Kinetics of High-Pressure Removal of Hydrogen Sulfide Using Calcium Oxide Powder

Shriniwas S. Chauk, Rajeev Agnihotri, Raja A. Jadhav, Santhosh K. Misro, and Liang-Shih Fan
Dept. of Chemical Engineering, The Ohio State University, Columbus, OH 43210

Sulfidation reaction of CaO at high pressure (up to 2 MPa) and high temperature (up to 900°C) to remove H_2S in a coal-fired gasifier was studied in a high-pressure and temperature differential-bed flow-through reactor. Experimental conditions selected are typical for pressurized gasifiers. Effects of total pressure, H_2S partial pressure, reaction temperature, fuel gas composition, and CaO surface area on the extent of sulfur capture and sorbent conversions were determined. The gasifier pressure affected the in-situ calcination of calcium carbonate particles through reduction in available surface area and pore volume of CaO formed, thus limiting the sulfidation conversion. Time-resolved conversion data of CaO sulfidation were analyzed using a modified grain model. The model incorporates external and internal diffusion, surface reaction, product layer diffusion, and the structural changes of the sulfiding CaO particle. The activation energy for the reaction was 37 kcal/mol. The estimated product layer diffusivity was 8×10^{-15} m^2/s at 800°C with an associated activation energy of 38.4 kcal/mol—typical of solid state diffusion of ionic species through the product layer. The extent of conversion increased with increasing initial surface area and porosity of CaO particles. The high-pressure sulfidation reaction data for CaO will be useful in understanding and optimizing the in-gasifier H_2S capture using calcium-based sorbents.

Introduction

Coal finds its principal use in electrical power generation. More than half of the electricity in the U.S. is generated from coal. Plentiful supplies of coal reserves distributed all over the globe should suffice for the next few centuries. In the light of rapidly diminishing fossil fuels other than coal, continued and increased use of coal certainly seems an economically attractive option. However, the environmental issues related to coal-fired power-generating plants could potentially limit its use and effectiveness (U.S. Dept. of Energy, 1992).

New clean coal technologies, such as Integrated Gasification Combined Cycle (IGCC), are projected to greatly improve efficiency while reducing air pollution. Commercial success of these advanced coal-based power-generating systems is greatly dependent on the accompanying air-pollution control systems. The IGCC technology with a projected efficiency of 52% is considered to be one of the potential technologies that would meet the energy and environmental demands of the future (U.S. Dept. of Energy, 1994a,b).

Under the reducing conditions encountered in the advanced integrated gasification systems, sulfur in the coal transforms into H_2S as the primary gas-phase sulfur species with COS (carbonyl sulfide) and CS_2 (carbon disulfide) forming the secondary sulfur species. Recent advances in high-efficiency power generating units (PFB/IGCC) (Frey and Rubin, 1992) require that gasifiers should be operated under higher pressures (1−2 MPa) and temperatures (800−950°C). In such processes, the fuel gases should be cleaned prior to sending them through the gas turbine. The gas cleanup is necessary not only for the protection of the gas turbine hardware, but also to comply with the stringent environmental regulations. It is also necessary to clean fuel gases at high temperatures and pressures in order to maintain the overall high efficiency of these processes. Coal gas desulfurization to sufficiently low levels at temperatures greater than 600°C and at gasifier pressures of 1−2 MPa is now recognized as a crucial step in realizing efficient and economical coal utilization in IGCC systems. One of the strategies to achieve this goal is to remove the majority of the fuel-bound sulfur in-gasifier by

---

Correspondence concerning this article should be addressed to L.-S. Fan.

using calcium-based sorbents. Post-gasifier desulfurization is undertaken to polish the product gas to reduce the remaining H_2S concentration to less than 50 ppm (Mojtahedi et al., 1994). Expensive novel sorbents (usually metal oxides) are used in the polishing units to reduce H_2S to desired levels. According to thermodynamic calculations, it is possible to reduce 98% of H_2S (from 4,000 ppmv to levels as low as 80 ppmv) (Fenouil et al., 1994) from fuel gases by using Ca-based sorbents and thereby reducing the load on expensive post-gasifier polishing units. However, there is a lack of relevant high-pressure sulfidation kinetic data to support this claim.

The high-pressure and high-temperature ''in-gasifier'' H_2S removal using calcium-based sorbents represents an attractive option from economic and reactivity aspects. The existing technologies developed for SO_2 removal from coal-fired combustors involving Ca-based sorbents ($Ca(OH_2)$ and $CaCO_3$) can also be applied to H_2S removal with suitable modifications (Borgwardt, 1984; Borgwardt et al., 1984). Sulfur capture in reducing conditions using Ca-based sorbents results in the formation of a higher molar volume product (CaS), however, theoretical calculations and experimental data have shown that complete sorbent utilization and higher levels of sulfur removal can be attained under these conditions (Efthimiadis and Sotirchos, 1992; Lindgren et al., 1992).

In a pressurized gasifier there exists a spatial distribution of temperature and gas-phase composition. At any location depending on the temperature, the CO_2 partial pressure may be higher or lower than the equilibrium partial pressure for limestone calcination. Thus, both calcined limestone (CaO) and uncalcined limestone ($CaCO_3$) can react with H_2S according to reactions

$$CaO + H_2S \leftrightarrow CaS + H_2O \qquad \text{(oxide sulfidation)} \qquad (1)$$

$$CaCO_3 + H_2S \leftrightarrow CaS + H_2O + CO_2 \quad \text{(carbonate sulfidation)} \qquad (2)$$

These reactions are well researched and a number of researchers have reported kinetic data pertaining to the reaction between CaO and H_2S at ambient and high pressures using gravimetric techniques in the temperature range of 650–1,050°C (Pell, 1971; Squires et al., 1971; Camp, 1979; Westmooreland et al., 1977; Borgwardt et al., 1984; Heesink and van Swaaij, 1995; Yrjas et al., 1996; Zevenhoven et al., 1998). However, there is no consensus regarding the magnitudes of basic kinetic parameters for this reaction, such as the order of reaction and activation energy. Squires et al. (1971) reported the ambient pressure sulfidation reaction of CaO to have an activation energy of 23 kcal/mol and the reaction to be first-order with respect to H_2S partial pressure. Attar and Dupuis (1979) reported an activation energy of 37 kcal/mol. Simons and Rawlins (1980) using the atmospheric pressure sulfidation data obtained by Kearins et al. (1973) reported the activation energy to be only 10 kcal/mol. Freund (1984), after taking pore-diffusion into account, determined the apparent activation energy to be 45.5 kcal/mol for 115 μm CaO particle in the temperature range of 1,125–1,425°C. Heesink and van Swaaij (1995) reported a value of 38 kcal/mol. The order of CaO sulfidation reaction with respect to H_2S partial pressure has been determined by various researchers to be in the range of 0.5 to 1 (Squires et al., 1971; Pell, 1971; Westmooreland et al., 1977; Camp, 1979; Heesink and van Swaaij, 1995).

Sulfidation reaction of CaO is relatively fast and conversions up to 100% can be obtained (O'Neil et al., 1972; Attar and Dupuis, 1979; Efthimiadis and Sotirchos, 1992). Sulfidation of CaO is thermodynamically favorable and is strongly dependent on equilibrium partial pressure of H_2S at all temperatures of interest (650–1,300°C) (Lindgren et al., 1992). Researchers have reported that in the temperature range of 550–1,015°C the sulfidation reaction of calcium-based sorbents is governed by thermodynamic variables, such as temperature, pressure, and gas-phase composition. Sintering kinetics of CaO and/or CaS also determined the rate of sulfidation of Ca-based sorbents. Efthimiadis and Sotirchos (1992) reported that the sulfidation of CaO is more efficient than sulfation and attributed that behavior to a lower molar volume of CaS (29 cm^3/mol) than that of $CaSO_4$ (46 cm^3/mol). Fenouil and Lynn (1995a,b,c) conducted extensive research to compare the reaction kinetics and the completeness of the sulfidation of CaO and $CaCO_3$ in three different types of Ca-based sorbents: limestone, dolomite, and dolomitic limestone. They concluded that, at atmospheric pressure and for temperatures slightly above the calcination temperature of $CaCO_3$, all three sorbents showed complete CaO utilization. Fenouil et al. (1994) have also reported that the sintering mechanism of the CaS product layer plays a significant role in determining the reaction rate and sorbent utilization. Efthimiadis and Sotirchos (1992) reported a strong dependence of sulfidation reaction rate on the particle size of the sorbent and its internal pore structure for atmospheric pressure CaO sulfidation in the temperature range of 750–850°C. Yrjas et al. (1996) reported the kinetic data for calcined and uncalcined limestone sulfidation at elevated pressure of 2 MPa in the temperature range of 750–950°C. Their experiments were conducted in pressurized thermobalance equipment. They concluded that under identical conditions calcined limestone reacted with H_2S to a much greater extent than the uncalcined limestone.

Mechanism of CaO-H_2S reaction has been examined by various researchers and two different reaction mechanisms are proposed (Borgwardt et al., 1984; Nguyen and Watkinson, 1993; Heesink and Van Swaaij, 1995; Agnihotri et al., 1999). Borgwardt et al. (1984) and Nguyen and Watkinson (1993) concluded that the initial rate of sulfidation reaction is determined by the reaction at the surface and the diffusion through the product layer becomes the rate-determining step at later stages of the reaction. From the activation energy values, it was concluded that the product layer diffusion may involve solid state diffusion with migration of S^{2-} ions through the CaS layer (Borgwardt et al., 1984). Contrary to the solid-state product layer diffusion mechanism, Heesink and van Swaaij (1995) proposed the sulfidation mechanism to involve pore diffusion though the porous CaS product layer. They proposed that during the initial stage of the reaction the entire CaO surface takes part in the reaction. However, as the reaction proceeds the CaO core becomes partly covered with CaS, which remains porous. These two proposed reaction mechanisms for atmospheric pressure sulfidation of CaO are derived from fitting the data to different models and are not experimentally verified in prior studies. In a recent study by Agnihotri et al. (1999), inert platinum marker experiments were conducted to obtain direct physical evidence for the CaO sulfidation reaction mechanism, which revealed that the reaction of CaO with H_2S is limited by transport and mobility of S^{2-} and O^{2-} ions through the CaS product layer.

It is well established that various species in reactant gas mixture interact in the gas phase, and the STP composition of the reactant gas mixture may not be representative of the composition under the actual reaction conditions. Water-gas-shift (WGS) reaction, CO-assisted H_2S decomposition, and thermal decomposition of H_2S are considered to be the main composition altering reactions in the pressure and temperature range of interest (Fenouil et al., 1994). These reactions can be represented as

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(Water-Gas-Shift reaction)} \tag{3}$$

$$CO + H_2S \leftrightarrow COS + H_2 \quad \text{(CO-assisted } H_2S \text{ decomposition)} \tag{4}$$

$$H_2S \leftrightarrow H_2 + 0.5\ S_2 \quad (H_2S \text{ thermal decomposition}) \tag{5}$$

They concluded that the equilibrium composition of the reacting gas could drastically change due to these reactions, and the effect of these reactions need to be taken into consideration, while studying the sulfidation characteristics of sorbents.

The objective of this study is to determine the kinetic parameters of high-pressure sulfidation of CaO. In this work, high-pressure and high-temperature sulfidation of CaO sorbent is studied in a flow-through differential-bed reactor. The reaction between CaO and H_2S is carried out under typical pressurized gasification conditions. Effects of various parameters, such as operating pressure, reaction temperature, H_2S partial pressure, gas-phase composition, and initial sorbent structural properties on sulfidation characteristics of fine CaO particles, are investigated.

Experimental Studies

Apparatus

For investigating the sulfidation kinetics at the gasifier conditions of higher pressures and temperatures, a novel reactor system is designed. This reactor has the flexibility of operating under fixed bed (differential), as well as fluidized bed mode, and can be used as an entrained flow reactor with minor modifications. The overall reactor assembly is shown in Figure 1. The high-pressure and temperature reactor (HPTR) vessel is shown in Figure 2. The pressure vessel is designed to operate at pressures of up to 5 MPa and temperatures of up to 1,000°C. The reactor involves a dual shell design concept with an internal diffusion furnace. The 30 in. (760 mm) tall internal diffusion furnace (Thremcraft) is a vertical three-zone heater. The use of an internal diffusion furnace is necessary because of the high gas flow rates required under elevated pressures. The pressure vessel is made of alonized SS 316 and has internal insulation to avoid contact with the heater.

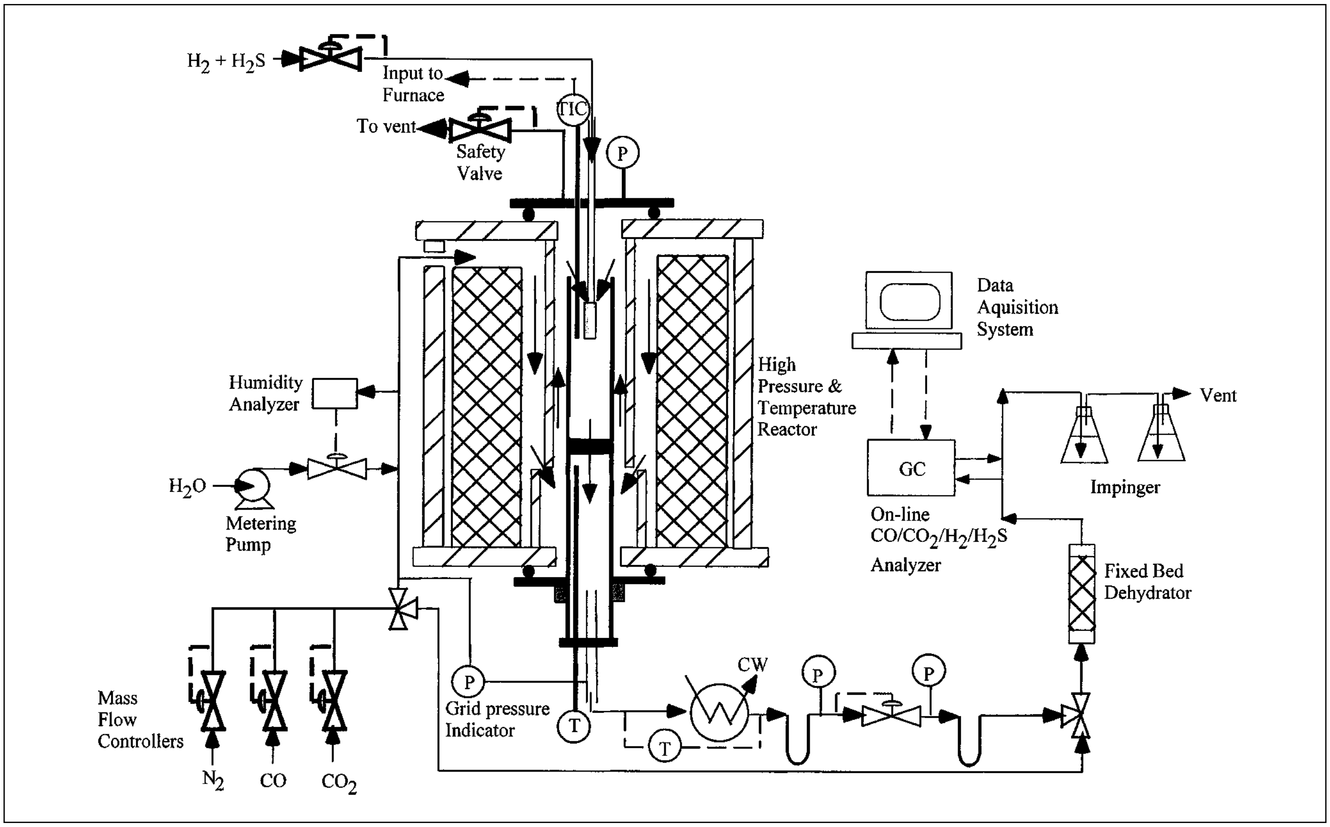


Figure 1. High-pressure and high temperature reactor (HPTR) assembly for studying CaO sulfidation.

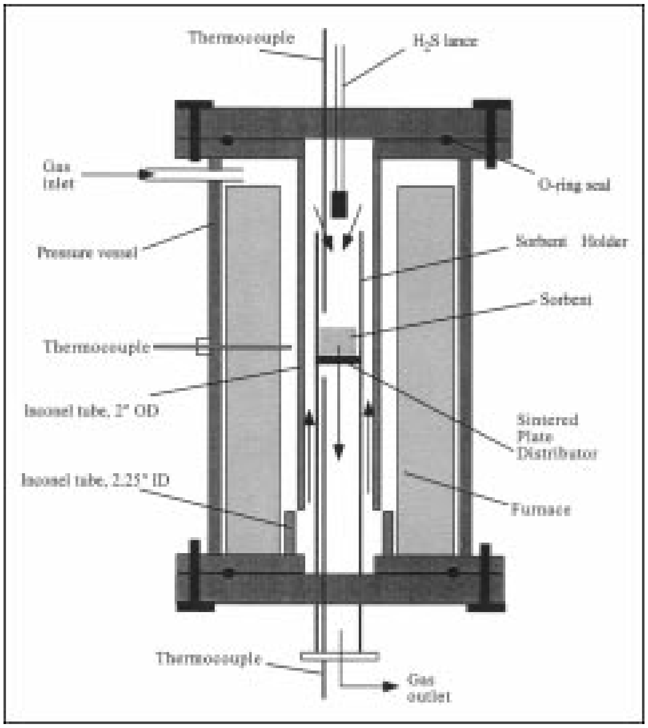


Figure 2. Details of the high-pressure and high temperature reactor (HPTR).

The main reactor consists of a 2 in. (51 mm) OD Inconel-600 tube housed in the pressure vessel. Inconel-600 is chosen due to its corrosion resistance against H_2S at the temperatures and pressures of interest here. In the dual-shell type of arrangement the reactor walls need not be thick due to the pressure balance. Furthermore, this type of reactor arrangement reduces the use of expensive materials of construction. The annular space between the Inconel tube and the inner core of internal diffusion furnace provides the preheating zone for the bulk of the reactant gases, and also provides enough time for all the gas-phase reactions, particularly the water-gas-shift reaction, to equilibrate. At the bottom of the reactor, the 2 in. (51 mm) OD Inconel tube slides inside a 2.25 in. (57 mm) ID Inconel tube, which allows the entry of the heated bulk gas into the 2 in. (51 mm) tube and also allows for the thermal expansion of the Inconel tubes. The 2 in. OD tube is 45 in. (1.1 m) long, whereas the 2.25 in. (57 mm) ID tube is 3 in. (76 mm) long. These two tubes are welded to the top and bottom flanges and sufficient clearance is left from the flanges to allow for thermal expansion. The flange plates at the top and bottom and the sidewalls of the pressure vessel have openings to accommodate thermocouples for close monitoring of gas temperatures both above and below the sorbent bed. The reactant gases (CO, CO_2 and N_2) are introduced in the outer shell of the pressure vessel, whereas H_2 and H_2S are introduced via a specially designed moveable lance, thus ensuring the alonized steel pressure vessel walls against coming in contact with H_2S.

A specially designed sorbent bed holder made from thick walled 0.5 in. (13 mm) OD quartz tube mounted on a kovar seal is inserted into the 2 in. tube from bottom and is held in position by a compression fitting welded to the lower flange. The quartz sorbent bed holder is designed to support the sorbent particles over a fritted ceramic disc, which can also act as a gas distributor for the fluidized-bed mode of operation. The total gas-flow rate through the sorbent bed at any given pressure and temperature condition is maintained at approximately 5 L/m.

The combination of individual gases is chosen such that the partial pressure of H_2S resulting from equilibrium gas-phase interactions (reactions 3, 4 and 5) would be at the desired value. The reactant gas selected in this study consists of 1–3 kPa H_2S, 2–5% CO, 1–3% CO_2 (calcining conditions), 2–10% H_2, and balance N_2. The presence of CO is essential to prevent oxidation of CaS to $CaSO_4$ by CO_2, whereas, H_2S thermal decomposition is reduced by the presence of H_2. Mass-flow controllers are used to deliver the precise amount of gases against the reactor pressure to give a predetermined reactant gas composition. In order to eliminate pressure fluctuations a line regulator is added downstream of the mass-flow controllers. The reactant gas mixture is introduced into the pressure vessel and is heated via direct contact with the internal diffusion furnace. Provision is made to determine the gas composition by the on-line gas chromatograph just prior to sending into the reactor and immediately after the gases exit the reactor. The exiting reactant gases from the reactor are quenched in a coiled condenser and condensed water is removed in the water knockout pot. A back-pressure regulator is used to maintain the reactor assembly at a predetermined pressure setting.

Procedure

High-pressure sulfidation of CaO is carried out in the differential-bed flow-through reactor at pressures in the range of 0.1 to 2 MPa and temperatures varying from 650 to 900°C. Differential conditions with respect to H_2S are maintained by using a high reactant gas-flow rate of 5 Lpm through the sorbent bed at the existing temperature and pressure. Prior to sulfidation, a small amount of calcium carbonate sorbent (20–25 mg) is dispersed finely on quartz wool and placed in the sorbent bed holder. The parent calcium carbonate sorbent is calcined *in-situ* by subjecting it to the reaction temperature and pressure under an inert nitrogen flow rate of 5 L/m for 10 min. The calcination step is analyzed for completeness using thermogravimetric analyzer. The calcined sorbent CaO (10–15 mg) is then subjected to the reactant gas. The extent of sulfidation is determined by wet chemistry methods after subjecting the CaO sorbent to the reactant gas stream for a specified time. Pre-weighted samples of partially sulfided CaO particles are dissolved in a standardized buffered iodine solution, and the resulting solution is titrated against a standardized arsenite solution to determine the amount of iodine unconsumed by reaction with CaS as per the reaction

$$CaS + I_2 \leftrightarrow Ca^{2+} + 2I^- + S \qquad (6)$$

From the amount of iodine remaining in the standard solution, the amount of sulfide and, hence, the CaO sorbent conversion is calculated.

Table 1. Chemical Composition and Initial Structural Properties of CaO Samples

	CaO-1*	CaO-2†	CaO-3‡
Composition (wt. %)			
CaO	97.0	97.0	99.0
SiO_2	0.8	0.8	0.2
Al_2O_3	0.5	0.5	0.2
MgO	1.0	1.0	0.4
Fe_2O_3	0.5	0.5	0.1
Trace Elements	0.2	0.2	0.1
Median Particle Size (d_{50}, μm)	7.8	7.7	6.3
BET Surface Area (m^2/g)	48.6	29.7	6.2
Pore Volume (cm^3/g)	0.18	0.12	0.042

*Obtained by calcination of High Reactivity Carbonate (Mahuli et al., 1997).

†Obtained by calcination of Linwood Carbonate (Linwood Mineral and Mining Co., Davenport, Iowa).

‡Aldrich Chemicals, Inc.

Sorbent materials

Sulfidation is conducted with three types of CaO sorbents, two prepared by an *in-situ* calcination of calcium carbonates and the other obtained from Aldrich Chemicals. Two different parent calcium carbonates are used: one is a commercially available Linwood Carbonate (LC) and the other is an in-house synthesized High Reactivity Carbonate (HRC). The sorbent structural properties, such as surface area, pore volume, pore-size distribution, and their alterations during conversion, greatly influence the sorbent conversion. Hence, the three CaO sorbents of varying structural properties (surface area and porosity) are used to study the effect of initial sorbent surface area on their sulfidation characteristics. The chemical compositions and structural properties of these CaO sorbents are presented in Table 1. Pore properties of the pre-calcined and commercial sorbents are determined by measuring the low-temperature nitrogen adsorption using the BET technique (Quantachrome NOVA 2000). The particle-size distribution is measured by Sedigraph 5100 (Micromeritics). The X-ray diffractograms (XRD) are used to identify the chemical species in partially sulfided CaO sorbents. The physical characteristics such as grain structure, surface morphology of CaO, and partially sulfided CaO are investigated using Scanning Electron Microscopy (SEM).

Calcium Oxide Sulfidation Model

The sulfidation reaction of CaO is analyzed based on a grain model (Szekely et al., 1976), and it is modified to account for the change in particle surface area and porosity. The overall concept of the model is illustrated in Figure 3. A single CaO particle is assumed to be composed of identical, spherical, nonoverlapping and nonporous grains (Figure 3a). The grains are considered to undergo sulfidation to varying extents depending on the local concentration of H_2S, which diffuses inward through the intergrain voids of the particle. Based on the findings of Agnihotri et al. (1999), the diffusion of S^{2-} ions (from H_2S) inwards through the nonporous product layer of CaS with eventual reaction at the CaO/CaS interface and counterdiffusion of O^{2-} ions (from CaO) outward to the CaS/H_2S interface are incorporated in the development of the model. CaS has a higher molar volume than CaO, which results in increased grain size and lowered surface area and porosity of the sulfiding particle. Thus, the partially sulfided CaO grains offer increased resistance to the transport of both H_2O and H_2S. At any given time, depending on the radial location of the grain, the grain size varies.

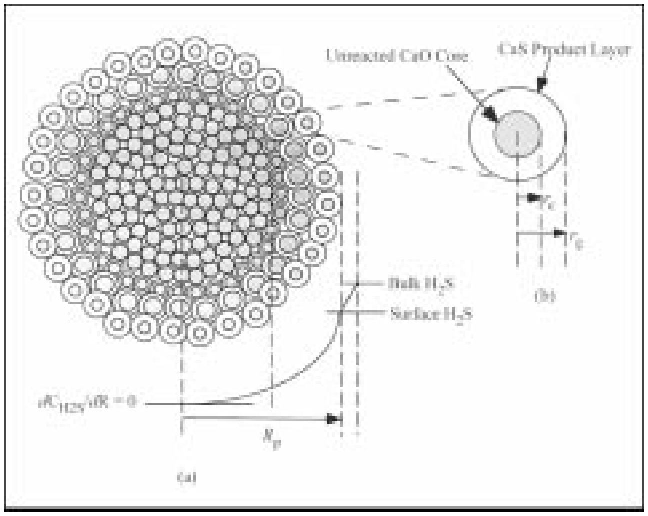


Figure 3. Sulfidation model.

(a) Single partially sulfided CaO particle; (b) partially sulfided CaO grain.

This model assumes that there are no intraparticle heat-transfer limitations. For small particles less than 10 μm in size, heatup and quenching have been shown to be extremely fast (Gullett et al., 1988; Alvfors and Svedberg, 1992). The model accounts for external mass-transfer resistance of H_2S from the bulk gas phase to the surface of the particle.

Model development

For irreversible reaction (reaction 1) and diffusion of H_2S in the CaO particle, assuming pseudo steady-state condition, the mass balance for H_2S can be written as

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2 D_{se}\frac{\partial C_{H_2S}}{\partial R}\right) - r_{H_2S} = 0 \qquad (7)$$

where

$$r_{H_2S} = \frac{3k_s r_c^2}{r_g^3}(1-\epsilon_s)C_{ion} \qquad (8)$$

C_{ion} represents the concentration of S^{2-} ions at the reaction interface. The local rate of reaction is assumed to be first-order with respect to ion concentration at the reaction interface. The boundary conditions are

$$D_{se}\frac{\partial C_{H_2S}}{\partial R}\bigg|_{R=R_p} = k_m\left(C_{bulk} - C_{H_2S}\right) \qquad (9)$$

$$\frac{\partial C_{H_2S}}{\partial R}\bigg|_{R=0} = 0 \qquad (10)$$

Both Knudsen and molecular diffusivities are considered to calculate D_{se}, the effective diffusivity of H_2S through the particle (m^2/s). The external mass-transfer coefficient k_m (m/s) is calculated using the Frossling correlation (Fogler, 1992). The local porosity following sulfidation is given as

$$\epsilon_s = \epsilon_0 - (z-1)(1-\epsilon_0)x_s \tag{11}$$

The reaction between S^{2-} and Ca^{2+} takes place at the interface of CaO/CaS. S^{2-} and O^{2-} ions counter-migrate in a coupled manner through the CaS layer to maintain the electrical neutrality of the product layer. The pseudo-steady-state condition can be applied (Bischoff, 1963; Bowen, 1965) and the radial concentration profile of the ions in the CaS layer is given by

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{\text{ion}}}{\partial r}\right) = 0 \tag{12}$$

with the following boundary conditions

$$C_{\text{ion}}|_{r=r_g} = C_{H_2S} \tag{13}$$

$$D_{\text{ion}} \left.\frac{\partial C_{\text{ion}}}{\partial r}\right|_{r=r_c} = k_s C_{\text{ion}} \tag{14}$$

where r_g and r_c represent the grain and the unreacted core radius (m), respectively.

The extent of sulfidation for a given grain can be determined by performing a solid reactant balance.

$$-\frac{dr_c}{dt} = \frac{k_s C_{\text{ion}}}{\rho_{\text{CaO}}} \tag{15}$$

The local conversion for a grain at a specific radial location inside the particle is given by

$$x_s = 1 - \left(\frac{r_c}{r_{go}}\right)^3 \tag{16}$$

The change in overall grain size is then obtained by taking into account the volume expansion due to sulfidation

$$r_g^3 = r_c^3 + z x_s r_{go}^3 \tag{17}$$

The overall conversion for the entire particle is calculated by integrating the local conversion over all the layers of grains

$$X_s = \frac{3\int_0^{R_p} x_s R^2 dR}{R_p^3} \tag{18}$$

The numerical simulation is carried out stepwise with time using the finite difference method. The equations for H_2S continuity and the solids conversion are coupled, and the implicit Crank-Nicolson technique is used to solve the initial value partial differential equations. The sulfidation model has two specific rate parameters k_s and D_{ion}, which are obtained from the best fit of experimental data and follow Arrhenius-type dependence with temperature.

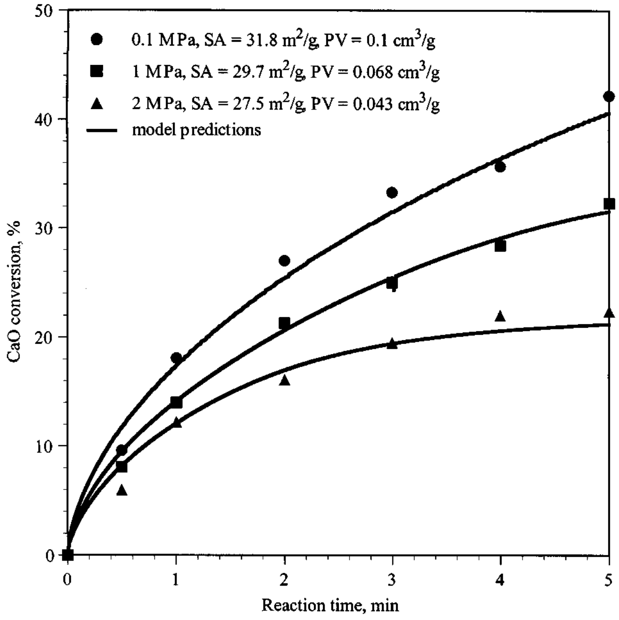


Figure 4. Effect of total pressure on CaO sulfidation.

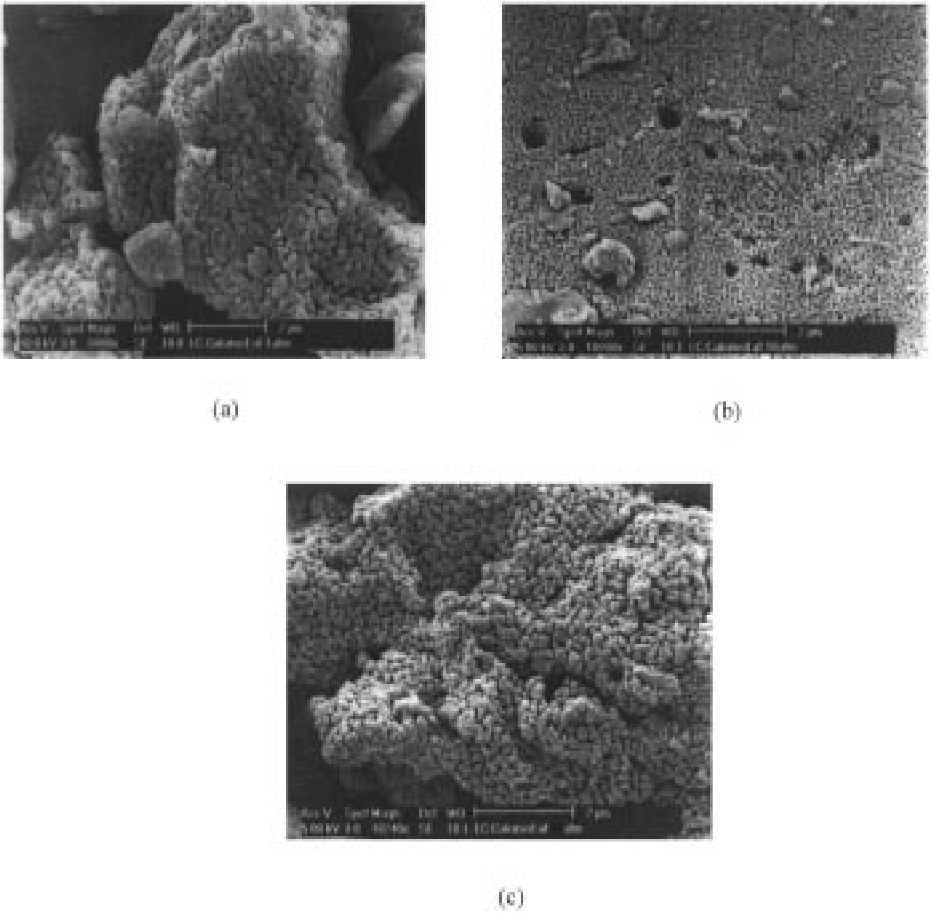
Reaction temperature: 800°C; H_2S partial pressure: 2,000 Pa.

Results and Discussion

Effect of total pressure

To study the effect of total pressure, the CaO sorbents are generated *in-situ* by calcining Linwood carbonate at the reaction pressure in the range of 0.1 to 2 MPa and temperature of 800°C under 5 L/m of N_2 flow. The *in-situ* generated sorbents are then exposed to the reactant gas mixture comprising of CO_2, CO, H_2, H_2S, and N_2. All the experiments are conducted under a constant H_2S partial pressure of 2 kPa. Figure 4 shows the effect of pressure on sulfidation conversion. As can be seen from the figure, increasing pressure had a negative effect on the combined calcination and sulfidation steps. Analyses of CaO generated by *in-situ* calcination at different total pressures revealed that total operating pressure had an adverse effect on its structural properties. Figures 5a, 5b, and 5c show the pressure induced morphological alterations of the CaO sorbents. The surface area decreased from 31.8 to 27.5 m^2/g, while the pore volume reduced drastically from 0.1 cm^3/g to 0.043 cm^3/g when the pressure increased from 0.1 to 2 MPa.

The loss in the surface area and porosity may be linked to the phenomenon of enhanced CaO sintering in the presence of CO_2. Calcination of calcium carbonate produces CO_2 at the $CaCO_3$/CaO interface, which diffuses out to the bulk through the CaO layer. The diffusivity of CO_2 is inversely proportional to pressure, which causes the CO_2 molecules to diffuse out relatively slowly at elevated pressures. It is well



(a)

(b)

(c)

Figure 5. Scanning electron micrographs of CaO sorbents generated by in-situ calcination at 800°C showing the pressure induced morphological alterations.

(a) Pressure: 0.1 MPa; surface area: 31.8 m^2/g; pore volume: 0.1 cm^3/g. (b) Pressure: 1 MPa; surface area: 29.7 m^2/g; pore volume: 0.068 cm^3/g. (c) Pressure: 2 MPa; surface area: 27.5 m^2/g; pore volume: 0.043 cm^3/g.

established that presence of CO_2 enhances the rate of sintering resulting in a loss of available surface area and porosity (Borgwardt, 1989). Thus, at elevated pressures, CO_2 molecules stay in the CaO layer for a relatively longer time causing reduction in the surface area and porosity due to increased sintering.

To discount the effect of pressure on CaO structural properties, high-pressure sulfidation experiments are conducted with precalcined and presintered CaO sorbents (CaO-2). These results indicated a negligible effect of total pressure (results not shown). However, in a pressurized gasifier, the calcium-based sorbents are introduced into the gasifier in the form of carbonate ($CaCO_3$), which calcines *in-situ* as calcination and sulfidation proceed simultaneously. Hence, it is important to study high-pressure sulfidation of CaO with varying initial structural properties.

Effect of sorbent surface area

Sorbent physical characteristics, such as surface area and pore volume also play a crucial part in determining the overall sorbent utilization and the rate of sulfidation reaction. In order to understand the effect of CaO surface area, sorbents with different surface areas (ranging from 6.2 m^2/g to 48.6 m^2/g) are used for sulfidation studies. All the CaO sorbents tested in this study (CaO-1, CaO-2, and CaO-3) have a mass median diameter (d_{50}) in the range of 6.3 to 7.8 μm to eliminate the effect of particle size on sulfidation characteristics of CaO. The effect of initial CaO surface area on the extent of sulfidation is shown in Figure 6. In each case the reaction is carried out at pressure of 1 MPa, temperature of 800°C, and a fixed H_2S partial pressure of 3 kPa. Figure 6 shows that the initial reaction rate and the extent of calcium oxide conversion at later stages of the reaction increase drastically with increasing initial sorbent surface area.

Sorbent particles with higher initial surface area and porosity offer higher reaction interface and lower diffusional resistance. This results in significantly higher overall sorbent conversions and higher initial reaction rates. A similar effect of initial sorbent surface area on sulfidation extent has also been reported by other researchers for calcined and uncalcined limestone sulfidation (Zevenhoven et al., 1998).

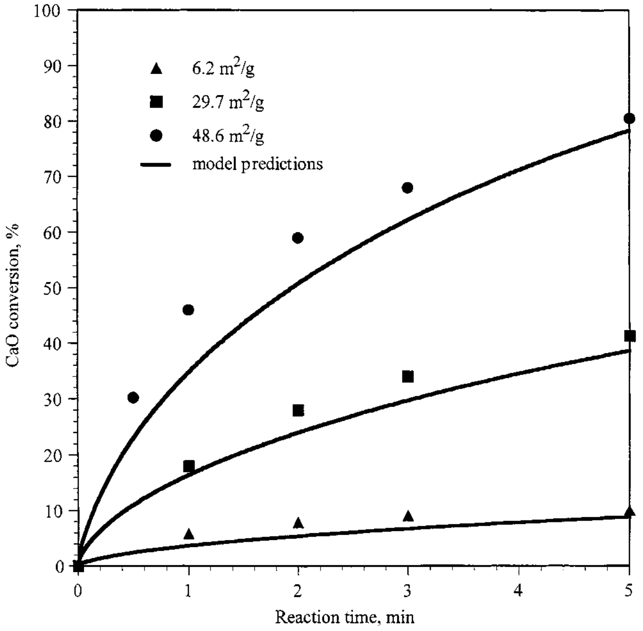


Figure 6. Effect of initial CaO specific surface area on sulfidation characteristics.

Total pressure: 1 MPa; reaction temperature: 800°C; H_2S partial pressure: 3,000 Pa.

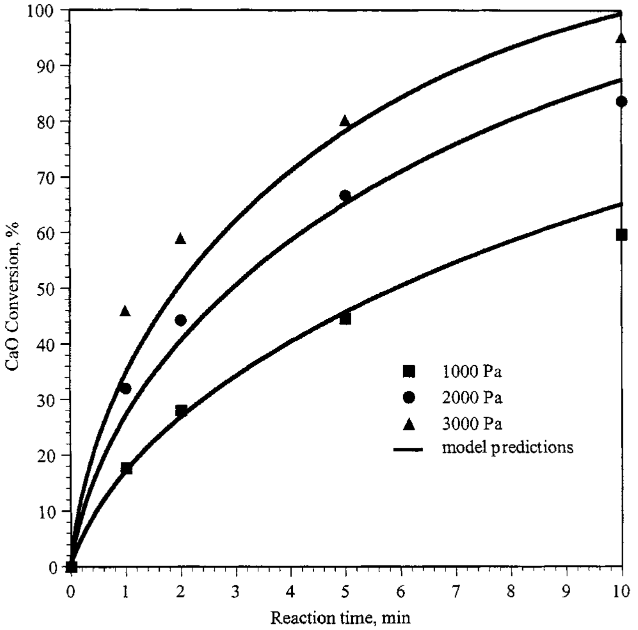


Figure 7. Effect of H_2S partial pressure on CaO sulfidation.

Total pressure: 1 MPa; reaction temperature: 800°C; CaO surface area: 48.6 m^2/g; pore volume: 0.18 cm^3/g.

Effect of H_2S partial pressure

Experiments are performed to determine the effect of H_2S partial pressure on the extent of CaO conversion. The overall pressure is maintained at a representative value of 1 MPa. Figure 7 shows the effect of H_2S partial pressure on sorbent conversion. The H_2S partial pressure is varied from 1 kPa (typical for low sulfur coal) to 3 kPa (typical for high sulfur coal). Experiments are conducted with pre-calcined CaO particles with initial specific surface area of 48.6 m^2/g and pore volume of 0.18 cm^3/g (CaO-1). As can be seen from the figure, the sulfidation of CaO increases with increasing H_2S partial pressure. From the initial rate of reaction, the order of reaction with respect to H_2S partial pressure is determined to be approximately 1, which compares favorably with the range of values reported in literature for ambient pressure sulfidation (Squires et al., 1971; Pell, 1971; Westmooreland et al., 1977; Camp, 1979; Borgwardt et al., 1984; Heesink and van Swaaij, 1995).

Effect of H_2 and CO partial pressure

Since H_2 is a major constituent of the coal gas, its effect on sulfidation of calcium oxide forms an integral part of this kinetic study. Figure 8 shows the effect of partial pressure of H_2 (in the form of H_2/H_2S ratio) on sorbent sulfidation conversion at 800°C and H_2S partial pressure of 3 kPa. Calcium oxide of initial surface area of 29.7 m^2/g and pore volume of 0.12 cm^3/g (CaO-2) is used. The total pressure is kept constant at 1 MPa. It can be seen from the figure that initially with increasing H_2 partial pressure the rate of sulfidation of CaO increases. The sulfidation conversion passes through a maximum at H_2/H_2S molar ratio of about 5 and then reduces as the partial pressure of H_2 is further increased. Initially, increasing the H_2 partial pressure retards the thermal decomposition of H_2S (reaction 5) and, thus, CaO particles are exposed to a higher partial pressure of H_2S.

As can be seen from Figure 8, CaO sulfidation is retarded at higher H_2 partial pressures. Attar (1982) concluded that

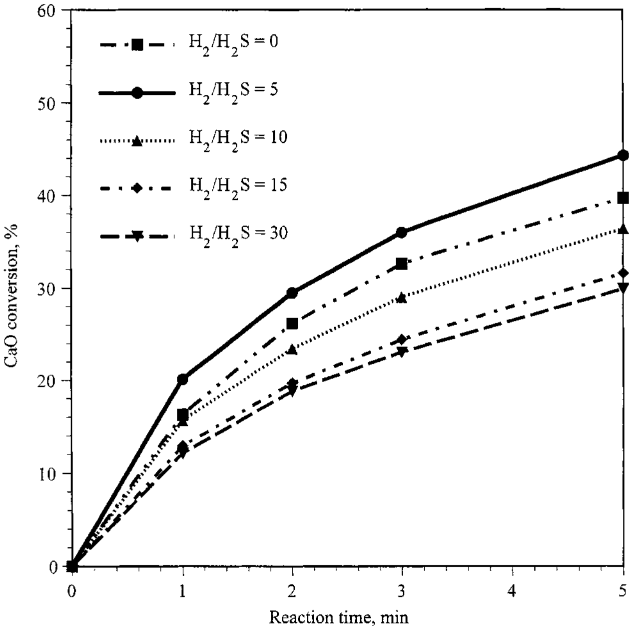


Figure 8. Effect of partial pressure of hydrogen on CaO sulfidation.

Total pressure: 1 MPa; reaction temperature: 800°C; CaO surface area: 29.7 m^2/g, H_2S partial pressure: 3,000 Pa.

the inhibitive effect of H_2 is due to the reversal of dissociation of the adsorbed surface complex to form H_2S rather than the desired product CaS. Borgwardt (1984) proposed an alternative to Attar's hypothesis by concluding that the permeability of CaS product formed in presence of H_2 is lower than that formed in absence of H_2. This hypothesis is based on the strong interaction between hydrogen inhibition and increased product layer diffusional resistance. Borgwardt et al. (1984) observed that the sulfidation reaction was product layer diffusion limited and, with increasing partial pressure of H_2, the sulfidation conversion was drastically reduced indicating that the pressure of H_2 was increasing the diffusional resistance through CaS product layer.

To study the effect of partial pressure of CO on CaO sulfidation, experiments are conducted with a pre-calcined and pre-sintered CaO (CaO-2) at 800°C and CO partial pressures ranging from 10 kPa to 100 kPa at a total pressure of 1 MPa and H_2S partial pressure of 3 kPa. It is found that CO partial pressure has a negligible effect on CaO sulfidation for the temperature and pressure ranges of study (results not shown).

Effect of temperature

To determine the effect of temperature on the reaction rate, pre-calcined and pre-sintered CaO sorbent particles of initial specific surface area of 29.7 m^2/g and pore volume of 0.12 cm^3/g (CaO-2) are exposed to 3 kPa of H_2S at a total pressure of 1 MPa and temperatures in the range of 650–900°C for varying reaction times. Figure 9 shows the conversion vs. time profiles for 7.8 μm CaO particles. It can be seen from the figure that sulfidation conversion is very sensitive to reaction temperature. It can also be noted that the rate of sulfidation during initial stages is significantly higher at higher temperatures. Sulfidation conversions in excess of 45% of the ultimate conversion are obtained within the first minute of reaction at 900°C. The rate of reaction tapers off as the conversion increases suggesting a change in the controlling mechanism. At higher temperature, the tapering off of the overall reaction rate is more drastic than at lower temperatures.

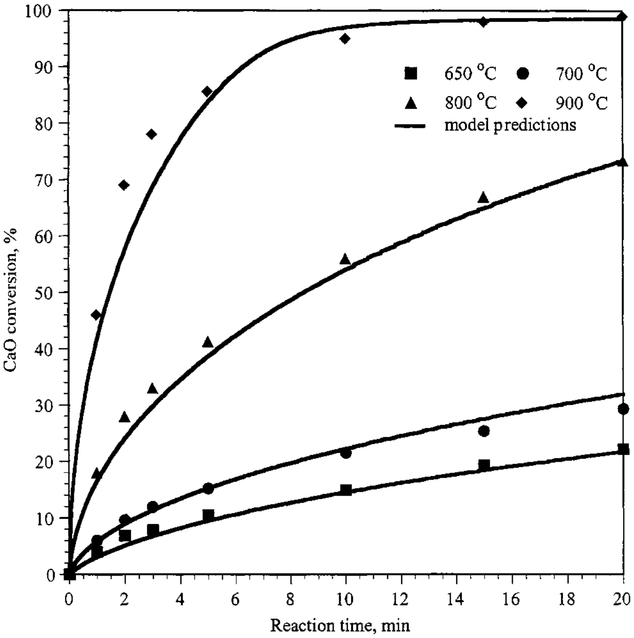


Figure 9. Effect of temperature on CaO sulfidation.

Total pressure: 1 MPa; H_2S partial pressure: 3,000 Pa; CaO surface area: 29.7 m^2/g; CaO pore volume: 0.12 cm^3/g.

Initially, the product layer buildup is limited and the surface reaction can be assumed to control the overall rate of CaO sulfidation. The rate of surface reaction increases exponentially with temperature, and this is evident from initial conversion data shown in Figure 9. After the first minute of exposure, sorbent conversion is nearly 45% at 900°C as compared to only about 5% at 650°C. As the reaction proceeds, the nonporous CaS product layer builds up resulting in decreased porosity of the partially sulfided particle, which in turn increases the diffusion resistance and shifts the overall rate controlling step from surface reaction to product layer diffusion. At higher temperatures, faster buildup of the product layer leads to an earlier transition to diffusion control regime.

Determination of kinetic parameters

Effects of various operating variables on sulfidation characteristics of calcium oxide are studied experimentally and the kinetic parameters of the reaction are obtained by fitting the time-resolved data at various temperatures (Figure 9) to the modified grain model. The proposed two-parameter model has k_s and D_{ion} as the fitting parameters. The estimated values of these parameters at different temperatures are used to calculate the activation energies using the Arrhenius-type equation, as shown in Figure 10.

The value of activation energy for the surface reaction rate constant k_s (m/s) is calculated to be 37 kcal/mol, which compares favorably with the values reported in literature. Attar and Dupuis (1979) reported CaO sulfidation activation energy to be 37 kcal/mol and Heesink and van Swaaij (1995) reported this value to be 38 kcal/mol. Borgwardt et al. (1984) reported the activation energy for CaO sulfidation to be 31.1

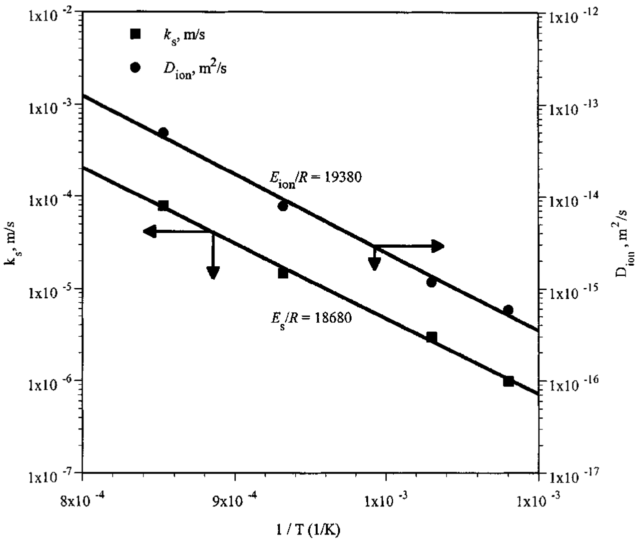


Figure 10. Arrhenius plot for the reaction rate constant k_s and product layer diffusivity D_{ion}.

kcal/mol, which is slightly lower than the estimated value in this study. Abbasian et al. (1991) reported the activation energy value for this reaction to be 40.2 kcal/mol.

The product layer diffusivity D_{ion} is estimated to be in the range of 6×10^{-16} to 5×10^{-14} for the temperature range of 650–900°C, and the corresponding activation energy value is determined to be 38.4 kcal/mol. This value is significantly higher than those typically encountered for diffusion of gaseous species through the cracked/porous CaS product layer. The high activation energy (38.4 kcal/mol) and low product layer diffusivity value (8×10^{-15} m^2/s at 800°C) suggest that the sulfidation reaction involves solid-state ionic diffusion and is consistent with the previous findings (Borgwardt et al., 1984; Nguyen and Watkinson, 1993; Agnihotri et al., 1999), which show that product layer diffusion in atmospheric pressure CaO sulfidation involves solid-state diffusion of S^{2-} and O^{2-} ions.

Conclusions

Experimental data for high-pressure sulfidation (up to 2 MPa) of calcined limestone is obtained in the temperature range of 650–900°C. The effects of total pressure, H_2S partial pressure, reaction temperature, fuel gas composition, and CaO initial surface area on the extent of sulfur capture and conversions of sorbent are studied. The sulfidation conversion is adversely affected by increasing pressure due to CaO sorbent morphological alterations, such as reduction in surface area and pore volume. The rate of formation of CaS is found to increase linearly with gas-phase H_2S partial pressure. Higher initial surface area and pore volume of CaO lead to higher levels of sulfidation conversion. The rate of sulfidation, as well as the extent of CaO conversion, increase with initial increase in the H_2 partial pressure, but reduce at high H_2 partial pressures. The sulfidation conversion is unaffected by varying CO partial pressure. The activation energy of high-pressure CaO reaction with H_2S is obtained to be 37 kcal/mol and product layer diffusivity value is obtained to be approximately 8×10^{-15} m^2/s at 800°C. The product layer diffusivity values measured for the temperature range of 650–900°C suggests that the sulfidation reaction involves solid-state diffusion. The modified grain model predicts the experimental data for the sulfidation reaction reasonably well. The high-pressure sulfidation kinetic data obtained in this study will be useful in understanding the sulfidation characteristics of calcium oxide particles under gasifier conditions.

Acknowledgments

This work was sponsored in part by Ohio Department of Development's Ohio Coal Development Office.

Notation

C_{bulk} = concentration of H_2S in the bulk gas phase, mol/m^3
C_{H_2S} = concentration of H_2S inside the CaO particle, mol/m^3
C_{ion} = concentration of sulfur ions at the reaction interface, mol/m^3
D_{ion} = diffusivity of sulfur ions, m^2/s
r = radial distance in the grain, m
r_{go} = initial grain radius, m
r_{H_2S} = mass rate of reaction of H_2S, mol/$m^2\cdot s$
R = radial distance in the CaO particle, m
R_p = overall particle radius, m
t = time, s
x_s = local extent of sulfidation
X_s = overall conversion of CaO to CaS
z = molar volume ratio of CaS to CaO
ϵ_s = local product layer porosity following sulfidation
ϵ_o = initial porosity of CaO
ρ_{CaO} = density of CaO, mol/m^3

Literature Cited

Abbasian, J., D. M. Rue, and F. S. Lau, "In-gasifier Sulfur Capture During Pressurized Fluidized-bed Hydrotreating of Eastern Oil Shales," *Fuel*, **70**, 1342 (1991).

Agnihotri, R., S. Chauk, S. Mahuli, and L.-S. Fan, "Mechanism of CaO Reaction with H_2S: Diffusion through CaS Product Layer," *Chem. Eng. Sci.*, **54**, 3443 (1999).

Alvfors, P., and G. Svedberg, "Modeling of the Simultaneous Calcination, Sintering and Sulphation of Limestone and Dolomite," *Chem. Eng. Sci.*, **47**, 1903 (1992).

Attar, A., "The Fundamental Chemistry and Modeling of the Reactions of Sulfur in Coal Pyrolysis," Interim report for U.S. EPA Research Grant No. R809274, North Carolina State University, Raleigh, NC (Dec. 1982).

Attar, A., and F. Dupuis, "The Rate and Fundamental Mechanism of the Reaction of Hydrogen Sulfide with the Basic Minerals in Coal," *Ind. Eng. Chem. Process Des. Dev.*, **18**, 607 (1979).

Bischoff, K. B., "Accuracy of the Pseudo-Steady State Approximation for Moving Boundary Diffusion Problems," *Chem. Eng. Sci.*, **18**, 711 (1963).

Borgwardt, R. H., "Reaction of H_2S and Sulfur with Limestone Particles," *Ind. Eng. Chem. Process Des. Dev.*, **23**, 742 (1984).

Borgwardt, R. H., N. F. Roache, and K. R. Bruce, "Surface Area of Calcium Oxide and Kinetics of Calcium Sulfide Formation," *Environ. Prog.*, **3**, 129 (1984).

Borgwardt, R. H., "Calcium Oxide Sintering in Atmospheres Containing Water and Carbon Dioxide," *Ind. Eng. Chem. Res.*, **28**, 493 (1989).

Bowen, J. R., "Comments on the Pseudo-Steady State Approximation for Moving Boundary Problems," *Chem. Eng. Sci.*, **20**, 712 (1965).

Camp, D. M., "The Formation of Artificial Dolomites and the Effects of the Calcium/Magnesium Ratio in Such Half-Calcined Dolomites on Reaction with Hydrogen Sulfide," PhD Diss., Massachusetts Institute of Technology, Cambridge, MA (1979).

Clean Coal Technology-Program Profiles, Office of Fossil Energy, US DOE (1994a).

Clean Power Systems-Program Profiles, Office of Fossil Energy, US DOE (1994b).

Efthimiadis, E. A., and S. V. Sotirchos, "Sulfidation of Limestone-Derived Calcines," *Ind. Eng. Chem. Res.*, **31**, 2311 (1992).

Fenouil, L. A., G. P. Towler, and S. Lynn, "Removal of H_2S from Coal Gas Using Limestone: Kinetic Considerations," *Ind. Eng. Chem. Res.*, **33**, 265 (1994).

Fenouil, L. A., and S. Lynn, "Study of Calcium-Based Sorbents for High-Temperature H_2S Removal. 1. Kinetics of H_2S Sorption by Uncalcined Limestone," *Ind. Eng. Chem. Res.*, **34**, 2324 (1995a).

Fenouil, L. A., and S. Lynn, "Study of Calcium-Based Sorbents for High-Temperature H_2S Removal. 2. Kinetics of H_2S Sorption by Calcined Limestone," *Ind. Eng. Chem. Res.*, **34**, 2334 (1995b).

Fenouil, L. A., and S. Lynn, "Study of Calcium-Based Sorbents for High-Temperature H_2S Removal. 3. Comparison of Calcium-Based Sorbents for Coal Gas Desulfurization," *Ind. Eng. Chem. Res.*, **34**, 2343 (1995c).

Fogler, H. S., *Elements of Chemical Reaction Engineering*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1992).

Freund, H., "Intrinsic Global Rate Constant for the High-Temperature Reaction of CaO with H_2S," *Ind. Eng. Chem. Fund.*, **23**, 338 (1984).

Frey, H. C., and E. S. Rubin, "Integration of Coal Utilization and Environmental Control in Integrated Gasification Combined Cycle Systems," *Environ. Sci. Tech.*, **26**, 1981 (1992).

Gullett, B. K., J. A. Blom, and G. R. Gillis, "Design and Characterization of a 1200°C Entrained Flow, Gas/Solid Reactor," *Rev. Sci. Instrum.*, **59**, 1980 (1988).

Heesink, A. B. M., and W. P. M. van Swaaij, "The Sulfidation of Calcined Limestone with Hydrogen Sulfide and Carbonyl Sulfide," *Chem. Eng. Sci.*, **50**, 2983 (1995).

Kearins, D. L., D. H. Archer, R. A. Newby, E. P. O'Neil, and E. J. Vidt, "Evaluation of the Fluidized Bed Combustion Processes," *Fluidized Bed Oil Gasification/Desulfurization*, Vol. IV, EPA-650/2-73-048d, NTIS PB 233 (1973).

Lindgren, E. R., D. W. Pershing, D. A. Kirchgessner, and D. C. Drehmel, "Fuel Rich Sulfur Capture in a Combustion Environment," *Environ. Sci. Technol.*, **26**, 1427 (1992).

Mahuli, S. K., R. Agnihotri, S. Chauk, A. Ghosh-Dastidar, S.-H. Wei, and L.-S. Fan, "Pore Structure Optimization of Calcium Carbonate for Enhanced Sulfation," *AIChE J.*, **43**, 2323 (1997).

Mojtahedi, W., K. Salo, and J. Abbasian, "Desulfurization of Hot Coal-Gas in Fluidized-Bed with Regenerable Zinc Titanate Sorbent," *Fuel Proc. Tech.*, **37**, 53 (1994).

Nguyen, Q. T., and A. P. Watkinson, "Sulfur Capture During Gasification of Oil Sand Cokes," *Can. J. Chem. Eng.*, **71**, 401 (1993).

O'Neil, E. P., D. L. Kearins, and W. F. Kittle, "A Thermogravimetric Study of the Sulfation of Limestone and Dolomite—The Effect of Calcination Conditions," 3rd Int. Conf. on Fluidized Bed Combustion, Heston Woods, OH, **I**, 6 (1972).

Pell, M., "Reaction of Hydrogen Sulfide with Fully Calcined Dolomite," PhD Diss., City Univ. of New York (1971).

Simons, G. A., and W. T. Rawlins, "Reaction of Sulfur Dioxide and Hydrogen Sulfide with Porous Calcined Limestone," *Ind. Eng. Chem. Process Des. Dev.*, **19**, 565 (1980).

Squires, A. M., R. A. Graff, and M. Pell, "Desulfurization of Fuels with Calcined Dolomite. I. Introduction and First Kinetic Results," *Chem. Eng. Progress Sym. Ser.*, **67**, 23 (1971).

Szekely, J., J. W. Evans, and H. Y. Sohn, *Gas-Solid Reactions*, Academic Press, London (1976).

U.S. Dept of Energy, "Annual Energy Review 1992," Energy Information Agency, U.S. DOE, (1992).

Westmooreland, P. R., J. B. Gibson, and D. P. Harrison, "Comparative Kinetics of High-Temperature Reaction between H_2S and Selected Metal Oxides," *Environ. Sci. Technol.*, **11**, 488 (1977).

Yrjas, K. P., C. A. P. Zavenhoven, and M. M. Hupa, "Hydrogen Sulfide Capture by Limestone and Dolomite at Elevated Pressure. 1. Sorbent Performance," *Ind. Eng. Chem. Res.*, **35**, 176 (1996).

Zevenhoven, C. A. P., K. P. Yrjas, and M. M. Hupa, "Product Layer Development during Sulfation and Sulfidation of Uncalcined Limestone Particles at Elevated Pressures," *Ind. Eng. Chem. Res.*, **37**, 2639 (1998).

Manuscript received Jan. 27, 1999, and revision received Jan. 28, 2000.