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Abstract

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Disciplines

Chemical Engineering

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A Plausible Model for the Sulfidation of a Calcium-Based Core-in-Shell Sorbent

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A promising reusable sorbent for desulfurizing hot coal gas is being developed in the form of core-in-shell pellets which consist of a highly reactive CaO core encased in a porous protective shell made largely of an inert material. The spherical pellets are made by pelletizing plaster of Paris and then applying a coating of alumina (80%) and limestone (20%) particles. Subsequent high temperature treatment converts the cores to CaO and sinters the coating material to form the porous shells. The pellets absorb and react with H₂S at high temperatures (e.g., 800–900 °C) to form CaS and are regenerated by applying a cyclic oxidation/reduction method. The rate of sulfidation does not appear to be controlled by chemical reaction but, instead, seems to be controlled by one or more of the following diffusion resistances: external gas film, porous shell, micropores between CaO grains in the core, and product layer surrounding CaO within each grain. After considering various models, a brief review of which is included in the paper, a semiempirical model was chosen which represents the process well over a limited range of conversion (approximately 0–85%). This is not a serious limitation for the model because above this range the rate of conversion becomes too slow for most applications. The model assumes that within this range the rate of conversion is controlled by the resistance to diffusion offered by the porous outside shell together with the resistance to diffusion presented by a porous layer of reacted material. The model is in effect an extension of the well-known shrinking, unreacted core model for gas–solid reactions. As more basic diffusion data become available, a more rigorous model, such as a modified grain model, is expected to be developed.

Introduction

There is a continuing need for an economical, regenerable sorbent for desulfurizing hot coal gas in advanced power generating systems which gasify coal to supply gas turbines. Such systems are likely to utilize an integrated gasification combined cycle (IGCC) or another hybrid cycle such as the “topping cycle” developed by British Coal.¹ Typically, the gas is produced by treating coal with steam and either air or oxygen at temperatures which may range from 700 to 1000 °C or higher. While the principal products are carbon monoxide and hydrogen, the gasifier effluent will also contain unreacted steam (1–18 mol %), CO₂ (2–15 mol %), H₂S (750–7000 ppm), and lesser amounts of other impurities such as COS, NH₃, HCN, and HCl, depending on the properties of the coal and the gasification method. The product of air blown gasifiers will also have a large concentration of nitrogen (45–55 mol %). In most cases, the gas will also be laden with dust. Although it has been common practice to cool the gas below 77 °C (350 K) to remove H₂S and other impurities by wet scrubbing, this practice reduces the overall efficiency of power generation significantly when the gas is used directly to fuel a gas turbine.

A more efficient alternative would be to clean the gas at the gasifier outlet temperature by utilizing an appropriate sorbent for H₂S and COS. An even better alternative would be to utilize a reusable sorbent which is also capable of serving as a filter medium for removing entrained dust. While a number of metal oxides have been proposed as sorbents for high temper-

ature desulfurization of coal gas, none are ideal in all respects. Only a few materials are effective at gasification temperatures.² Among these materials, calcium oxide stands out because it is highly reactive, readily available, and low in cost. Furthermore, it should reduce the H₂S content of the gas produced by a modern entrained flow gasifier to 20 ppmv which is considered adequate for a turbine powered IGCC system.³ To achieve this level, the gas should not contain more than 2.0 mol % each of H₂O and CO₂ and have a total pressure of 30 bar and a temperature between 815 and 845 °C.

Unfortunately, CaO also tends to be weak and friable, difficult to regenerate, and subject to a loss in reactivity when regenerated and reused repeatedly.⁴ Regeneration is especially difficult because there is a greater tendency for CaS to be converted into CaSO₄ than into CaO upon oxidation except at very high temperature.⁵

Several methods have been suggested for overcoming these problems. One approach is to utilize the sorbent once and then discard the spent material since lime is so plentiful and inexpensive.^{4,6} The spent sorbent will be largely in the form of CaS due to the following reaction:



Unfortunately, the sulfided sorbent cannot be placed directly in a landfill where it would react slowly with water and release H₂S. Therefore, it has been proposed to oxidize the spent sorbent so as to convert CaS to CaSO₄ which can be disposed. But it has proved difficult to convert CaS completely into CaSO₄ by a single-step, air oxidation process at elevated temperatures because of pore blockage.^{4,7}

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Another approach suggested in the literature is to employ half-calcined dolomite as a sorbent to take advantage of the following forward reaction:⁸



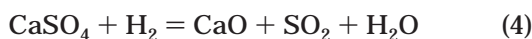
The sorbent is regenerated by employing the reverse reaction. However, since the forward and reverse reactions are carried out at widely different temperatures and pressures and with different gas compositions, the method has not proved very practical or economical.

Another proposed method of gas cleaning utilizes calcined limestone as a sorbent and a complex method of regeneration.³ Although the method produces elemental sulfur as a byproduct, it suffers from having to move the sorbent particles around a three-reactor system operating at different temperatures which presents a difficult materials handling and heat recovery problem.

A more promising method of gas cleaning has been proposed and demonstrated which utilizes a reusable calcium-based sorbent in the form of core-in-shell pellets wherein each pellet consists of a CaO core surrounded by a porous shell made largely of an inert material such as aluminum oxide.⁹ The structure provides a highly reactive core encased in a strong, protective shell and seems somewhat similar to a "geode-like" pellet structure proposed by others for a zinc oxide-based sorbent.¹⁰ The spent calcium-based sorbent can be regenerated by a unique process and reused repeatedly. The method of regeneration first treats the spent material with an oxidizing gas (e.g., air) at 1000–1100 °C to convert an outer layer of each core from CaS to CaSO₄ by the following reaction:⁵



The reaction does not proceed to completion because of pore blockage. Therefore, the material is treated next with a reducing gas such as H₂ to convert the CaSO₄ layer to CaO as shown:



The material is converted layer by layer until after several cycles it is entirely converted into CaO.¹¹ Although the regeneration method has only been demonstrated on a laboratory scale, it lends itself to application in either fixed bed, moving bed, or fluidized bed reactors.^{12,13}

Pellet cores with good sorption and regeneration characteristics have been made from either limestone or plaster of Paris.¹¹ When the cores have been subjected to repeated sulfidation with H₂S and regeneration by the cyclic oxidation and regeneration method, there has been a gradual decline in the rate of reaction of the sorbent. However, the reactivity of the sorbent seems to stabilize after 18–20 cycles.

Development of the core-in-shell sorbent is continuing to improve the performance and durability of the material. To guide this development and possible future applications of the material, consideration has been given to the selection and verification of a model which will adequately represent the kinetics of sulfidation. The models which have been considered are reviewed in following paragraphs. Similar consideration has not been given to regeneration which always proceeds rapidly.

Overview of Gas–Solid Reaction Models

The first model for describing the behavior of a solid as it undergoes reaction with a gas was proposed over a half a century ago by Yagi and Kunii.¹⁴ This is the shrinking core model (SCM), also called the sharp interface model (SIM). Several other models have been proposed since then, such as the expanding core (as an extension of SCM), volume reaction, reaction zone, particle–pellet, crackling core, grain–micrograin, nucleation, computational, and percolation models. The percolation models are based on the statistical physics of disordered media and include such phenomena as aggregation processes, scaling, network modeling of the pore space, discretization, and random walk representation of diffusion processes. An increasing number of papers are being published on percolation models (see Sahimi et al.¹⁵ for a review), but research on the other models continues because of the practical usefulness of these models (see, e.g., Szekely et al.;¹⁶ Ramachandran and Doraiswamy;¹⁷ Doraiswamy and Sharma;¹⁸ Doraiswamy and Kulkarni;¹⁹ Mazet;^{20,21} Bhatia and Gupta²²). In reactions involving high temperatures, such as the present one, the solid tends to sinter, but studies on the analysis of sintering are sparse.

The simplest examples of these models are those in which the internal structure of the pellet is not considered and its behavior as a whole is modeled. These are normally called the macroscopic models. In all other models, the behavior of the distinctive elements of a pellet such as the grain, micrograin, or the pore constitutes the central feature of the models. The first such models did not account for pore evolution (through changes in particle size distribution) with progress of reaction. The later models that took this into account, the so-called structural models, can roughly be divided into two categories: grain models and pore models.

A particularly important class of nonstructural models is the group of zone models in which a reaction zone is sandwiched between the ash layer and the unreacted core (Bowen and Cheng;²³ Mantri et al.;²⁴ Bowen et al.;²⁵ Dudukovic and Lamba²⁶). The experimental results of Prasannan and Doraiswamy²⁷ on the oxidation of zinc sulfide clearly reveal all three stages of the reaction.

The original grain model is based on an explicit recognition of the granular structure of the pellet (Szekely and Evans²⁸). The overall behavior of the pellet itself is assumed to be identical to that of the grain, i.e., shrinking core behavior. Several extensions of the grain model have been proposed, and the important ones are considered in the following sections.

Structural changes can be analyzed by considering the changes in the grains due to reaction or by corresponding changes in the pore structure (pore evolution). It is relatively simple to calculate grain size distributions using pore size distribution data obtained from mercury porosimetry measurements. The parent grain model mentioned earlier has been modified in different ways to account for changes in grain size and grain size distribution due to reaction. Alternatively, in the pore models, the pore has directly been considered to be the chief parameter.

In a particularly useful grain model, proposed by Heesink et al.,²⁹ the original model is made much more acceptable by accounting for grain size distribution, change in grain size with conversion, and pore blocking. Instead of using a continuous distribution of grain size, the grains are divided into a number of groups, and the

conversion is calculated for each group using the SCM. This study is particularly important from the point of view of the present work since the present authors used a similar experimental system for validating the model.

Another, more sophisticated, model is the so-called grain–micrograin model proposed by Dam-Johanson et al.³⁰ and Prins et al.³¹ In this model, the solid (pellet) is assumed to consist of porous grains which in turn are made up of nonporous micrograins that react according to the SCM under product layer diffusion control. When the pores within the micrograin get blocked (resulting in significant reaction rate reduction), the pores between the grains are still open for mass transfer; the grains then react, also according to the SCM (partially reacted).

In contrast to the grain models in which the grains are, in a sense, assumed to be dispersed in a continuous gas phase, in the pore models the solid is regarded as the continuous phase. A number of pore models have been proposed over the years, the earliest (and perhaps the most fundamental) being that of Ramachandran and Smith.³² Perhaps the most realistic model is the random pore model of Bhatia and Perlmutter.^{33–36} This model assumes that the actual reaction surface of the reacting solid is the result of the random overlapping of a set of cylindrical pores. Equations for calculating the evolving reaction surface have been developed. Several refinements of this model have been proposed (see Bhatia and Gupta²²), a particularly interesting one being the inclusion of “newly discovered” pores (Delikouras and Perlmutter³⁷).

Choice of Model for the Present Reaction. The experimental results obtained in this study using CaO pellets, and reported later in the paper, clearly show a shrinking core. Further, when a pellet core is encased in a shell of stronger material, there is a built-in case for adding an additional resistance to the SCM, thus making this model a prime candidate for describing the sulfidation reaction. It is noteworthy, however, that the grain model has been successfully used for the sulfidation of precalcined limestone with different microstructures (Heesink et al.²⁹). The micrograin–grain model has also been successfully used in the sulfidation of calcium oxide (Dam-Johanson et al.³⁰). More extensive experimental data involving several physicochemical property measurements are needed to examine the suitability of these models.

Thus, considering the a priori acceptability of the SCM, the emphasis of the present work on pellet development, and the need for a simple (semiempirical) equation for purposes of reactor design, it was considered desirable to confine the modeling to the SCM at this stage.

Experimental Results

Sorbent pellets both with and without supporting shells were prepared, and their absorption characteristics were determined and analyzed to select an appropriate model for representing the H₂S absorption process. The pellet cores were derived from calcium sulfate hemihydrate (i.e., plaster of Paris) while the shells were made of sintered alumina and lime.

Methods and Materials. The calcium sulfate hemihydrate was a commercial grade of plaster from U. S. Gypsum Co. with a purity of 98 wt % and a mean particle size of 1 μm . The limestone had a CaCO₃ content of 97 wt % and was obtained from the Martin Marietta Aggregates quarry located near Ames, Iowa.

The limestone was ground and screened to provide $-210/+44 \mu\text{m}$ size particles for the pellet shells. The other shell materials were two different grades of alumina from Alcoa. One grade was T-64 tabular alumina with a median particle diameter of 8.65 μm , and the other grade was A-16 SG alumina powder with a median particle diameter of 0.88 μm .

A two-stage pelletization process was used for preparing the core-in-shell sorbent pellets. The pellet cores were prepared first by placing a measured amount of plaster of Paris in a 25 cm diameter drum which revolved between 60 and 80 rpm. As the drum revolved, the powder was sprayed intermittently with water causing the powder to ball up. The size of the resulting pellets was increased by adding more material to the drum. After reaching an appropriate size, the pellets were tumbled for some time with additional spraying to complete their hydration and to improve their sphericity and uniformity. The finished cores were then screened, and cores of a selected size were returned to the pelletizer for coating with the shell material which consisted of 48 wt % T-64 tabular alumina, 32 wt % A-16 SG alumina powder, and 20% limestone. This material was added gradually as the drum revolved and the pellets were sprayed with a dilute lignin solution. Once coated, the pellets were tumbled and sprayed intermittently for another 2 h to consolidate and strengthen the coating. The pellets were again screened, and selected pellets were calcined in air at 1100 °C for 2 h to sinter the shell material.

The absorption and regeneration characteristics of the sorbent were determined by employing thermogravimetric analysis (TGA) to observe the change in weight of a single pellet as it reacted with H₂S or as it was regenerated in a vertical tubular reactor. The pellet was suspended in a quartz basket from a sensitive electrobalance which was connected to a computer/recorder. The quartz reactor had a diameter of 2.5 cm and length of 41 cm, and it was surrounded by an electric furnace for temperature control. The temperature of the reaction zone was measured with a protected thermocouple which was located inside the reactor and approximately 1 cm below the quartz basket. The reactor was supplied with an appropriate mixture of gases at a flow rate of 500 cm³/min measured at room temperature and pressure. The mixtures were prepared by combining and mixing the individual component gases which were obtained in high pressure cylinders and supplied to the TGA system through calibrated rotameters at controlled rates. These gases included prepurified N₂ with not over 50 ppm of impurities and technical grade H₂S and H₂.

The CaSO₄ core of a new pellet was converted to CaO by a cyclic process conducted at 1050 °C which involved reduction with 9 vol % H₂ and then oxidation with 13 vol % O₂, both gases being diluted with N₂. The cycle was repeated until the pellet weight became constant which indicated that 98% or more of the CaSO₄ had been converted to CaO. To conduct a subsequent sulfidation test, the temperature of the system was first lowered to a preselected level (e.g., 880 °C) while passing only N₂ through the reactor. When this temperature was reached, the gas composition was changed to include appropriate concentrations of H₂S and H₂, and sulfidation was allowed to proceed isothermally for an extended time, usually until the rate of change of pellet weight was very small. At this point, either the test was discontinued or the sorbent was regenerated and an-

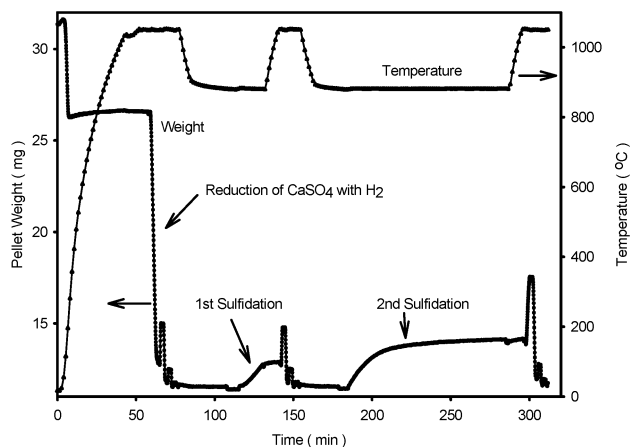
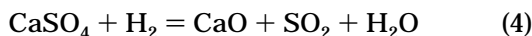


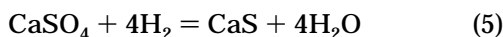
Figure 1. Results of a two-cycle sulfidation and regeneration test with a pellet core using 1.0 vol % H_2S and 24 vol % H_2 for sulfidation.

other sulfidation test was conducted. To regenerate the sorbent, the temperature of the system was raised to 1050 °C while passing only N_2 through the reactor, and the pellet was treated by a cyclic process which involved oxidation with 13 vol % O_2 followed by reduction with 9 vol % H_2 . The cycle was repeated until the pellet weight became constant. This usually required about three cycles.

Absorption Characteristics. The results of a typical sulfidation and regeneration test of a single pellet core derived from plaster of Paris are shown in Figure 1. Since the pellet initially consisted entirely of hydrated calcium sulfate, it experienced an initial loss in weight due to dehydration as the temperature was raised. Upon reaching 1050 °C, the pellet was treated with 9 vol % H_2 which produced a large, precipitous drop in weight due to reaction 4.



Before this reaction had gone to completion, its rate had fallen off, in part because of the following side reaction:

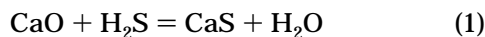


Therefore, it became necessary to switch back to an oxidizing gas (13 vol % O_2) to eliminate the CaS, and this caused an increase in pellet weight due to reaction 3.



The reduction/oxidation cycle was subsequently repeated two more times to achieve a constant weight and essentially complete conversion to CaO.

The sorbent was then cooled in N_2 to 880 °C and sulfidized with a mixture consisting of 1.0 vol % H_2S , 24 vol % H_2 , and 75 vol % N_2 . Hydrogen was included to inhibit thermal decomposition of H_2S . This treatment was continued for 15 min, which produced an increase in pellet weight corresponding to a 30% conversion of CaO to CaS by way of reaction 1.



At this point, sulfidation was discontinued, the temperature was increased to 1050 °C, and the sorbent was regenerated by applying the cyclic oxidation/reduction process. This caused the pellet weight to increase as CaS

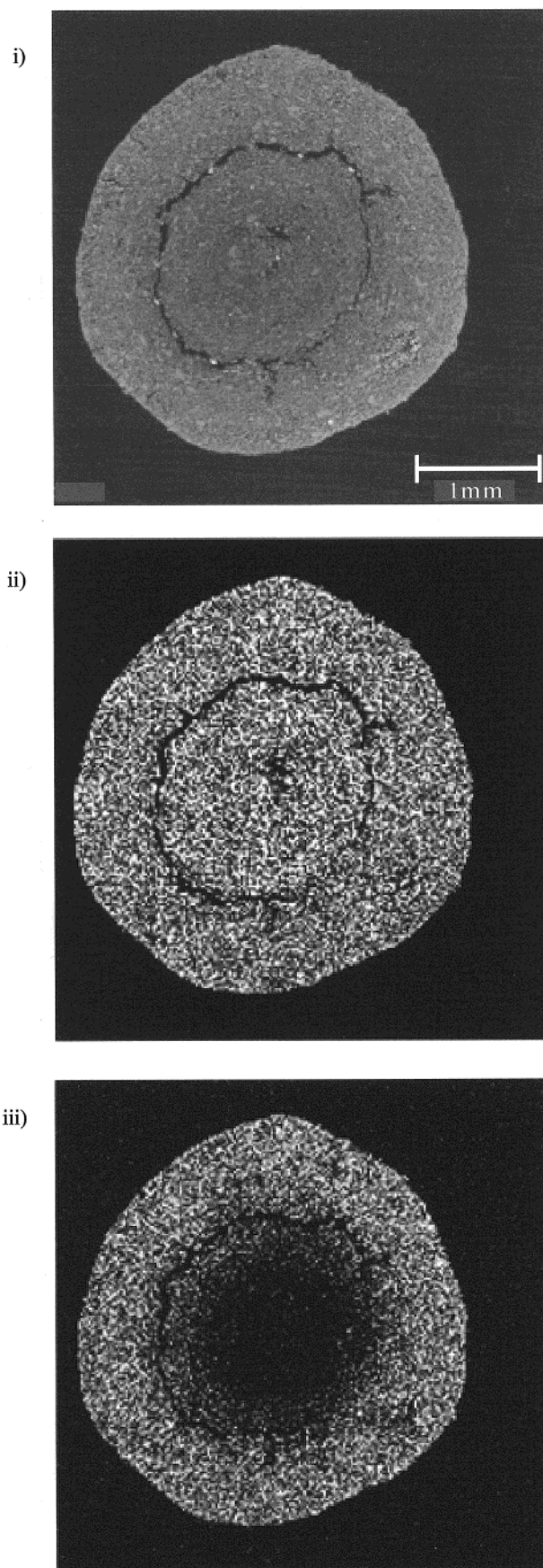


Figure 2. Micrograph of an incompletely sulfided, 3.2 mm diameter pellet core: (i) SEM view, (ii) calcium map, and (iii) sulfur map.

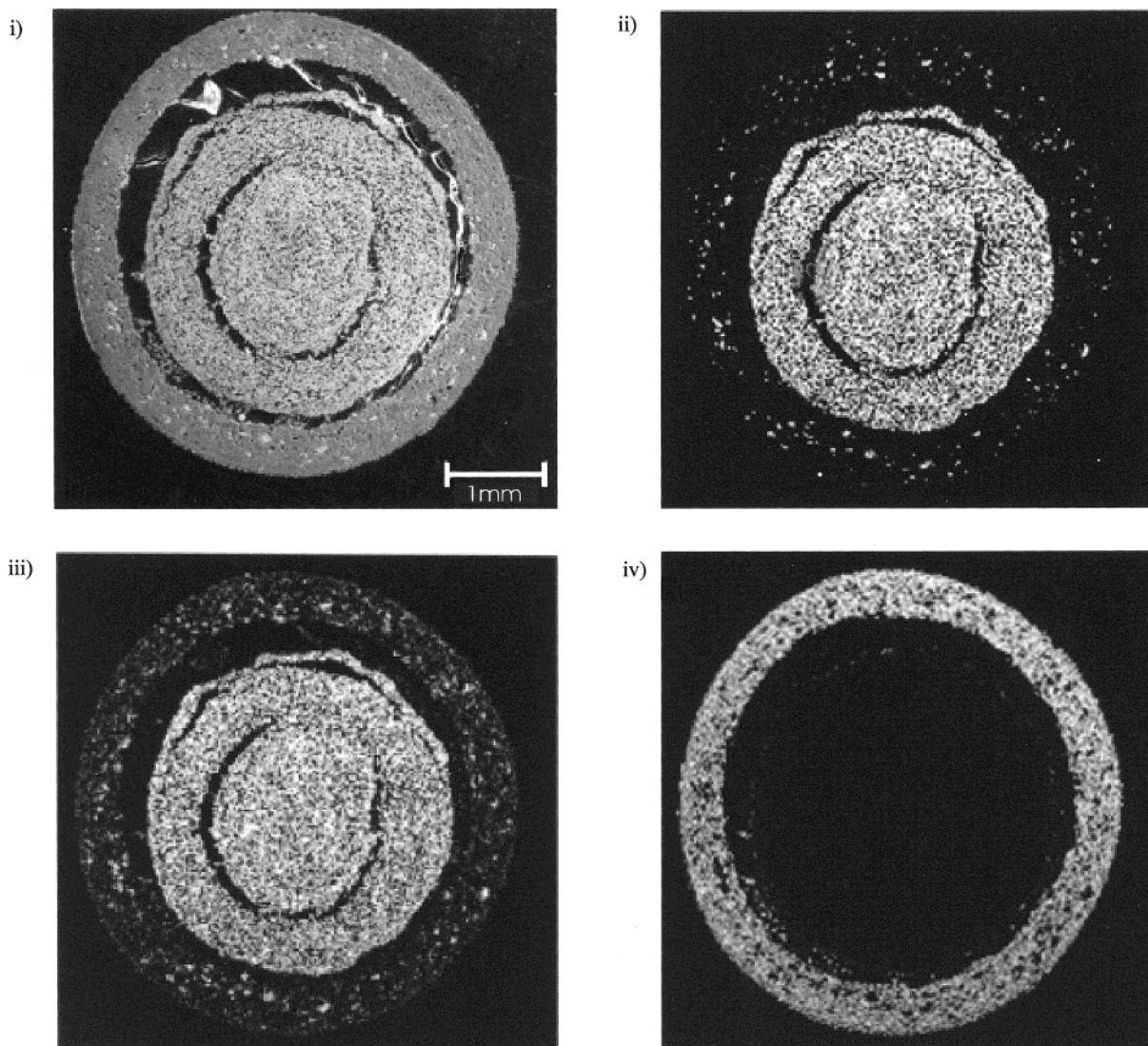


Figure 3. Micrograph of a highly sulfided, 4.4 mm diameter core-in-shell pellet: (i) SEM view, (ii) sulfur map, (iii) calcium map, and (iv) aluminum map.

was oxidized to CaSO_4 and then decrease as CaSO_4 was reduced to CaO . It can be seen that, after three cycles, the sorbent was completely regenerated.

The sorbent was then subjected to a second cycle of sulfidation and regeneration. However, this time sulfidation was continued for 100 min which converted 90% of the CaO to CaS . Figure 1 indicates that the rate of conversion was very slow after the first 45 min. During the following 55 min, the conversion only increased from 80% to 90%. Another pellet which was sulfided for 155 min under similar conditions was still only 96% sulfided.

Several pellets which had been sulfided for different lengths of time were cross-sectioned and examined by scanning electron microscopy (SEM) to observe the physical structure and by the associated energy dispersive spectroscopy (EDS) to observe the distribution of sulfur, calcium, and aluminum. Typical results are presented in Figure 2 for a CaO core which had been 70% converted to CaS . It can be seen that the structure is granular with several major cracks, the principal one being a concentric circular crack midway between the center and outer edge. There are also several minor cracks which radiate outward from the circular crack. While the calcium is distributed uniformly throughout the pellet, the sulfur is nonuniformly distributed sug-

gesting the results of a modified shrinking core process. Although sulfur appears to be uniformly distributed in a wide outer band or rim of the pellet and the dark inner core appears largely free of sulfur, there is not a sharp boundary between these two regions. Instead, there is an intermediate region where the concentration of sulfur declines gradually from the outer uniformly sulfided region to the inner almost barren region. The results suggest that the rate of conversion is controlled by diffusion both between grains and within grains.

A core-in-shell pellet which had been reacted more completely and then cross-sectioned presented a different appearance (see Figure 3). The plaster-based core had shrunk and pulled away from the shell which seemed to have partly detached a thin layer of core material. Again, there was a concentric circular crack within the core, but there were very few radial cracks. Both calcium and sulfur appeared to be uniformly distributed throughout the core. The sulfur distribution confirmed that the core was almost completely reacted. Also, both calcium and sulfur appeared to be present in the shell with calcium being much more in evidence than sulfur. The presence of sulfur in the shell showed that at least some of the calcium in the shell was available for reaction. Of course, the predominant shell

material was alumina which created the bright image for aluminum.

The appearance of the core-in-shell pellet cross-section differed markedly from that of a similar pellet in which the core had been derived from limestone. It had been found and reported previously that for such a pellet the calcined core was free of obvious cracks, and it had not shrunk away from the shell.⁹ Hence, the shrinking and cracking so apparent in Figure 3 was the result of the volume change which accompanied the dehydration of the core that was largely gypsum after pelletization.

Model Selection and Validation. In selecting an appropriate model to represent the lime sulfidation process, consideration was given to previous studies of the reaction kinetics and to models which were likely to apply. Among the noteworthy experimental studies, two in particular seem most applicable. The first by Borgwardt³⁸ showed that for micrometer size particles of CaO the rate of CaS formation is most probably limited by diffusion through the product layer surrounding individual CaO grains. Also, it was observed that the activation energy of 31.0 kcal/mol seemed more indicative of solid state ionic diffusion than of gaseous diffusion through a porous layer. These observations were corroborated more recently by Agnihotri et al.³⁹ who concluded that the reaction of CaO with H₂S is limited by the diffusion of S²⁻ and O²⁻ ions through the CaS layer. In addition, they showed that for micrometer size particles not limited by external film diffusion, the process is well represented by the SCM with diffusion of the gaseous reactant through the product (ash) layer as the controlling step.

While the preceding results should also apply to the individual grains of CaO which made up the pellet cores of the present sorbent, they do not account for other potential diffusion resistances offered by the core-in-shell pellets. These resistances include the resistance of the gas film surrounding the pellet, the resistance of the porous supporting shell, and the resistance of the pores between the CaO grains. It seems likely that a combination of the last resistance and the resistance of the product layer surrounding individual grains accounted for the zone of partially converted material between the outer band of fully reacted material and the core of unreacted material so apparent in Figure 2. Also, either or both of these resistances could have accounted for the very slow rate of reaction which occurred after a pellet was approximately 80% sulfided.

A review of existing models showed that none were likely to fit the core-in-shell pellet very well because of the widely different properties of the core and shell. While the grainy pellet model seemed to offer the greatest likelihood of representing the behavior of the pellet core by itself, and possibly that of the shell by itself, the model required extensive modification to fit the combined core and shell. Therefore, a simpler, semiempirical approach was taken which gave reasonable results. This was accomplished by fitting the classical, shrinking core model over the initial and subsequent portions of the sulfidation process which proceed rapidly but not the final, much slower portion which would not be used in most practical applications. For the bare pellet cores, the transition from the rapid to the slow rate of conversion generally took place at approximately 78% conversion. Therefore, model fitting was limited to the range 0–78%.

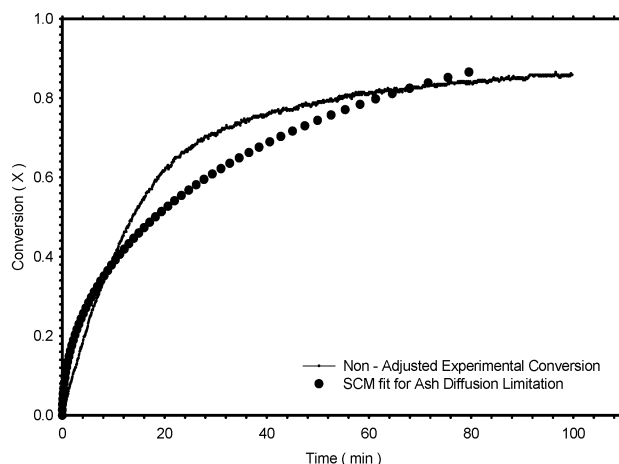


Figure 4. Results of fitting the shrinking core model to the unadjusted conversion data for a pellet core sulfided with 1.0 vol % H₂S and 24 vol % H₂ at 880 °C.

For the bare pellet cores, it was found that the effect of external gas film diffusion could not be ignored. Consequently, it was necessary to consider the effect of both film diffusion and ash layer diffusion in selecting an appropriate model for a pellet core. The two effects are accounted for in the following expressions provided by Levenspiel:⁴⁰

$$t_{\text{total}} = t_{\text{film,alone}} + t_{\text{ash,alone}}$$

$$t_{\text{total}} = \tau_{\text{film}}X + \tau_{\text{ash}}[1 - 3(1 - X)^{2/3} + 2(1 - X)] \quad (6)$$

The two coefficients which appear in this equation are defined as follows:

$$\tau_{\text{film}} = \frac{\rho_{\text{CaO}}R}{3k_g C_{\text{H}_2\text{S}}} \quad (7)$$

$$\tau_{\text{ash}} = \frac{\rho_{\text{CaO}}R^2}{6D_e C_{\text{H}_2\text{S}}} \quad (8)$$

When eq 6 was fitted to the results of the second sulfidation test shown in Figure 1 by applying nonlinear regression analysis, the best fit indicated by a relatively large correlation coefficient ($r = 0.965$) resulted in a negative value of τ_{film} . Since a negative value is unacceptable, the equation was refitted assuming this coefficient to be zero, and the results are compared with the experimental results in Figure 4. The visual appearance suggests a poor fit even though the correlation coefficient of 0.933 was still relatively high.

To achieve a better fit, the conversion versus time data were transformed by assuming that the pellet conversion was 100% for an actual conversion of 78%. In other words, for a given reaction time the adjusted conversion X_A was related to the actual conversion X by the following expression:

$$X_A = \frac{X}{X_{\text{limit}}} = \frac{X}{0.780} = 1.282X \quad (9)$$

Refitting eq 6 to the adjusted conversion data produced the final result:

$$t = 7.91X_A + 40.8[1 - 3(1 - X_A)^{2/3} + 2(1 - X_A)] \quad (10)$$

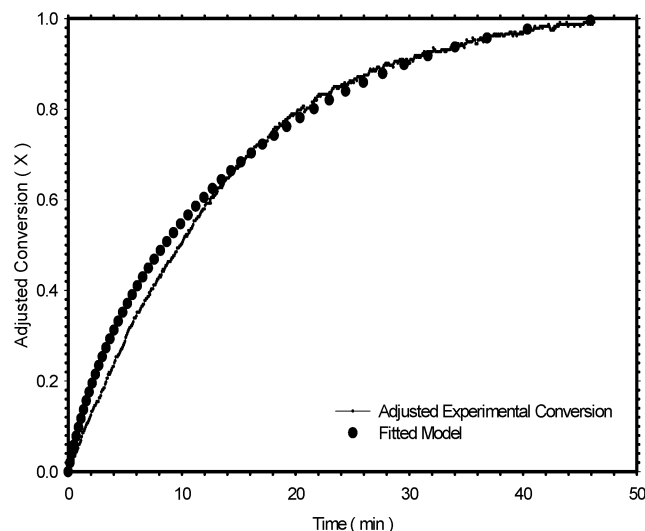


Figure 5. Comparison of adjusted experimental conversion and the fitted model conversion for pellet 2 sulfided with 1.0 vol % H₂S and 24 vol % H₂ at 880 °C.

Table 1. Results of Fitting Equation 6 to Adjusted Conversion Data for Sulfided Pellet Cores^a

pellet	wt, ^b mg	R, mm	X _{limit}	τ _{film} , min	τ _{ash} , min
1	10.8	1.40	0.78	7.91	40.8
2	10.6	1.36	0.78	5.94	46.0
3	12.7	1.47	0.78	11.15	38.4
av	11.37	1.41		8.33	41.7

^a With 1.0 vol % H₂S, 24 vol % H₂, at 880 °C. ^b Initial weight of pellet just prior to sulfidation.

This equation fit the experimental data quite well as can be seen in Figure 5 and from the very high correlation coefficient (0.997). Both τ_{film} and τ_{ash} proved to be statistically significant. During the initial period of sulfidation, the rate of conversion was controlled by film diffusion, and as conversion increased, diffusion through the ash layer became more rate limiting. Of course, eq 10 could not represent the constant rate period of sulfidation above 78% actual conversion where the rate was probably controlled by a combination of diffusion between and within the pellet grains.

The results of sulfiding two other pellet cores were analyzed by the same procedure. In each case, the data collected during the second sulfiding cycle were utilized, and eq 6 was fitted to the adjusted conversion data over the range 0–78% actual conversion. For each pellet tested, the model fitted the adjusted conversion data very well resulting in a correlation coefficient of 0.997 or higher. The results of this analysis presented in Table 1 indicate some variation in the τ coefficients of similar size. The variation in τ_{film} was larger than the variation in τ_{ash} and seemed to correlate with pellet size. The variation in τ_{film} may also have been partly due to some variation in the sphericity and/or smoothness of the pellets, whereas the variation in τ_{ash} may have been the result of differences in the structural integrity of different pellets which displayed small cracks and other imperfections.

The usefulness of the model was demonstrated by using eq 6 together with the average τ values listed in Table 1 to predict the results of two different sulfidation tests. In one case, the results of the sulfidation test conducted with pellet 2, listed in Table 1, were predicted by using the average value of each coefficient listed in

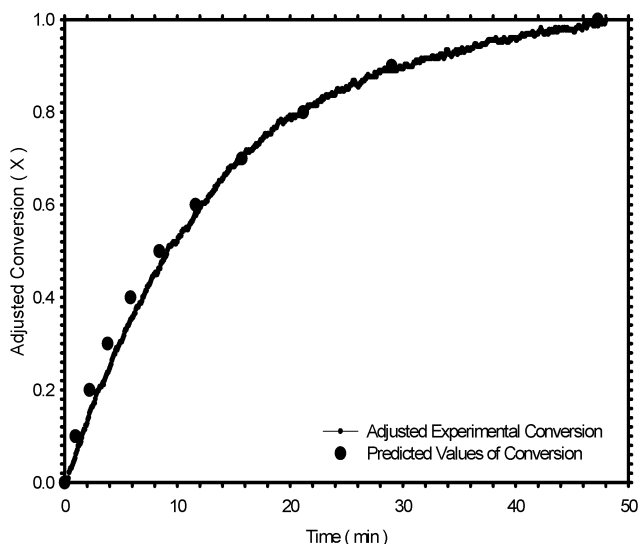


Figure 6. Comparison of adjusted experimental conversion and predicted conversion for pellet 2 sulfided with 1.0 vol % H₂S and 24 vol % H₂ at 880 °C.

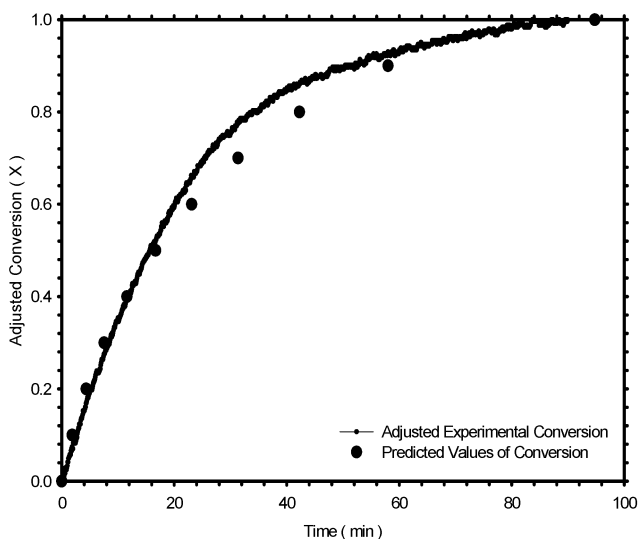


Figure 7. Comparison of adjusted experimental conversion and predicted conversion for a pellet sulfided with 0.5 vol % H₂S and 24 vol % H₂ at 880 °C.

the table adjusted to account for the difference between the radius of pellet 2 and the average pellet radius. The adjustment was made to reflect the effect of pellet radius on the two coefficients as indicated by eqs 7 and 8. Figure 6 shows that for this case the predicted values of adjusted conversion compare well with experimental values.

In another case, the average τ values were adjusted to match the conditions of a different sulfidation test which had been conducted with 0.50 vol % H₂S instead of 1.0 vol %. Again, the predicted conversion compared well with the adjusted experimental conversion (see Figure 7).

Therefore, the model appears to lend itself to account for some variation in pellet size or H₂S concentration.

A similar procedure was used to extend the semiempirical model to core-in-shell pellets. For these pellets, the diffusion resistance of the porous shell had to be considered. For a homogeneous shell, Akiti⁴¹ had shown previously that if it were the only controlling resistance, the time required to react a core-in-shell pellet would

Table 2. Results of Fitting Equation 6 (Modified) to Adjusted Conversion Data for Sulfided Core-in-Shell Pellets

pellet	wt, ^b mg	R ₁ , mm	R ₂ , mm	T, mm	X _{limit}	τ _{shell} , min	τ _{ash} , min
1	62.3	2.22	1.86	0.36	0.80	58.9	20.7
2	54.3	2.17	1.87	0.30	0.87	61.8	16.4
3	63.0	2.27	1.96	0.31	0.85	67.2	19.2
av	59.9	2.22	1.90	0.32		62.6	18.8

^a With 1.0 vol % H₂S, 24 vol % H₂, at 880 °C. ^b Initial weight of pellet just prior to sulfidation.

be determined by the following relation:

$$t_{\text{shell}} = \frac{\rho_{\text{CaO}} R_2^3}{3D_{\text{es}} C_{\text{H}_2\text{S}}} \left[\frac{1}{R_2} - \frac{1}{R_1} \right] X = \tau_{\text{shell}} X \quad (11)$$

where R₁ is the outer shell radius and R₂ is the inner shell radius. Therefore, this term can be added to eq 6 to account for shell diffusion resistance. As it turned out, τ_{shell} was so much greater than τ_{film} that the external film resistance could be neglected for a core-in-shell pellet. Therefore, eq 6 was adapted to a core-in-shell pellet by substituting τ_{shell} for τ_{film}. Although the shell contained some reactive CaO, its effect was not accounted for separately which seemed to make little difference when the model was applied to a core-in-shell pellet with a relatively thin shell. The actual conversion for a core-in-shell pellet was estimated by employing

$$X = \frac{3.5(W_f - W_i)}{M_{\text{CaO}}} \quad (12)$$

The mass of reactive CaO in the denominator, M_{CaO}, is the sum of the CaO in the core and the reactive portion of the CaO in the shell. This portion was determined by conducting an actual sulfidation test on some of the shell material by itself, and it amounted to about 4% of the shell mass. As before, the model was fitted to the adjusted conversion for a limited range of actual conversion. The upper limit of this range was marked by the transition from an increasing rate of conversion to a much slower, constant rate of conversion.

The results of fitting the model to the data collected in three separate sulfidation tests with core-in-shell pellets are presented in Table 2. Again, the data collected during the second sulfidation cycle of each test were utilized. For each pellet, the model was fitted to the adjusted conversion which was determined by eq 9 with the appropriate value of X_{limit} which was higher for a core-in-shell pellet than for a bare pellet core; i.e., X_{limit} ranged from 0.80 to 0.87 for the core-in-shell pellets, whereas it was 0.78 for the pellet cores. In each case, the model fitted the adjusted data for a core-in-shell pellet so closely that the correlation coefficient was essentially unity. Therefore, the fit was better and over a wider range than the fit for the bare cores. Although there was some variation in τ_{shell} and τ_{ash} among pellets, the differences were not unreasonable considering the cracks and imperfections which are so apparent in Figure 3. The relative values of τ_{shell} and τ_{ash} indicate that the shell provides a much greater resistance to diffusion than the ash layer provides over the entire range of adjusted conversion. Therefore, increasing the porosity of the shell would have a greater effect on the rate of conversion than increasing the porosity of the ash layer.

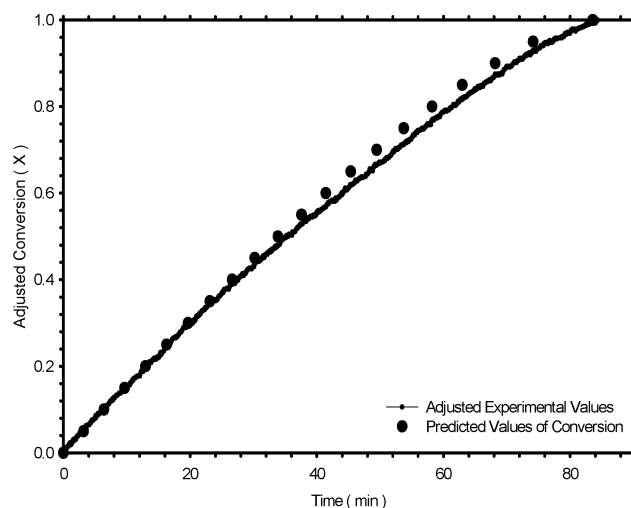


Figure 8. Comparison of predicted and experimental values of adjusted conversion for core-in-shell pellet 3 sulfided with 1.0 vol % H₂S and 24 vol % H₂ at 880 °C.

The model was used to predict the results of the sulfidation test with core-in-shell pellet 3 by employing average values of τ_{shell} and τ_{ash} which had been adjusted to reflect the difference in shell dimensions between pellet 3 and the average pellet. The adjustments for pellet radius were based on eqs 8 and 11. It can be seen that predicted values of adjusted conversion compare well with experimental values in Figure 8.

Additional insight is gained by combining the average τ values over the fitted range of conversion (i.e., X_A = 1.00) for the two cases as shown. For pellet cores,

$$t_{\text{total}} = \tau_{\text{film}} + \tau_{\text{ash}} = 8.3 + 41.7 = 50.0 \text{ min} \quad (13)$$

For core-in-shell pellets,

$$t_{\text{total}} = \tau_{\text{shell}} + \tau_{\text{ash}} = 62.6 + 18.8 = 81.4 \text{ min} \quad (14)$$

In the first case, since the ash layer is the controlling resistance for diffusion, τ_{ash} is relatively large, whereas in the second case since the resistance of the ash layer is not as important as the resistance of the shell, τ_{ash} is relatively small.

Conclusions

The results of this work indicate that the sulfidation of a calcium-based, core-in-shell sorbent can be represented over a wide range of conversion by a semiempirical model which accounts for the resistance to gas diffusion presented by the porous shell and by a layer of reaction product or “ash”. The model is basically an extension of the well-known SCM which has been widely used for gas–solid reactions. Although the model does not apply to high levels of conversion where the rate of reaction seems to be controlled by a combination of diffusion between and within grains, it provides a means for analyzing and predicting sorbent performance over a practical and, most likely, economical range of application.

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standard texts for many university courses, both graduate and undergraduate. The field of reactor modeling is also richer for his own unique contributions to model development and to the design of gas–solid fluidized-bed reactors. This report was prepared with the support of the U.S. Department of Energy (DOE), under Award DE-FG26-99FT40587. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.

Nomenclature

$C_{\text{H}_2\text{S}}$ = concentration of H_2S , mol/cm³

D_e = effective diffusivity, cm²/s

D_{es} = effective diffusivity in shell, cm²/s

k_g = mass transfer coefficient, cm/s

M_{CaO} = mass of CaO, g

R = pellet core radius, cm

R_1 = outer shell radius, cm

R_2 = inner shell radius, cm

T = shell thickness, cm

t = time, s

W_f = final pellet weight, g

W_i = initial pellet weight, g

X = conversion of CaO to CaS

X_A = adjusted conversion of CaO to CaS

Greek Symbols

ρ = molar density, mol/cm³

ρ_{CaO} = density of CaO, g/cm³

τ = time for complete conversion, s

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