davison et al., 1974; Kaakinen and Jorden, 1974). Their investigations show an increase in trace element concentration with decreasing ash particle size. Davison et al. (1974) reported that the concentration of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr, and S were found to increase markedly with smaller particle size. However, nickel and chromium belong to Class I elements, and a major portion of these elements is already retained in the slag. Natusch et al. (1974) and Lee and von Lehmden (1973) also reported the inverse relationship between concentrations of some elements and the fly ash particle size. 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-stack. Table 6.3 shows the concentration of a number of Class II elements on fly ash as reported in Valkovic (1983b). The range of concentration increase in the $<$ 3 $\mu$m fraction compared to the $>$ 15 $\mu$m is 10-fold for Se and As and 4-fold for Pb. Markowski and Filby (1985) have reported that the sub-micrometer fly ash (0.04 - 0.15 $\mu$m) is highly enriched in As, Se, Sb and Ga. Kaakiken and Jorden (1974) observed that the concentrations of Zn, As, Mo, Sb, Pb, Cd, and Se were lowest in the bottom ash and increased progressively in fly ashes collected downstream toward the stack.

Linton et al. (1976) have showed that Pb, Zn and Cr were some of the elements particularly concentrated on particle surface as compared to their concentration at the distance 50 nm from the surface. Based on the above two phenomena, Natusch et al. (1974) developed a volatilization adsorption-condensation mechanism to explain the observed size-concentration and surface predominance phenomena. Those elements (and their compounds) which have their boiling points comparable or less than the temperature of combustion zone (1300-1600°C) will volatilize and enter the gas phase. When the flue gas cools down, these species condense and adsorb onto the surface fly ash particles. Adsorption and condensation are surface phenomena and surface area increases with decreasing particle size (in the case of highly nonporous particles), hence the smallest fly ash particles will have the highest concentration of the volatile species. Davison et al. (1974) list how nearly all the chalcophilic elements, irrespective of their chemical state (elemental, oxides or
sulfides) have their boiling points below 1550°C. Those elements not volatile in the combustion zone form the fly ash matrix and have been mechanically transported by the gas stream. The condensation is probably not complete and at least some species are given off into the atmosphere where they remain in gas phase or form aerosols. Mercury, chlorine undoubtedly vaporize and would be predicted to exhibit the same inverse concentration dependence if the mechanism were valid but their vapor pressure is too high for them to adsorb/condense at the output temperature. Other exceptions to the volatilization adsorption-condensation hypothesis also exist and are discussed by Klein et al. (1975).

6.3 Mass Balance Closures for the most volatile elements

Of special interest are the toxic heavy metals which are emitted to the atmosphere in substantial amount from the coal burning utility plants. These emissions can occur in both solid and vapor forms. Very fine fly ash particles which escape to the atmosphere are preferentially enriched with some of the heavy metals by as much as 100- to 1000- fold over their natural crustal abundance. A fraction of some of these heavy metals does not condense in the stack and escape as vapor to the atmosphere. Especially, nearly the total mercury content of the parent coal escapes as vapor (Germani and Zoller, 1988; Kaakinen et al., 1975).

Germani and Zoller (1988) have calculated mass balances for some of the trace elements in Chalk Point Electric Generating Station. Their report also shows that the chalcophilic elements of Class II, e.g. Zn, As, Se, Cd, and Pb, typically have the
largest $EF_{coal}$ (Enrichment factor) values on in-stack suspended particles. In their
work, the elemental enrichment factor is defined as

$$EF_{coal} = \frac{(X/Al)_{susp}}{(X/Al)_{coal}}$$ (6.1)

where $(X/Al)_{susp}$ is the ratio of the concentration of an element $X$ to $Al$ in the
suspended particles in the stack flue gas and $(X/Al)_{coal}$ is the same ratio for the coal.

Failure to achieve closure for the mass balance of mercury and selenium indicates that
at least a portion of these elements is present in vapor phase upon release from the
stack. 98% of the total in-stack Hg concentration was found to be in vapor phase in
their work. For selenium, this value was about 59% with the average in-stack
concentration being 33 (±5) $\mu$g/m$^3$. This compares well with the work of Gladney
et al. (1976) also at the Chalk Power Generating Station, who calculated (from mass
balance closure condition) that about 61% of the Se would have to be in the vapor
phase. Germani and Zoller (1988) measured the As concentration at 140 (±80) $\mu$g/m$^3$
with about 13% of it in vapor form (the % of As in vapor varied from 0.7-52%).
They also reported that the vapor phase As decreases linearly with increase in the in-
stack total particulate mass loading over the entire range of their study from 11-245
mg/m$^3$. Unlike As, the decrease in Se vapor concentration is not very well correlated
with increasing in-stack mass loading. Kaakiken et al. (1975) also carried out a mass
balance of certain trace elements in Valmont Power Station near Boulder, Colorado.
Their results also indicate a large imbalance for Se and Hg, confirming that major portions of the inputs of these elements leave as vapors and/or very fine particles in the flue gas. Andren et al. (1975) carried out a rigorous mass balance for selenium in Allen Steam Plant. Their findings suggest that extensive fractionation of selenium takes place during combustion of coal. Selenium is very poorly incorporated into slag; only 0.3% of the coal derived Se leaves the system via slag. For a selenium input rate of 3.23 g/min, approximately 68% of it is carried into fly ash, whereas the rest 32% leaves as vapor. Other works such as of Ondov et al. (1989) also suggest that about 30% of Se present in the parent coal escapes as vapor. Outgoing Se vapor concentration lies somewhere between 25 and 75 μg/m³.

6.4 Chemical State of volatiles in coal and in emissions

Most of the Class I elements are known to occur mostly as oxides or form oxides upon heating (such as SiO₂, Al₂O₃, CaO, MgO, K₂O). They come under the category of lithophiles (aluminosilicate-associated elements) in Goldschmidt’s geochemical classification. The Class II elements are known to occur most possibly as sulfides (Se, Pb, Zn, Sb, Cd). These belong to the class of elements known as chalcophiles, sulfide-associated elements (Mason, 1966; Chigier, 1981). Trace elements can be distributed in the following forms inside the coal matrix:

Extremely small but discrete or free mineral matter with very little organically associated matter (mainly aluminosilicates, metal carbonates, sulfides, sulfates and silica).
In association with organic matter: either trapped as inorganic compounds in an organic matrix or bonded in organic compounds (as organic salts, organometallic species, chelates etc)

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 etc al., 1974). During combustion, trace elements associated with the organic fraction may be volatilized or form aerosol particles and have a much higher probability of being transferred to the gas phase. Hence, such trace elements associated with the organic fraction in coal play an important role in the particulate and gaseous emissions from coal combustion. Attempts to correlate the oxide boiling-points of the trace elements with the observed enrichment factors (EF) show some pattern for most minor elements. The lithophiles exhibit high oxide boiling points and have small EF's. Such a correlation does exist for some chalcophiles also, but their sulfide boiling points correlate better with the observed behavior (Chigier, 1981).

Various researchers have investigated the chemical state in which selenium is emitted from a coal-fired power plant. Billings et al. (1973) suggested that Se vapor in the stack exists as elemental form. Ondov and co-workers (1989) estimated the in-stack Se concentration to be about 50 μg/m³ from mass balance in a large western power plant. They mentioned that this estimate agrees quite well with the equilibrium vapor concentration (34 μg/m³) of Se metal (including Se₂, Se₄, Se₂ and Se₆) at the stack temperature (117°C) of the ESP unit, considering the large uncertainty in measuring the former and the sensitivity of the latter to fluctuating stack temperature
Andren et al. (1975) performed a host of experiments to determine the state of selenium in the slag, fly ash, and flue gas. They started with the assumption that the expected forms of Se in emissions from combustion processes are Se°, SeO₂, SeO₃⁻, and SeO₄²⁻ (Chizhikov and Shchastilivy, 1968). Their experimental approach was based on different chemical properties of selenium compounds. Following a process of elimination, they concluded that all Se in the vapor phase, fly ash, and slag exists as elemental Se. Since the formation of SeO₂ in the furnace is most likely, Andren et al. (1975) postulated that the excess SO₂ produced during the coal combustion processes acts as a reducing agent to yield elemental Se. Sarquis and Mickey (1980) also support the occurrence of such a reaction in the coal-fired furnace. The formation of Se° can be described by the following equations:

$$\text{SeO}_2 + 2 \text{SO}_2 \rightarrow \text{Se}^0 + 2 \text{SO}_3$$ (6.2)

$$\text{H}_2\text{SeO}_3 + 2 \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Se}^0 + 2 \text{H}_2\text{SO}_4$$ (6.3)

The above reactions are purely speculative and it is left to be seen whether they are thermodynamically favorable anywhere in the coal-fired furnace. Moreover, a number of researchers (Davison et al., 1974; Oehm et al., 1991) have suggested that the most probable chemical state of Se in vapor state is SeO₂. Davison et al. (1974) concluded from the thermodynamic data that it is SeO₂ which escapes to the atmosphere and at 25°C as much as 80 μg/m³ of Se can exist as SeO₂. Oehm et al. (1991) reported that
the predominant form of selenium in atmospheric aerosols is selenious acid, and suggested the reaction of SeO$_2$ with moisture to be the possible formation pathway. Later studies (Dismukes, 1994) indicate that selenium exists as SeO$_2$ for almost the entire course of its stay in the combustion environment, but at the lower temperatures of the stack, could be partially reduced to Se by the presence of SO$_2$. A thermodynamic calculation shows that the possibility of Se oxidation to SeO$_2$ is higher than the formation of Se$_6$, the predominant form of elemental Se at high temperatures (800-1200°C).

6.5 Selenium & Arsenic emissions

Selenium concentration in coal varies widely with geographical locations. Average worldwide concentration of selenium in coal approximately equals 3 parts per million. In United States, the average selenium content of coal is higher than the worldwide average equalling nearly 4 ppm (Valkovic, 1983b). An extensive study was conducted by Department of Natural Resources, State of Ohio (Knapp, 1977) to measure the trace element concentrations in Ohio Coals. Samples from 53 sites were tested and average selenium concentration was found to be slightly higher (4.31 ppm) than the national average. However, an average seam Se content as high as 6.27 ppm was detected in Meigs Creek. The highest seam level of Se among Ohio Coals was found in Lower Freeport, reaching 18.6 ppm. Andren et al. (1975) report that in the U. S. alone, $0.25 \times 10^9$ g of Se are discharged annually into the atmosphere and $1.0 \times 10^9$ g of Se are mobilized by rivers as a result of natural and coal combustion.
As is present at an average concentration of 5 ppm worldwide, while U. S. coal contains 15 ppm of As (Valkovic, 1983a). Arsenic concentration in Ohio coals shows a large variation with 2 ppm being the lowest and 110 ppm the highest recorded concentration (Botoman and Stith, 1978).

Dutkiewicz and Husain (1988) studied the spatial pattern of non-urban Se concentrations in the northeastern U.S. and made an effort to determine the possible pollution sources. Their extensive set of Se concentration data showed a systematic decrease of Se concentration with distance from the midwest region. In their study, the common border between Ohio, Pennsylvania, and West Virginia was chosen as the reference point, since it is within the area of high coal combustion emissions. The spatial concentration data indicated that Se concentration at Steubenville, Ohio is the highest (5.3 ng/m$^3$) among all the locations covered under this study. The concentration gradually decreased eastward, to a level of 0.5 ng/m$^3$ at a distance of 800 km. from the reference point. Shaw and Paur (1983) investigated the source of high Se concentration at the Ohio River Valley sites. They suggested that this high Se concentration is primarily associated with coal combustion, which is spread throughout the industrial midwest. Sarquis and Mickey (1980) reported that nearly 62% of industrial selenium emission is linked to coal-burning facilities.

The fate of selenium once released from the power plant either in vapor form or in enriched concentration in very fine fly ash particles has been an area of study by various researchers. Andren and his co-researchers (1975) postulate that since, Se has a boiling point of about 680°C, the vapor should condense shortly after
atmospheric release to form a solid. Tuncel et al. (1985) also suggest that vapor phase Se coalesces into submicron particles within short distance from the emission point and settles on the nearby soil or remains suspended as atmospheric aerosol. Gutenmann et al. (1976) observed high concentration of selenium in white sweet clover voluntarily growing on beds of fly ash landfills. Since elemental selenium is unavailable for plant uptake, they suggest subsequent oxidation of selenium in the fly ash to higher valence and more water soluble forms may be responsible for its leachability and availability to growing plants. Oehm et al. (1991) propose that the predominant form of selenium in aged atmospheric aerosol is not selenium dioxide as presumed by previous investigators, but as selenious acid. They present the reaction between selenium dioxide and atmospheric moisture as the possible reason.

Selenium is a nutrient in small doses and a toxin in higher concentrations. Selenium in the range of from 0.04-2 μg/g is required in animal diet to prevent deficiency. However, at slightly higher levels (4 or 5 μg/g) it becomes toxic (Allaway, 1969). The unique feature of selenium is that the line between too little and too much is unusually narrow. High level of Se concentration has been held responsible for the loss of fish populations in cooling reservoirs adjacent to coal-fired plants at three sites in North Carolina and Texas. It has also been blamed for the death and deformity in migratory waterfowl, birds, fish, frogs and other marsh-related wildlife in a wildlife refuge in San Joaquin valley, California (Marshall, 1986). Excessive selenium intake produces "blind staggers" in cattle, monstrosities in chickens and, in 1961-64 was responsible for poisoning among the population of Enshi
Different selenium compounds exhibit different levels of toxicity. Water-soluble Se(VI) and Se(IV) compounds are the most toxic of all. Elemental Se, on the other hand, is probably harmless and not available for plant uptake. However, this elemental form in fly ash landfills gradually oxidizes to higher valence and more water soluble forms, thus becoming readily available to growing plants. Insoluble Se (VI), Se(IV), and Se (-II) compounds have variable toxicities depending on the ease with which they are absorbed (Oehm et al., 1991).

Gissel-Nielsen and Bisbjerg (1970) indicate that the physical and chemical forms of Se in soils determine the availability to plants and subsequently to animals. Factors controlling the chemical forms of Se are soil pH, redox potentials, microbial activity, and soil mineralogy. In acid soils, any SeO$_4^{2-}$ is sorbed into ferric oxides and made unavailable for further oxidation. In alkaline soils, Se may be oxidized to SeO$_4^{2-}$, which easily enters into plants.

6.6 Control of heavy metal emissions

Very little attention has been given so far by researchers to the emission control of selenium from coal burning power plants. Since the particulate matter in a power plant ESP is separated at an elevated temperature (150-200°C), substantial amount of selenium remains in the vapor form and escape to the atmosphere. Although in principle it would be possible to remove selenium by a condensation procedure, reduction in temperature would seriously diminish the buoyancy of the
plume from the stack. It would then be necessary to reheat the flue gas before discharge, which would be uneconomical (Wouterlood and Bowling, 1979). Yodnane and coworkers (1992) worked on removing arsenic and selenium from fly ash leachate, in an effort to reducing their concentration in fly ash ponds to current drinking water standards set by U.S. EPA. Results of their study showed that arsenic can be removed effectively from fly ash leachate by both iron coprecipitation and activated alumina. However, selenium removal by iron coprecipitation did not meet the EPA standard. In case of removal with activated alumina, final selenium concentration was very close to the permit limit. Oehm et al. (1991) achieved nearly 100% recovery of selenious acid aerosols on glass fiber filters, working with the presumption that atmospheric selenium exists as selenious acid. However, removing Se by this technique demands additional design features which may prove highly expensive.

Rothenberg et al. (1991) studied the rates of adsorption of m-Xylene by fly ash. The authors found that the half-times required for monolayer 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 Cheng (1980a, 1980b) measured the rates of desorption of water from fly ash at different temperatures and concluded that there exists strong chemical interaction between water and ash. They also reported that fly ash includes several components which can react chemically with water but did not elaborate further.
Uberoi and Shadman (1990, 1991a) tested a host of sorbents to investigate their efficiency in trapping cadmium and lead vapors from hot flue gases. Those sorbents included silica, alumina, kaolinite, bauxite, emathlite, and lime. The reaction was carried out in a differential reactor, and at temperatures in the range of 700-800°C. Their studies indicated that alumina, kaolinite and bauxite are most promising among naturally occurring materials for both cadmium and lead removal. The efficiency of metal removal by these sorbents ranged from 50 to 80%. The leachability tests performed afterward showed that about 90% of the metal trapped by the above sorbents is not soluble in water. On contrary, lime exhibited only a 20% capture, almost all of which was soluble in water. In an effort to determine the chemical or physical process involved in the metal capture, Uberoi and Shadman (1990, 1991a) performed an XRD analysis of the reacted sorbents and observed the presence of a metal-aluminosilicate compound. They concluded that chemical reaction, not physical adsorption, is the dominant method in metal removal. Injection of CaO at furnace atmosphere has been observed to capture arsenic in the form of calcium arsenate (Benson, 1993).
Table 6.1: Distribution of elements among bottom ash, fly ash and flue gas (from Valkovic, 1983b).

<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>
<tbody>
<tr>
<td>Aluminum</td>
<td>20.5</td>
<td>78.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Antimony</td>
<td>2.7</td>
<td>93.4</td>
<td>3.9</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.8</td>
<td>99.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Beryllium</td>
<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>
<tr>
<td>Chromium</td>
<td>13.9</td>
<td>73.7</td>
<td>12.4</td>
</tr>
<tr>
<td>Cobalt</td>
<td>15.6</td>
<td>82.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Copper</td>
<td>12.7</td>
<td>86.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Fluorine</td>
<td>1.1</td>
<td>91.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Iron</td>
<td>27.9</td>
<td>71.3</td>
<td>0.8</td>
</tr>
<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>
<td>82.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Mercury</td>
<td>2.1</td>
<td>0</td>
<td>97.9</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>12.8</td>
<td>77.8</td>
<td>9.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>13.6</td>
<td>68.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Selenium</td>
<td>1.4</td>
<td>60.9</td>
<td>27.7</td>
</tr>
<tr>
<td>Silver</td>
<td>3.2</td>
<td>95.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.4</td>
<td>8.8</td>
<td>87.8</td>
</tr>
<tr>
<td>Titanium</td>
<td>21.1</td>
<td>78.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Uranium</td>
<td>18.0</td>
<td>80.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>15.3</td>
<td>82.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Zinc</td>
<td>29.4</td>
<td>68.0</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Table 6.2: Elemental Concentrations and Concentration Ratios (from Klein et al., 1975).

<table>
<thead>
<tr>
<th>Element</th>
<th>Element Concentration, ppm</th>
<th>Slag/Coal</th>
<th>(i fa)/Slag</th>
<th>(o fa)/(i fa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Slag</td>
<td>i fa</td>
<td>o 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>
<td>32,000</td>
</tr>
<tr>
<td>Fe</td>
<td>10,850</td>
<td>112,000</td>
<td>121,000</td>
<td>150,000</td>
</tr>
<tr>
<td>K</td>
<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>
</tr>
<tr>
<td>Si</td>
<td>23,100</td>
<td>229,000</td>
<td>196,000</td>
<td></td>
</tr>
<tr>
<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>
<td>1.1</td>
<td>8.0</td>
<td>51</td>
</tr>
<tr>
<td>Se</td>
<td>2.2</td>
<td>0.080</td>
<td>25</td>
<td>88</td>
</tr>
<tr>
<td>Pb</td>
<td>4.9</td>
<td>6.2</td>
<td>80</td>
<td>650</td>
</tr>
<tr>
<td>Sb</td>
<td>0.5</td>
<td>0.64</td>
<td>12</td>
<td>55</td>
</tr>
<tr>
<td>Zn</td>
<td>46</td>
<td>100</td>
<td>740</td>
<td>5,900</td>
</tr>
<tr>
<td>Cl</td>
<td>914</td>
<td>&lt;100</td>
<td>&lt;200</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>3.7</td>
<td>2</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.122</td>
<td>0.028</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3: Concentration (in ppm) of some Class II elements as a function of fly ash size.

<table>
<thead>
<tr>
<th>Element</th>
<th>&gt;15</th>
<th>8-15</th>
<th>3-8</th>
<th>&lt;3</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>13.7</td>
<td>56</td>
<td>87</td>
<td>132</td>
</tr>
<tr>
<td>Cd</td>
<td>0.4</td>
<td>1.6</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Ga</td>
<td>43</td>
<td>116</td>
<td>140</td>
<td>178</td>
</tr>
<tr>
<td>Pb</td>
<td>73</td>
<td>169</td>
<td>226</td>
<td>278</td>
</tr>
<tr>
<td>Sb</td>
<td>2.6</td>
<td>8.3</td>
<td>13</td>
<td>20.6</td>
</tr>
<tr>
<td>Se</td>
<td>19</td>
<td>59</td>
<td>78</td>
<td>198</td>
</tr>
<tr>
<td>Zn</td>
<td>71</td>
<td>194</td>
<td>304</td>
<td>550</td>
</tr>
<tr>
<td>Mn</td>
<td>207</td>
<td>231</td>
<td>261</td>
<td>317</td>
</tr>
<tr>
<td>Cr</td>
<td>28</td>
<td>49</td>
<td>59</td>
<td>63</td>
</tr>
</tbody>
</table>
CHAPTER VII
SELENIUM REMOVAL USING SORBENTS:
MECHANISM OF CAPTURE USING Ca(OH)$_2$

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

7.1 Introduction

The high volatility and its existence in the form of vapor make selenium emission control a very difficult task. A reduction in the operating temperature of the stack could enhance condensation of the vapor and hence metal removal, but the resulting loss in buoyancy of the stack emission eliminates this as a feasible technique. Improving performance of the particulate control device can lead to better capture of the finer metal aerosols, however, it fails to lessen the gas phase emission. 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 SO$_2$ 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) 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 (9) 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 selenium with hydrated lime compared to the other sorbents. In their baseline runs without any sorbent injection, they observed that nearly 50% of the recovered selenium was concentrated in the submicrometer range (filter and impinger solutions) indicating ineffectiveness of the larger fly ash particles to capture Se. With hydrated lime injection, there was a reduction of the submicrometer selenium fraction and a significant increase in the selenium content of the larger size sorbent/fly ash mixture. 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 $\text{As}_2\text{O}_3$ 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.

In this study, the effectiveness of hydrated lime, limestone, kaolinite and alumina is tested for removal of selenium. Investigations are conducted with hydrated lime sorbent to identify the mechanism of Se/Ca interaction and the chemical state and characteristics of the adsorbed species.

7.2 Differential 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.

7.2.1 Vapor generation setup

The selenium source is held in a Pt sample pan suspended by a Pt hangdown wire from the ATI Cahn D-200 digital microbalance. $\text{SeO}_2$ is used as the selenium 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 selenium source. In order to achieve vaporization and transfer of SeO₂ into gas phase, the vaporization tube is wrapped with heating tape and closely maintained at a specific temperature using the thermocouple and a temperature controller. Solid SeO₂ sublimes at a temperature of 317°C. The desired concentration of selenium in the gas phase dictates the temperature at which the vaporization tube is maintained. Some preliminary vaporization studies along with the vapor pressure data of SeO₂ are utilized to determine the vaporization temperature and the carrier gas flow rate. A vaporization temperature of about 160°C gives the desired uniform vaporization rate to achieve the objective of a very small yet uniform concentration of selenium. 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 SeO₂-carrying gas from the vaporization tube to the top of the reactant tube. In order to avoid condensation of the Se 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 or nitrogen is used as the diluent stream. This serves to adjust the concentration of the Se species in the reactor to the desired levels. Typically, for all the reaction studies, diluent gas flow is maintained at 1 lpm (STP). In order to avoid any selenium 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 SeO₂ before being vented to exhaust. 7% HNO₃ solution is used as the impinger solution. The connecting line between the reactor and the impinger is also kept heated.

7.2.3 Experimental Procedures and Analyses

During actual experiments, a small amount of preweighed 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 SeO$_2$ sample in the vaporization tube is initiated by heating to 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 selenium concentration is calculated from a knowledge of the vaporization rate and the gas flow rates. All the experiments are performed with the selenium concentration at 8 ppmv with the carrier gas and diluent gas flow rates at 200 and 1000 ml/min respectively.

Initial experimental runs involved testing various sorbents for their selenium capture ability at two representative temperatures of 500 and 900°C. Along with Ca(OH)$_2$, limestone, kaolinite, and alumina are included among the sorbents tested. Further studies are then carried out with Ca(OH)$_2$ powder for sorption temperatures ranging from 400 to 1000°C thus covering both medium and high temperature windows. For the sorption run at 400°C, where the calcination of Ca(OH)$_2$ is much slower, complete calcination is first ensured by raising the reactor temperature to 550°C. The temperature is then lowered to 400°C before commencing selenium vaporization. All the sorption runs are conducted for 4 hours.

The amount of selenium captured is determined by measuring the selenium content of the sorbent after the experiment. The water soluble fraction is determined by leaching with de-ionized water. 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 a ultrasonic bath for about 4 hours which is found to be adequate to leach out all the
selenium. The selenium 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 available in the Materials Science and Engineering Department. X-ray photoelectron spectroscopy (XPS), available in the Chemistry Department is also used to identify the chemical state of the material upon sorption. The dispersant quartz wool itself exhibits no significant capture (<25 ppm) of selenium.

7.3 Results and Discussion

The results obtained from the screening experiments under diluent air at 500°C and at 900°C are shown in Figure 7.2. Of the various sorbents tested, hydrated lime exhibits much higher capture at both the temperatures and for all the sorbents the amount of selenium captured is much less at 900°C than at 500°C. The results showed good reproducibility from the multiple experiments performed with some sorbents. Hydrated lime proved to be the most effective for removing selenium and is chosen for conducting thorough mechanistic studies which are described below.

Figure 7.3 shows the results of the sorption studies in terms of overall capture at different temperatures in the medium and high temperature ranges. The overall sorption is seen to increase with temperature between 400 to 600°C, however, it reduces drastically at higher temperatures yielding a maxima at 600°C. Figure 7.4 compares the selenium capture by Ca(OH)₂ in the presence of air with that under inert nitrogen at medium temperature conditions. The amount of sorption under diluent air
is observed to be less than that under nitrogen and the difference is more pronounced at the lower temperatures of 400 and 500°C. Carbonation of CaO to CaCO$_3$ due to the presence of CO$_2$ in air appears to be the most probable reason for reduced metal capture under air. 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). This is verified by heating a small amount of the post-reaction sorbent in a TGA immediately after withdrawal from the reactor. The TGA result indicates that significant portion (30-50%) of the sample CaO is carbonated to CaCO$_3$ during the sorption run. Carbonation occurs preferentially on and near the CaO surface, and CaCO$_3$ being highly non-porous may block SeO$_2$ access to the interior oxide surface. This phenomenon in association with loss of overall CaO can be used to explain the reduction in metal capture observed for 400 and 500°C runs. At 600°C and higher temperatures, carbonation of CaO is not very significant and the results are nearly identical for both nitrogen and air.

The actual mechanism of Se sorption by CaO could involve either physisorption of SeO$_2$ or some chemisorbed complex or some chemical reaction product from CaO and SeO$_2$ (to yield a calcium-selenium-oxygen compound such as CaSeO$_4$ or CaSeO$_3$) or a combination of all these phenomena. Physical adsorption involves relatively weak attractive forces between the adsorbent and adsorbate, and the physisorbed amount decreases rapidly with increasing temperature (Gregg and Sing, 1982). Further, physisorption is a nonactivated process and easily reversible. 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.

Water-leachability tests indicate that practically all the selenium captured at medium temperatures is in the water soluble form. $\text{SeO}_2$ is highly water soluble, as well as $\text{CaSeO}_4$ and $\text{CaSeO}_3$; hence water-leachability characteristics alone cannot distinguish between capture by physical adsorption and chemical reaction process. Analysis of the water leached solution of the 600$^\circ$C sample using Alltech ion chromatography (IC) system showed the selenium to be present entirely in the form of selenite ($\text{SeO}_3^{2-}$) ion indicating a valence state of +4 for the selenium. This result demonstrates that Se content of the sample is present as either $\text{SeO}_2$ or calcium selenite, but not as more oxidized form of $\text{CaSeO}_4$ in which the valence state of the metal is +6. No appreciable difference in selenium capture between air and nitrogen environments at 600$^\circ$C also suggests to an insignificant role of oxygen in the overall reaction process. The IC analysis also quantitatively corroborated the selenium concentration results obtained from AAS.

Desorption studies were carried out with the post-sorption sample by passing $\text{SeO}_2$-free nitrogen gas at the same flow rate at a specific temperature. Figure 7.5 shows the result of such isothermal desorption for the sorbent following sorption at 500$^\circ$C. Negligible loss of selenium is observed following 2 hours of desorption at the temperature of sorption, i.e., at 500$^\circ$C. Further desorption of the sample for 2 hours at higher temperatures of up to 700$^\circ$C did not lead to any appreciable loss of selenium content. However, most of the selenium is released upon desorption at a much higher temperature of 825$^\circ$C. The 400$^\circ$C and 600$^\circ$C samples also showed similar results.
following desorption for 2 hours at the respective sorption temperatures, which possibly indicate an irreversible capture of selenium, thus eliminating physical adsorption as a dominant mechanism in the sorption process.

In order to gain further insights into the actual mechanism of Se/sorbent interaction, sorption experiments are conducted for much longer time scale, and XRD/XPS are performed on the sorbent. Figure 7.6 shows the XRD spectrum of the sorbent following 48 hours of sorption at 500°C and at the same selenium concentration of 8 ppmv. From AAS analysis, the selenium sorption is about 150,000 μg Se/g sorbent. XRD spectra are also performed for pure CaSeO₄ and CaSeO₃, in addition to SeO₂. Pure calcium selenate is procured from commercial sources as hydrated salts (CaSeO₄·2H₂O), and calcium selenite is prepared by decomposition of calcium selenate in the TGA at 700-800°C (Selivonava, 1958). XRD seems to confirm the formation of calcium selenite on the sorbent from a comparison of these spectrums. On the other hand, the presence of physically adsorbed SeO₂ could not be confirmed by XRD. XPS results, figures 7.7(a) and 7.7(b) also verified presence of selenium species on the sorbent surface, and a comparison of the sample spectrum with the CaSeO₃ and CaSeO₄ spectra indicated that CaSeO₃ is the most likely chemical state of the captured selenium. Based on these findings, the following reaction scheme can be proposed for CaO/SeO₂ interaction:

$$CaO(s) + SeO₂(g) \rightarrow CaSeO₃(s)$$  \hspace{1cm} (7.1)

This reaction process does not require the participation of oxygen, which is
further corroborated by XPS analysis on 600°C sample, reacted under air, which indicates presence of only CaSeO₃, but no CaSeO₄. Confirmatory tests are also performed in a TGA to study the stability of pure CaSeO₃ in the presence of oxygen at 600°C. Negligible weight gain following overnight exposure proves that CaSeO₃ does not react with oxygen to form selenate.

Results of the high-temperature studies indicate much reduced capture at these temperatures with negligible selenium sorption above 900°C. In contrast to the medium-temperature runs, results at these temperatures show a decreasing selenium capture by the sorbent as temperature increases. Investigations of decomposition of pure CaSeO₃ with temperature were performed under inert nitrogen flow. Unlike the sulfur salts of calcium for which vapor pressure and decomposition characteristics have been thoroughly investigated (Schwitzgebel, 1973), no such information is available for the selenium salts of calcium in the literature. Calcium selenite is observed to undergo decomposition after 800°C with the rate of decomposition increasing with temperature. The weight loss upon completion of decomposition corresponds to the formation of CaO. This indicates that in the reaction (7.1), the backward reaction becomes prominent at higher temperatures due to increasing vapor pressure of CaSeO₃. This is similar to the Ca(OH)₂/SO₂ reaction which shows an increasing rate of reaction up to about 1400 K and reduced sulfation at higher temperatures due to the decomposition of the reaction product CaSO₄ (Milne et al., 1990).
7.4 Conclusions

The results of this study indicate that calcium hydroxide is an effective sorbent in capturing selenium from hot flue gas at temperatures around 400 to 600°C. The metal capture occurs by a chemical reaction between CaO and SeO$_2$, forming calcium selenite. Consequently, selenium is transferred from vapor to a solid phase, and can be controlled more easily in the baghouse or electrostatic precipitator of the coal-burning utility system. The thermodynamic equilibrium criteria show that this reaction is not favored at high temperatures which suggests that sorbent injection in the economizer region of the utility plant will result in better selenium removal compared to in-furnace sorbent injection.

This study is conducted at a selenium concentration of 8 ppm, which is higher than the typical selenium concentration in the coal-generated flue gas. In addition, presence of CO$_2$, SO$_2$, and H$_2$O in the flue gas will lead to a host of competing reactions with CaO which will influence the CaO/SeO$_2$ 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 and in short-time entrained-flow system. Nevertheless, this work has revealed the mechanisms involved in CaO/SeO$_2$ interaction and has shown that it is possible to capture selenium from hot flue gas by calcium hydroxide injection.
Table 7.1: Composition of sorbents investigated (wt%).

<table>
<thead>
<tr>
<th></th>
<th>lime</th>
<th>kaolinite</th>
<th>limestone</th>
<th>alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>94.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.9</td>
<td>45.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.6</td>
<td>38.5</td>
<td>0.5</td>
<td>99.99</td>
</tr>
<tr>
<td>MgO</td>
<td>1.0</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>1.0</td>
<td></td>
<td></td>
<td>97.0</td>
</tr>
<tr>
<td>CaO</td>
<td>1.0</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.5</td>
<td>0.41</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

* Linwood Mining & Minerals Co.  ^ Albion Kaolin Co.  ^ Johnson Matthey
Figure 7.1: Schematic of high-temperature differential reactor assembly.
Figure 7.2: Amount of selenium capture by various sorbents; concentration of Se: 8 ppm; diluent stream: air.
Figure 7.3: Selenium uptake by Ca(OH)$_2$ sorbent in 4 hours; selenium concentration: 8 ppm; diluent stream: air.
Figure 7.4: Comparison of selenium capture by Ca(OH)$_2$ sorbent under different diluent streams; concentration of Se: 8 ppm
Figure 7.5: Effect of desorption temperature on selenium retention by Ca(OH)$_2$ sorbent following 2 hours of desorption under Se-free flow.
Figure 7.6: X-ray diffractograms of (a) post-sorption sample, (b) pure calcium selenite, (c) pure calcium selenate, and (d) pure SeO$_2$; sorption conducted at 500°C for 48 hours under diluent air at selenium concentration of 8 ppm.
Figure 7.7: XPS spectra of (a) post-sorption sample, and (b) selenium 3d peak; sorption conducted at 600°C for 48 hours under diluent air at selenium concentration of 8 ppm.
CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The influence of internal pore structure and its interaction with reaction kinetics has been the main focus of this research. The high temperature interaction of SO$_2$ with calcium-based sorbents, though a subject of numerous investigations, cannot be said to have been completely understood. The three different phenomena of calcination, sintering and sulfation, each with their own influence and interaction with the internal pore structure, make this a complicated and challenging problem to study. Further more, their ultrafast nature and thereby their concomitant occurrence under the high temperature conditions adds more complexity. This research has contributed to a more thorough understanding of the various processes and has led to the identification and initial development of a new carbonate sorbent based on the principle of tailoring the pore structure to optimize reactivity.

The Ca(OH)$_2$-SO$_2$ interaction phenomena has been investigated in two stages: first, the calcination and sintering alone in the absence of SO$_2$; and second, the combined calcination, sintering and sulfation reaction in the presence of SO$_2$. While the ultrafast nature of calcination reaction is well investigated in the available literature, an understanding of the influence of sintering under such short-contact time
conditions was lacking. This research has experimentally investigated the enormous effect of sintering and has successfully modeled the kinetics and structural evolution of the calcine during ultrafast calcination and sintering. The mathematical model developed for small Ca(OH)$_2$ particles visualizes the CaO formed as micrograins surrounding the unreacted Ca(OH)$_2$, and takes into account the age distribution and varying levels of sintering of the CaO micrograins formed at various times. The extremely high initial calcination rate and the sudden attenuation and subsequent levelling-off has been observed. A mechanism is proposed to explain this behavior based on the increased resistance to outward diffusion of H$_2$O due to the drastic sintering of the product CaO layers. The model explains and fits the experimental data very well at temperatures of 950°C and higher, but at lower temperatures, it under-predicts the initial reaction rate.

In addition to surface area and porosity, the size distribution of the pores plays a crucial role in the kinetics and utilization. The investigations of transformations in the pore size distribution both in the absence and presence of SO$_2$ were carried out. During calcination and sintering, there is initially a generation of pores in the smallest size range of less than 50 Å (due to calcination). This is more prominent at temperatures lower than 1000°C, where calcination initially dominates sintering leading to increased porosity and generation of pores. However, as time proceeds, sintering leads to loss of continuous loss of pores, starting with the smallest pores first. This is enhanced at higher temperatures where the porosity reduces drastically and the small pores formed cannot sustain themselves due to increased sintering rate.
Moreover, sintering is shown to be more sensitive to temperature than calcination reaction (due to its much higher activation energy). In the presence of SO$_2$, this study has clearly shown the preferential filling of the smallest pores by the higher molar volume product, CaSO$_4$. Further, the enhanced loss of overall pore volume over the entire size range is clearly demonstrated. This study has shed more light on the evolution of pores of various size ranges and the implications of the loss of the smallest pores.

The investigation and development of modified and improved (high surface area and porosity) calcium-based sorbents has been an important part of this research towards improving the sorbent reactivity and utilization. Investigations performed with the high surface area carbonate and hydrate and a critical comparative investigation with unpromoted hydrate and carbonate have been able to correlate the pore structure and reactivity. Previous researchers have acknowledged the importance of the optimum size range of pores but an definite knowledge of the "best" range and the advantage to be derived had been missing. Pores smaller than 50 Å in diameter are likely to be quickly filled or plugged with sulfation and pores larger than 200 Å in diameter possess much smaller surface area to contribute significantly to sulfation rate. Both the high surface area as well as the non-porous carbonate are shown to possess inherently lower sintering characteristics and the ability to retain the pores smaller than 100 Å in diameter. However, what sets the high surface area carbonate apart is that in addition to the optimum distribution, it also possesses a substantial amount of pore volume. The non-porous carbonate, despite the availability of "good" pores
possesses them in very small amount which leads to its poor utilization. The modified hydrate is shown to be superior to the low surface area hydrate but only in the initial 50 milliseconds or so. The modified hydrate is observed to have very high sintering rate and looses most of its high surface area and porosity within the first 50 to 100 milliseconds after which it behaves very similar to the unpromoted hydrate. However, the advantage derived in the first 50 milliseconds or so is retained by the modified hydrate leading to its higher ultimate utilization. The results indicate about 20% improvement in utilization of the modified hydrate compared to the pure. This work has laid the foundation and background for harnessing the sorbent pore structure and tailoring it to develop sorbents with very high reactivity.

This research has also investigated the interaction of selenium, a trace heavy metal pollutant, with sorbents. Selenium is a highly volatile trace toxic and is emitted to the atmosphere with the flue gas during fossil-fuel combustion and its toxicity and damaging effects are well-documented. This research has shown that calcium-based sorbents seem to possess high sorption capability compared with other alumino-silicate based sorbents tested. Thorough mechanistic investigations have revealed the mechanism of SeO$_2$/Ca interaction. The CaO reacts with SeO$_2$ to lead to the formation of calcium selenite, which does not require the presence of oxygen. Moreover, due to the high vapor pressure and decomposition characteristics of CaSeO$_3$ above 700°C, the most favorable temperature range lies at 600°C or below.
This research work, with its time-resolved kinetic data and on-line measured residence time, has contributed to a more thorough understanding of the short-time \( \text{SO}_2/\text{Ca} \) interaction and the mechanism of Se/Ca-sorbent. However, there most certainly remain a number of unaccomplished tasks, shortcomings and improvements that warrant further research work.

In this work, the calcination and sulfation reactions are studied for their inherent characteristics, however, under actual conditions, the \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are major constituents of the flue gas. The presence of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) can not only influence the calcination of the sorbent thermodynamically (due to its reversible nature), they also influence and accelerate the sintering characteristics. Hence, in order to accurately predict and model the reaction kinetics and pore structure transformations under actual boiler conditions, studies with simulated flue gas will be very useful.

The structural studies have clearly shown certain important transformations such as the preferential loss of small pore sizes and the effectiveness of pores of certain optimum size. However, an exact quantitative analysis of pore structure transformations has not been attempted. Firstly, because this research represents the first experimental study of its kind at such short-contact times and the amount of data collected though sufficient for a qualitative analysis, cannot be said to be adequate for a thorough mathematical modeling. Secondly, the analysis itself would demand a high degree of advanced mathematical formulations for the pore structure and its variations. Hence, a necessary step towards that ultimate objective would be to gather more data on the pore structure transformations, while the model development is in progress.
Such a model and its experimental validation would not only represent an important advancement in this field, it could also serve in the theoretical predictions of the sorbent tailoring work that is outlined below.

The framework of the comprehensive model development work is discussed in chapter V. However, in this work, a simplified form of the sulfation model scheme has been used for prediction of experimental data. The sulfation model itself utilizes the predictions of the calcination and sintering model as its input. The combination of the sulfation model with the calcination and sintering model needs to be improved upon. These shortcomings may be largely responsible for the mediocre model prediction ability. Incorporating these improvements will be very useful in making the model more robust and comprehensive. Further, application of the model to predict the high reactivities of the high surface area carbonates could yield some interesting theoretical insights for future work.

This work has shown for the first time that carbonate-based sorbents, if modified or synthesized suitably to enhance their structural characteristics, have the potential to improve upon the utilization by a large factor over the hydrate-based sorbents. The work shows great promise in the future in terms of direct economic benefits derived through high reactivity sorbents. This work could be conducted on two fronts, first, synthesis of high-surface area, porous sorbents, and second, the testing and characterization of these powders for SO$_2$ reactivity. Precipitation synthesis in the presence of suitable additives/dispersants is a promising technique which if optimized could yield very effective sorbents.
On the heavy metals removal, this work has served to identify Ca(OH)$_2$ as a good sorbent for selenium as well, and has revealed the exact mechanism of interaction. However, the kinetics of the interaction, which will determine the utility of this process for heavy metal removal, was beyond the scope of this work. Hence, the next important research area would be to study the kinetics under more representative conditions. Studies under entrained flow conditions at short contact time scales of 2-3 seconds will be very useful.
APPENDIX A

FORTRAN program of Calcination and Sintering Model.

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/ A(5000),B(5000),CBC(5000)
COMMON /BLOCK6/ B(5000),RCN(5000),CN(5000)
COMMON /BLOCK7/ BN(5000),SC(5000),SCPGMN(5000),STOTGN(5000)
COMMON /BLOCKS/ TOTCAO

WRITE(6,*) 'ENTER NAME OF DATA FILE, INCLUDE DAT'
READ(5,'(A20)') FILEINP
OPEN(UNIT=4,FILE=FILEINP,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')

NOMENCLATURE:

DP: Diffusivity, H2O in N2, m2/s
AKC: Reaction constant
AKS: Sintering constant
CBS: Concentration of H2O at saturation, gmol/m3
SCA: Asymtotic S.A of CaO, m2/gmol
SCNA: Nascent S.A. of CaO, m2/gmol
SHNA: S.A. of Caoh2, m2/gmol
RHOH: True density of Caoh2, g/m3
RHOC: True density of CaO, g/m3
CSO: Solid reactant concentration, gmol/m3
DELTA: DELTA TIME
NT: Total no. of iterations

Arrays:

T,TN: Time, s
X,XX: Conversion,
B,BN: Amount of CaO formed, gmol
A,AN: Amount of Caoh2 left, gmol
A+B=1, basis: 1 gmol of Caoh2.
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 CaOH₂, m² per gram basis, remains constant

SH: S. A. of Ca(OH)₂, 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.

TEMK=1173.

DP=9.5E-5*(TEMK/1223.)**1.5

IF(TEMK.EQ.1223.) GOTO 1
IF(TEMK.EQ.1323.) GOTO 2
GOTO 3

CBS=1.3E+3
GOTO 4
CBS=3.35E+3
GOTO 4
CBS=1.1E+3
GOTO 4

SHNA=16.9*74.
RHOH=2.4E+6
RHOC=3.32E+6
DELT=0.1E-3
CSO=RHOH/74.
NIT=299.5E-3/DELT

INITIAL CONDITIONS

=0.0
=0.0

Values of all variables (which are functions of X)

=X(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.

WRITE(3.21)T(I),X(I),RG(I),RC(I),CBC(I),STOTG(I)

ICTR=1
CALL RK(I)


C CALCULATE VALUES OF SURFACE 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)
C
I=I+1
C
=BN(I-1)

=TN(I-1)
C
RG(I)=RGN(I-1)
RC(I)=RCN(I-1)
SC(I)=SCN(I-1)
SCPGM(I)=SCPGMN(I-1)
CBO(I)=CBCN(I-1)
STOTG(I)=STOTGN(I-1)
C
ICTR=ICTR+1
IF(ICTR.NE.21) GO TO 40
C
WRITE(6,21)T(I),X(I),RG(I),RG(I),RC(I),STOTG(I)
WRITE(3,21)T(I),X(I),RG(I),RG(I),RC(I),STOTG(I)
FORMAT(IX,E10.5,1X,E10.5,1X,E12.5,1X,E12.5,1X,E12.5,1X,E12.5)
C
ICTR=1
IF(I.GT.NIT) GO TO 20
GO TO 10
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)
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
\[ X_{N(I)} = X(I) + DXDT \cdot \text{DELT} \]
\[ T_{N(I)} = T(I) + \text{DELT} \]
\[ \text{CALL FUNCT}(T_{N}, X_{N}, T_{X}, X_{I}, DXDT) \]
\[ CAY4 = DXDT \]
\[ X(I+1) = X(I) + \text{DELT} \cdot (CAY1 + 2 \cdot CAY2 + 2 \cdot CAY3 + CAY4) / 6. \]
\[ T(I+1) = T(I) + \text{DELT} \]
\[ \text{RETURN} \]
\[ \text{END} \]

```
SUBROUTINE FUNCT(TN,XN,T,X,XD)
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)
COMMON /BLOCK6/ RGN(5000),RCN(5000),CBCN(5000)
C
CALL SURFRAD(TN,XN,T,X)
C
C CALCULATE DXDT
C
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)
C
RETURN
END
```

```
SUBROUTINE SURFRAD(TN,XN,T,X)
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 /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
C This is the real work-horse subroutine, it calculates everything!!!
C
DIMENSION X(5000),T(5000),XN(5000),TN(5000)
DIMENSION AN(5000),SHN(5000)
DIMENSION STOTN(5000),RHON(5000)
C
C Calculate incremental CaO formed over the previous
C
BN(I)=XN(I)-X(I)
```
AN(I)=1.-BN(I)
C
SURFACE AREA CALCULATION
C
C Calculate modified AKS using previous CBC over 2.
C
AKSN=AKS*(1.+CONKS*(CBC(I-100)/2.))**0.17
TERM1=SCNA*BN(I)
TERM11=SCNA
SCPGMN(I)=TERM11
C
C Term2 is the single most important term calculated,
C
TERM2=0.
DO 100 J=1,1
AKSN=AKS*(1.+CONKS*(CBC(J-100)/2.))**0.17
TERM2=TERM2+((SCA+17((iy(SCP(GM(J)-SCA)+AKSN*(TN(J)-T(J)))))*B(J)
FORMAT(1X,E10.5,1X,E10.5,1X,E12.5,1X,E12.5,1X,E12.5)
C
C Total CaO S. A, m2
C
SCN(I)=TERM1+TERM2
C
AMOUNT CAO CALCULATION
C
ANEWCAO=BN(I)
OLDCAO=0.
DO 200 K=1,1
OLDCAO=OLDCAO+B(K)
C
TOTCAO=ANEWCAO+OLDCAO
C
Calculate S.A per g. gmol etc.
C
SHN(I)=SHNA*(1.-TOTCAO)
STOTN(I)=SCN(I)+SHN(I)
TOTGN=TOTCAO*56.+(1.-TOTCAO)*74.
C
IF(TOTCAO.EQ.0.) GOTO 36
CAOPERG=SCN(I)/(TOTCAO*56.)
HYDPERG=SHN(I)/(1.-TOTCAO)*74.
STOTGN(I)=CAOPERG*XN(I)+HYDPERG*(1.-XN(I))
GOTO 37
C
STOTGN(I)=STOTN(I)/TOTGN
C
"Average true" DENSITY CALCULATION
C
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 CALCULATION
C
RGN(I)=3.*STOTGN(I)/RHON(I)
RCN(I)=RGN(I)*(1.-XN(I))**(1./3.)

AN(I)=1.-BN(I)
C
SURFACE AREA CALCULATION
C
C Calculate modified AKS using previous CBC over 2.
C
AKSN=AKS*(1.+CONKS*(CBC(I-100)/2.))**0.17
TERM1=SCNA*BN(I)
TERM11=SCNA
SCPGMN(I)=TERM11
C
C Term2 is the single most important term calculated,
C
TERM2=0.
DO 100 J=1,1
AKSN=AKS*(1.+CONKS*(CBC(J-100)/2.))**0.17
TERM2=TERM2+((SCA+17((iy(SCP(GM(J)-SCA)+AKSN*(TN(J)-T(J)))))*B(J)
FORMAT(1X,E10.5,1X,E10.5,1X,E12.5,1X,E12.5,1X,E12.5)
C
C Total CaO S. A, m2
C
SCN(I)=TERM1+TERM2
C
AMOUNT CAO CALCULATION
C
ANEWCAO=BN(I)
OLDCAO=0.
DO 200 K=1,1
OLDCAO=OLDCAO+B(K)
C
TOTCAO=ANEWCAO+OLDCAO
C
Calculate S.A per g. gmol etc.
C
SHN(I)=SHNA*(1.-TOTCAO)
STOTN(I)=SCN(I)+SHN(I)
TOTGN=TOTCAO*56.+(1.-TOTCAO)*74.
C
IF(TOTCAO.EQ.0.) GOTO 36
CAOPERG=SCN(I)/(TOTCAO*56.)
HYDPERG=SHN(I)/(1.-TOTCAO)*74.
STOTGN(I)=CAOPERG*XN(I)+HYDPERG*(1.-XN(I))
GOTO 37
C
STOTGN(I)=STOTN(I)/TOTGN
C
"Average true" DENSITY CALCULATION
C
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 CALCULATION
C
RGN(I)=3.*STOTGN(I)/RHON(I)
RCN(I)=RGN(I)*(1.-XN(I))**(1./3.)
WRITE(6,*) 'RGN(I), RCN(I) :RGN(I),RCN(I)
C
C CALCULATE POROSITY & DIFFUSIVITY EFFECTIVE
C ONE WAY OF CALCULATING POROSITY OF PRODUCT, HOME-DEVISED
C
C IF(RGN(I).EQ.RCN(I)) GOTO 51
C ANUM=TOTCAOM73.*(22./7.)*(RG(I)**3)*RHOH/74.
C ANUM=ANUM1/(RHOH/56.)
C ADEN=4./3.*(22./7.)*(RGN(I)**3-RCN(I)**3)
C PORPRO=1.-ANUM/ADEN
C
C ANOTHER WAY OF CALCULATING POROSITY OF PRODUCT, FROM MILNE
C
IF(I.GT.2) GO TO 34
PORPRO1=0.4529-(0.4529/(SCPGM(I)-SCA))*(SCPGM(I)-SCPGMN(I))
GOTO 35
SHPRO=SCA+1/((1./SCPGM(2)-SCA)+AKSN*(TN(I)-T(2)))
PORPRO1=0.4529-(0.4529/(SCPGM(I)-SCA))*(SCPGM(I)-SHPRO)
C
C35 RCN(I)=RG(I)*(1.-XN(I))**2
c WRITE(6,*) RCN(I)
C TERMA=RCN(I)**3.
C TERMB=(RHOH/74.)*(RG(I)**3.-RCN(I)**3.)
C TERMB=TERMB/(RHOH/74.)/(1.-PORPRO1)
C TFIN=(TERMA+TERMB)
C RGN(I)=TFIN**(1./3.)
C RCN(I)=TERMA**(1./3.)
C WRITE(6,*) TERMA,TERMB
C WRITE(6,*) RGN(I),RCN(I)
C
C Calculate Knudsen diffusiity
C
PORRAD=2.*PORPRO1/(SCPGMN(I)*RHOH/56.)
DK=97.*PORRAD**(TEMK/18.)**0.5
DPEFF=1./DK+1./DP
DPN=DPEFF*PORPRO1**2
GO TO 32
C
C CALCULATE PRODUCT GAS CONCENTRATION AT INTERFACE.
C
C31 DPN=DP
C RGN(I)=RG(1)
C RCN(I)=RG(1)
C
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
APPENDIX B

QuickBasic program for pore size distribution analysis for parallel plate pore structure.

'*****************************************************************************
'THIS IS A QUICKBASIC PROGRAM TO PERFORM PORE SIZE DISTRIBUTION FOR Ca(OH)2 POWDER BASED ON THE WORKSHEET IN INNES (1957)
'*****************************************************************************
DIM P(130), AD(130), D(130), X(130), XL(130), DELX(120), DELT(120)
DIM DELA(120), AVA(120), C(120)
DIM E(120), F(120), DELV(120), V(120), AT(130), T(130), A(120), R(120)
DIM ADA(100), DELP(100), DAV(100), DELD(100), YAX(100)
DIM AV(100), DDA(100), DLDA(100), DL(100), VCORR(100)

PRINT "OPTIONS"
PRINT "1. DATA IN GAS VOLUME"
PRINT "2. DATA IN LIQUID VOLUME"
INPUT "CHOOSE OPTION 1 OR 2"; OPT
IF OPT = 1 THEN
READ N
FOR J = 1 TO N ' INPUT GAS VOLUME IN CC
READ P(J), X(J)
XL(J) = X(J) * .00154
' convert to liquid nitrogen volume
NEXT J
ELSE
READ N
FOR J = 1 TO N
READ P(J), XL(J)
NEXT J
END IF
FOR J = 1 TO N
IF P(J) = 1! THEN
AD(J) = 1000000
AT(J) = 26.2
' AD IS THE PORE WIDTH AND AT IS THE FILM THICKNESS IN ANGSTROMS FROM INNES (1957), KELVIN EQUATION
ELSEIF P(J) = .985 THEN AD(J) = 680!
AT(J) = 23.92
ELSEIF P(J) = .96 THEN AD(J) = 273.76
AT(J) = 20.12
ELSEIF P(J) = .95 THEN AD(J) = 225!
' END OF PROGRAM
AT(J) = 18.6
ELSEIF P(J) = .93 THEN AD(J) = 165.67
AT(J) = 17.16
ELSEIF P(J) = .925 THEN AD(J) = 156!
AT(J) = 16.8
ELSEIF P(J) = .9 THEN AD(J) = 120!
AT(J) = 15!
ELSEIF P(J) = .98 THEN AD(J) = 518!
AT(J) = 23.16
ELSEIF P(J) = .85 THEN AD(J) = 90!
AT(J) = 12.8
ELSEIF P(J) = .8 THEN AD(J) = 69!
AT(J) = 11.4
ELSEIF P(J) = .75 THEN AD(J) = 52!
AT(J) = 10.3
ELSEIF P(J) = .7 THEN AD(J) = 46!
AT(J) = 9.4
ELSEIF P(J) = .65 THEN AD(J) = 39!
AT(J) = 8.6
ELSEIF P(J) = .6 THEN AD(J) = 35!
AT(J) = 8!
ELSEIF P(J) = .55 THEN AD(J) = 30!
AT(J) = 7.5
ELSEIF P(J) = .5 THEN AD(J) = 28!
AT(J) = 7!
ELSEIF P(J) = .45 THEN AD(J) = 25!
AT(J) = 6.6
ELSEIF P(J) = .4 THEN AD(J) = 23!
AT(J) = 6.2
ELSEIF P(J) = .35 THEN AD(J) = 21!
AT(J) = 5.9
ELSEIF P(J) = .3 THEN AD(J) = 19!
AT(J) = 5.6
ELSEIF P(J) = .25 THEN AD(J) = 17!
AT(J) = 5.2
ELSEIF P(J) = .2 THEN AD(J) = 15!
AT(J) = 4.8
ELSEIF P(J) = .15 THEN AD(J) = 13!
AT(J) = 4.4
ELSEIF P(J) = .1 THEN AD(J) = 11!
AT(J) = 4!
ELSEIF P(J) = .05 THEN AD(J) = 9!
AT(J) = 3.6
ELSEIF P(J) = .025 THEN AD(J) = 6!
AT(J) = 3.2
ELSEIF P(J) = .02 THEN AD(J) = 4!
AT(J) = 2.8
ELSEIF P(J) = .1 THEN AD(J) = 2!
AT(J) = 2.2
ELSEIF P(J) = .01 THEN AD(J) = 1!
AT(J) = 1.8
ELSEIF P(J) = .001 THEN AD(J) = 0.1!
AT(J) = 1.6
ELSEIF P(J) = .0001 THEN AD(J) = 0.01!
AT(J) = 1.4
ELSEIF P(J) = .00001 THEN AD(J) = 0.001!
AT(J) = 1.2
ELSEIF P(J) = .0000001 THEN AD(J) = 0.0001!
AT(J) = 1.1
ELSEIF P(J) = .00000001 THEN AD(J) = 0.00001!
AT(J) = 1
ELSE IF P(J) = .000000001 THEN AD(J) = 0.000001!
AT(J) = 1
ELSE
PRINT "THERE IS AN ERROR IN DATA"
END IF

' CONVERT FROM ANGSTROMS TO CM
D(J) = AD(J) * 1E-08
T(J) = AT(J) * 1E-08
NEXT J
V(1) = XL(1)
R(1) = 100
A(1) = 0
'A IS SURFACE AREA
DAV(1) = D(1)
DL(1) = LOG(D(1))
ADAV(1) = DAV(1) * 1E+08
DDAV(1) = LOG(ADAV(1))
FOR J = 2 TO N - 1
DELX(J) = XL(J) - XL(J - 1)
DELT(J) = T(J) - T(J - 1)
C(J) = A(J - 1) * ABS(DELT(J))
\[
\begin{align*}
E(J) &= \text{ABS}(\text{DELX}(J)) - \text{ABS}(C(I)) \\
F(J) &= (D(J - 1) / (D(J - 1) - 2 * T(J - 1))) \\
\text{DELV}(J) &= \text{ABS}(E(J)) \times \text{ABS}(F(J)) \\
\text{DELV INCREMENTAL VOLUME} \\
V(J) &= \text{ABS}(V(J - 1)) - \text{ABS}(\text{DELV}(J)) \\
A(J) &= (X(J) - V(J)) / T(J) \\
\text{DAV}(J) &= (D(J) + D(J - 1)) / 2 \\
\text{ADAV}(J) &= \text{DAV}(J) \times 1E+08 \\
\text{DL}(J) &= \log(D(J)) \\
\text{DELD}(J) &= (\text{DL}(J) - \text{DL}(J - 1)) \\
\text{YAX}(J) &= \text{ABS}(\text{DELV}(J)) / \text{ABS}(\text{DELD}(J)) \\
\text{'YAX IS THE PORE SIZE DISTRIBUTION FUNCTION} \\
R(J) &= (V(J) / V(1)) \times 100 \\
\text{'R(J) IS THE CUMULATIVE PORE SIZE DISTRIBUTION} \\
\text{NEXT J} \\
\end{align*}
\]

'PRINT OUR RESULTS

\[
\begin{align*}
\text{INPUT "ENTER FILENAME TO STORE RESULTS IN"; NAMES} \\
\text{OPEN NAMES FOR OUTPUT AS #1} \\
\text{FOR J = 1 TO N - 1} \\
\text{PRINT #1, USING "###.###  #.####  ##.####  ####.####"; AD(J); R(J); YAX(J); ADAV(J)} \\
\text{PRINT USING "###.###  #.####  ##.####  ####.####"; AD(J); R(J); YAX(J); ADAV(J)} \\
\text{NEXT J} \\
\text{PRINT #1, "PORE VOLUME="}, V(1) \\
\text{PRINT "PORE VOLUME="}, V(1) \\
\end{align*}
\]

'EXAMPLE DATA INPUT FORMAT

'FOLLOWING DATA FOR PURE LINWOOD CALCIUM HYDROXIDE P.S.D.

'DATA 14

'EXAMPLE DATA

'FOLLOWING DATA FOR PURE LINWOOD CALCIUM HYDROXIDE P.S.D.

'DATA 14

'EXAMPLE DATA

'FOLLOWING DATA FOR PURE LINWOOD CALCIUM HYDROXIDE P.S.D.

'DATA 14

END
QuickBasic program for surface area distribution analysis for cylindrical and parallel plate pore structure.  

' THIS IS A QUICKBASIC PROGRAM TO CALCULATE CUMULATIVE SIZE DISTRIBUTION FROM CUMULATIVE PORE VOLUME DISTRIBUTION FOR A CYLINDRICAL PORE MODEL.

DIM P(12), VG(12), RK(12), T(12), RP(12), RKA(12), DT(12)
DIM DVG(12), DVL(12), DTSA(12), VP(12), A(12), SA(12)
READ N
FOR J = 1 TO N
READ P(J), VG(J)
' P IS RELATIVE PRESSURE AND VG IS VOLUME UPTAKE OF NITROGEN GAS FROM BET.
NEXT J
IF P(J) = .98 THEN
  RK(J) = 473
  T(J) = 22.1
ELSEIF P(J) = .96 THEN RK(J) = 234
  T(J) = 17.3
ELSEIF P(J) = .95 THEN RK(J) = 186.1
  T(J) = 16.2
ELSEIF P(J) = .94 THEN RK(J) = 154
  T(J) = 15.3
ELSEIF P(J) = .925 THEN RK(J) = 122.5
  T(J) = 14
ELSEIF P(J) = .9 THEN RK(J) = 90.6
  T(J) = 12.7
ELSEIF P(J) = .88 THEN RK(J) = 74.7
  T(J) = 11.9
ELSEIF P(J) = .8 THEN RK(J) = 42.8
  T(J) = 9.9
ELSEIF P(J) = .6 THEN RK(J) = 18.7
  T(J) = 7.5
ELSEIF P(J) = .35 THEN RK(J) = 9.1
  T(J) = 5.9
ELSE
  PRINT "ERROR IN DATA"
END IF
RP(J) = RK(J) + T(J)
' THIS IS A QUICKBASIC PROGRAM TO CALCULATE CUMULATIVE SURFACE AREA DISTRIBUTION FROM CUMULATIVE PORE VOLUME DISTRIBUTION FOR A PARALLEL PLATE MODEL. THIS METHOD IS SIMILAR TO THE CYLINDRICAL PORE MODEL.

DIM P(12), VG(12), RK(12), T(12), RP(12), RKA(12), DT(12)
DIM DVG(12), DVL(12), DTSA(12), VP(12), A(12), SA(12)
READ N
FOR J = 1 TO N
READ P(J), VG(J)
NEXT J
FOR J = 1 TO N
IF P(J) = .98 THEN
RK(J) = 471.6
T(J) = 23.2
ELSEIF P(J) = .96 THEN RK(J) = 233.6
T(J) = 20.1
ELSEIF P(J) = .95 THEN RK(J) = 187.8
T(J) = 18.6
ELSEIF P(J) = .925 THEN RK(J) = 122.4
ENDIF
NEXT J

NEXT J
FOR J = 1 TO N - 1
RKA(J) = (RK(J) + RK(J + 1)) / 2
RPA(J) = (RP(J) + RP(J + 1)) / 2
DT(J) = T(J) - T(J + 1)
DVG(J) = VG(J) - VG(J + 1)

's CONVERT TO VOLUME OF LIQUID NITROGEN
DVL(J) = DVG(J) * .00154
NEXT J

FOR J = 1 TO N - 1
IF J = 1 THEN
DTSA(J) = 0!
ELSE
DTSA(J) = DT(J) * 1E-10 + SA(J - 1) * 100000!
ENDIF
ENDIF
FOR I = 1 TO J
SUM = SUM + A(I)
NEXT I
SA(J) = SUM
PRINT RP(J + 1), SA(J)
NEXT J

' EXAMPLE DATA ENTRY FORMAT
' FORSBY 4" CALCINATION 1080, FEB8-2
' DATA .98,140.,.96,84.,.95,79.4,.925,67.2,.9,64.4,.8,49.,.6,33.6,.35,16.8
END
T(I) = 16.8
ELSEIF P(I) = .9 THEN RK(I) = 90!
T(J) = 15!
ELSEIF P(J) = .85 THEN RK(J) = 64.4
T(I) = 12.8
ELSEIF P(J) = .8 THEN RK(J) = 46.2
T(J) = 11.4
ELSEIF P(J) = .6 THEN RK(J) = 19!
T(J) = 8!
ELSEIF P(J) = .5 THEN RK(J) = 14!
T(J) = 7!
ELSEIF P(J) = .45 THEN RK(J) = 11.8
T(J) = 6.6
ELSEIF P(J) = .4 THEN RK(J) = 10.6
T(J) = 6.2
ELSEIF P(J) = .35 THEN RK(J) = 9.2
T(J) = 5.9
ELSE
PRINT "ERROR IN DATA"
END IF
RP(J) = RK(J) + 2! * T(J)
NEXT J
FOR J = 1 TO N - 1
RKA(J) = (RK(J) + RK(J + 1)) / 2
RPA(J) = (RP(J) + RP(J + 1)) / 2
DT(J) = T(J) - T(J + 1)
DVG(J) = VG(J) - VG(J + 1)
DVL(J) = DVG(J) * .00154
NEXT J
FOR J = 1 TO N - 1
IF J = 1 THEN
DTSA(J) = 0!
ELSE
DTSA(J) = DT(J) * 1E-10 * SA(J - 1) * 1000000!
END IF
VP(J) = (DVL(J) - DTSA(J)) * (RPA(J) / RKA(J))
A(J) = 2! * VP(J) / RPA(I) * 10000!
SUM = 0!
FOR I = 1 TO I
SUM = SUM + A(I)
NEXT I
SA(T) = SUM
PRINT RP(J), SA(J)
NEXT J

EXAMPLE DATA ENTRY FORMAT
'linwood caoh2 1080 4'calcination, jul26-1
'data 8
'data .98,57.4,.96,40.9,.95,37.1,.925,29.5,.9,23.4,.8,15.6,.6,9.87,.35,6.4

END
FORTRAN Program for the comprehensive calcination, sintering and sulfation model.

```fortran
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/ RNG(5000),RCN(5000),CBCN(5000)
COMMON /BLOCK7/ BN(5000),SCN(5000),SCPGMN(5000),STOTGN(5000)
COMMON /BLOCK8/ TOTCAO
COMMON /BLOCK9/ porprol,caoperg,caoperv,proavg
COMMON /block10/ akss,dps,epsilon,beta,tau,xs,alo

character*20 fileinp, fileout

WRITE(6,*) 'ENTER NAME OF DATA FILE, INCLUDE DAT'
READ(5,'(A20)') FILEINP
OPEN(UNIT=4,FILE=FILEINP,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')
write(6,*) 'give values of akss and dps and alo'
read(5,*) akss, dps, alo

NOMENCLATURE:

DP: Diffusivity, H2O in N2, m2/s
AKC: Reaction constant
AKS: Sintering constant
CBS: Concentration of H2O at saturation, gmol/m3
SCA: Asymtotic S. A. of CaO, m2/gmol
SCNA: Nascent S. A. of CaO, m2/gmol
SHNA: S. A. of Caoh2, m2/gmol
RHOH: True density of Caoh2, 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 Caoh2 left, gmol
A+B=1, basis: 1 gmol of Caoh2.

APPENDIX D
```
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 Ca(OH)₂, m² per gram basis, remains constant
SH: S. A of Ca(OH)₂, 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.

TEMK=1173.
DP=9.E-5*(TEMK/1223.)**1.5

IF(TEMK.EQ.1223.) GOTO 1
IF(TEMK.EQ.1323.) GOTO 2
IF(TEMK.EQ.1308.) GOTO 101
IF(TEMK.EQ.1353.) GOTO 201
GOTO 3
1  CBS=1.8E+3
   GOTO 4
2  CBS=3.35E+3
   GOTO 4
101 CBS=2.95E+3
   GOTO 4
201 CBS=3.67E+3
   GOTO 4
3  CBS=1.6E+3
   GOTO 4

4  SHNA=16.9*74.
   RHOH=2.4E+6
   RHOC=3.32E+6
   DELT=0.02E-3
   CSO=RHOH/74.
   NII=299.E-3/DELT

INITIAL CONDITIONS

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

Values of all variables (which are functions of X)

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.

WRITE(6,*') T(I),X(I),T(I),X(I)

ICTR=1
10 IF(T(I).GT.0.05) DELT=0.1E-3
CALL RK(I)

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+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)
SC(I)=SCN(I-1)
SPGM(I)=SPGMN(I-1)
CBC(I)=CBCN(I-1)
STOTG(I)=STOTGN(I-1)

CALL sulfation(T,X,I)

WRITE(5,21)(i),proavg,caoperv,epsilon,beta
WRITE(3,21)(i),proavg,caoperv,epsilon,beta


ICTR=1
40 IF(T(I).GT..29) GO TO 20
GO TO 10

20 WRITE(3,*') AKC,AKS,CONKS,SCNA,TEMK,SCA
write(3,*') akss,dps,alo
STOP
END

subroutine sulfation (T,X,I)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON /BLOCKS/ TOTCAO
common /block9/ porprol,caoperg,caoperv,proavg
common /block10/ akss,dps,epsilon,beta,tau,xs,alo
COMMON /BLOCK7/ BN(5000),SCN(5000),SPGMN(5000),STOTGN(5000)
COMMON /BLOCK3/ RC(5000),RG(5000),RHO(5000),SPGM(5000),SHGM(5000)
COMMON /BLOCK1/ AKC,DP,CBS,AKS,SCA,SCNA,SHNA,RHOH,ROC,CSO,CONKS
COMMON /BLOCK4/ SC(5000),SH(5000),STOT(5000),STOTG(5000)

spro = sc(i)/totcao
PROAVG = 0.49 - 0.49/(SCPGM(1)-SCA)*(SCPGM(1)-Spro)

totvol = caovol
caovol = totcao * 56.332/1000000
C
totvol is in m3
caoperv = caoperg * totcao * 56. / totvol
C
cao is in m2/m3

epsilon = 4.227 * alo * (1. - proavg) / caoperv / caoperv
betal = 2. * akss * 3.32 * (1. - proavg) / 56. / caoperv
beta = (betal + betaold) / 2.
beta = 40.

C
cbulks = 3900. / 22.4 / 1000.
C
cbulks is in gmol/m3

tau = akss * cbulks * caoperv * T(I) / (1. - proavg)
z = 2.86

C
term1 = sqrt(1. + beta * z * tau)
term2 = (1. - beta * z / epsilon)
term3 = (term1 - term2) * (term1 - term2)
term4 = epsilon / beta / beta / z / z

term5 = 1. / epsilon - term4
xs = 1. - exp(term5)
betaold = beta

return
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 /BLOCK5/ B(5000),A(5000),CBC(5000)
COMMON /block9/ porprol,caoperg,caoperv,proavg

C

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

C

CAY1 = DXT
XN(I) = X(I) + DXT * DELT/2.
TN(I) = T(I) + DELT/2.
CALL FUNCT(TN,XN,T,X,IDXDT)
CAY2 = DXDT
XN(I) = X(I) + DXDT * DELT/2.
CALL FUNCT(TN,XN,T,X,I,DXDT)

CAY3 = DXDT
TN(I) = TN(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), TN(5000), XN(5000), TN(5000)
COMMON / BLOCK6/ RGN(5000), RCN(5000), CBCN(5000)
COMMON / BLOCK7/ BCAO, CAO, CAOP, CAOPR, CAOPC, CAOPFR, PROCA, PROCAO
CALL SURFRAD(TN,XN,T,X,I)
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)
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
CALL SURFRAD(TN,XN,T,X,I)
RETURN
END

C
CALL SURFRAD(TN,XN,T,X,I)
C
CALCULATE DXDT
C
CRITERIA = 0.99 * CBS
IF(CBCN(I) .GE. CRITERIA) CBCN(I) = CRITERIA
DXDT = 3 * RCN(I) ** 2 * AKC * (CBS - CBCN(I)) / (RGNa) ** 3 * CSO)
C
RETURN
END
This is the real work-horse subroutine. It calculates everything!!

```fortran
DIMENSION X(5000), T(5000), XN(5000), TN(5000)
DIMENSION AN(5000), SHN(5000)
DIMENSION STOTN(5000), RHON(5000)

Calculate incremental CaO formed over the previuos

BN(I)=XN(I)-X(I)
AN(I)=1.-BN(I)

SURFACE AREA CALCULATION

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

Term2 is the single most important term calculated,

TERM2=0.
DO 100 J=1, I
AKSN=AKS*(1.+CONKS*(CBC(J-100)/2.))**0.17
TERM2=TERM2+((SCPM(I)-SCA)+AKSN*(TN(I)-T(J)))*B(J)
100 FORMAT(1X,E10.5,1X,E10.5,1X,E12.5,1X,E12.5,1X,E12.5)

Total CaO S. A. m2

SCN(I)=TERM1+TERM2

AMOUNT CAO CALCULATION

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

Calculate S.A per g, g/mol etc.

SHN(I)=SHNA*(1.-TOTCAO)
STOTN(I)=SCN(I)+SHN(I)
TOTGN=TOTCAO*56.+(1.-TOTCAO)*74.

IF(TOTCAO.EQ.0.) GOTO 36
CAOPRG=SCN(I)/(TOTCAO*56.)
HYDPERG=SHN(I)/((1.-TOTCAO)*74.)
STOTGN(I)=CAOPRG*XN(I)+HYDPERG*(1.-XN(I))
GOTO 37

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

"Average true" DENSITY CALCULATION

37 FRACH=(1.-TOTCAO)*74./TOTGN
FRACC=TOTCAO*56./TOTGN
RHON(I)=FRACH*RHOH+FRACC*RHOC
```
ONE WAY OF CALCULATING RADIUS OF GRAIN AND CORE CALCULATION

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

CALCULATE POROSITY & DIFFUSIVITY EFFECTIVE
ONE WAY OF CALCULATING POROSITY OF PRODUCT, HOME-DEVISED

IF(RGN(I).EQ.RCN(I)) GOTO 51
C
ANUM1=TOTCAO*4./3.*(22./7.)*(RG(I)**3)*RHOH/74.
C
ANUM=ANUM1/(RHO/56.)
C
ADEN=4./3.*(22./7.)*(RGN(I)**3-RCN(I)**3)
C
PORPRO=1.-ANUM/ADEN
C
ANOTHER WAY OF CALCULATING POROSITY OF PRODUCT, FROM MILNE
IF(I.GT.2) GO TO 34
C
PORPRO1=0.4529-(0.4529/(SCPGM(I)-SCA))*(SCPGM(I)-SCPGMN(I))
GOTO 35
C
SHPRO=SCA+I/(1./(SCPGM(2)-SCA)+AKSN*(TN(I)-T(2)))
PORPRO1=0.4529-(0.4529/(SCPGM(I)-SCA))*(SCPGM(I)-SHPRO)
C
35
RCN(I)=RG(I)*(1.-XN(I))**(1./3.)
C
WRITE(5,*) RCN(I)
C
TERMA=RCN(I)**3.
C
TERMB=(RHOH/74.)*(RG(I)**3.-RCN(I)**3.)
C
TERMB=TERMB/(RHO/56.)/(1.-PORPRO1)
C
TFIN=(TERMA+TERMB)
C
RGN(I)=TFIN**(1./3.)
C
RCN(I)=TERMA**(1./3.)
C
WRITE(5,* ) TERMA,TERMB
C
WRITE(5,* ) RGN(I),RCN(I)
C
Calculate Knudsen diffusivity

PORRAD=2.*PORPRO1/(SCPGMN(I)*RHO/56.)
D=97.*PORRAD*(TEMK/18.)**0.5
DPEFF=1./(1./DK+1./DP)
DPN=DPEFF*PORPRO1**2
GO TO 32
C
CALCULATE PRODUCT GAS CONCENTRATION AT INTERFACE.

32
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))
C
CBCN(I)=UP/DOWN
C
RETURN
END
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