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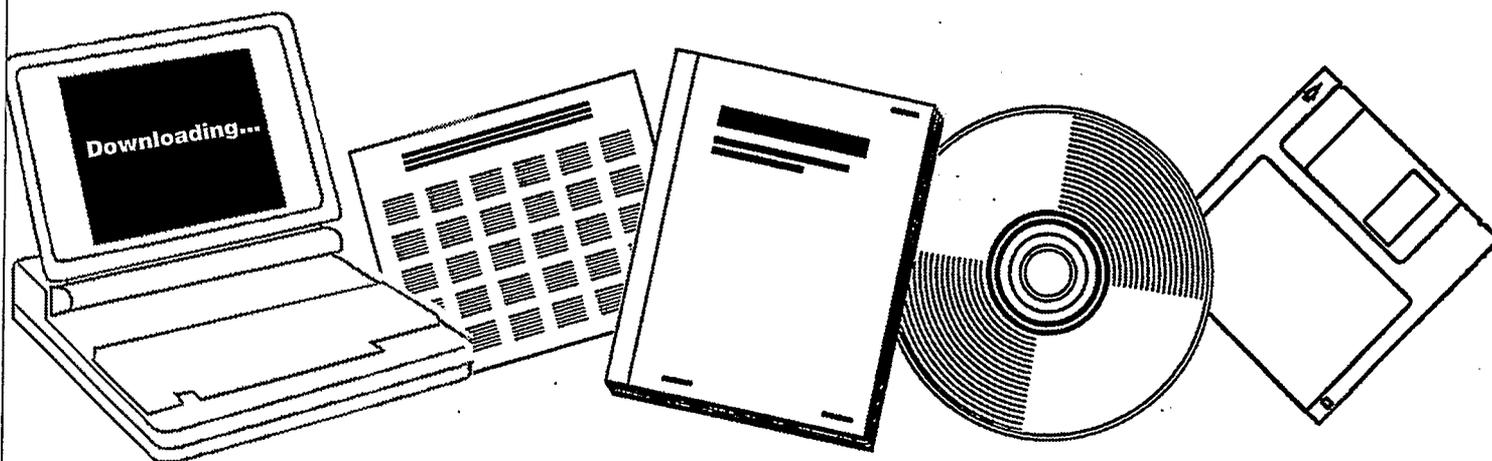
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REPORT ON REVIEW OF HOT-GAS-DESULFURIZATION SIMULATION MODELS

DEPARTMENT OF ENERGY, MORGANTOWN, WV.
MORGANTOWN ENERGY TECHNOLOGY CENTER

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A Report On
Review of Hot Gas Desulfurization Simulation Models

by

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Extended Abstract

The removal of hydrogen sulfide and other sulfur gaseous compounds from the fuel gas of coal gasification plants using iron and zinc oxides has been accomplished with promising success. Associated with this desulfurization process is the problem of regeneration of the metal sulfides formed back to the oxide state for reuse. For the efficient design and optimum operation of process plants, it is imperative that the reaction mechanism for the gas-solid reactions be known as also the gas and solids dispersion and movement in the reactor. In recent years, four mechanistic models have been developed and proposed for this purpose. In section II, models intended for use in connection with the noncatalytic gas-solid reactions are briefly described. They are: shrinking core model, homogeneous model, grain model and pore model. All the four models have been employed to mechanistically describe the desulfurization process in a fixed bed of granular metal oxide.

Schrodt has investigated in detail both the theoretical and experimental aspects of desulfurization and regeneration phenomena. For the former, he considered fixed and fluid beds and modeled the process first on the basis of a chemical reaction controlled grain model where the particle grains react in a spatially uniform way with a uniform concentration of gaseous reactant. In the second alternative, he adopted the pore diffusion controlled model where the reactant gas diffuses through the interstices of the particle and reacts rapidly at a sharp solid-product-reactant interface limited by the diffusion of reactant through the pores. Comparisons of these model predictions have been made against the limited experimental data. This analysis suggests that neither of the two models could adequately reproduce the experimental data over the entire concentration range. The film-kinetic model fits the data quite well for the mole fraction range 0.0 to ~ 0.8 , and

the film-pore diffusion model fits the remainder of the concentration range data. Schrodt also attempted to correlate his regeneration data on the basis of film-kinetic model but difficulties arise here due to large temperature excursions in the reactor temperature due to excessive amount of heat released in the oxidation reaction. He, therefore, examined the alternative of a fluidized-bed reactor and found that the shrinking-core model is inappropriate to represent the experimental data. On the other hand, he found the homogeneous model to be relatively superior.

Joshi and coworkers developed the shrinking core model by considering singly or in combination the three resistances viz., intermolecular gas film, intraparticle diffusion and gas-particle chemical reaction, to mimic the desulfurization of producer gas and regeneration of sulfided iron oxide. They found that the models are inadequate to predict the shape of the breakthrough curves as well as in their ability to predict sorption efficiency at ten percent breakthrough. By empirically modifying the expression for the film-kinetic model, they proposed an expression between sorption efficiency and fractional breakthrough which satisfied both of the above mentioned criteria. These workers have further developed their most successful kinetic-film model to allow for the different values of the temperatures for the gas and the solid. This model which contains three parameters is quite flexible. The lack of adequate available data prevented definitive conclusions concerning the capabilities of the models and all the three simulation models are found to be defective to some degree. This is not very surprising in view of the general agreement that the shrinking core model is quantitatively incapable of simulating gas-solid reaction kinetics for porous solids as in the present case of iron oxide-ash.

A pore plugging model was developed at Giner Inc., under well defined

approximations to simplify the mathematical formulation. Thus, the reaction rate constant, which in general depends on the sorbent conversion and is therefore a function of both reactor location and time, is assumed arbitrarily to decrease exponentially with time having a characteristic time constant, t_p . t_p represents how fast or slow the sorbent will become inactive either due to saturation or due to plugging of the pores at the external particle surface. Further, it is assumed that only the average bed conversion is followed so that the Damkohler number is only a function of time and this easily leads to the establishment of the hydrogen sulfide concentration as a function of time. The model thus has two unknown parameters viz., the pore plugging time constant t_p , and the reaction time constant t_r . t_p characterizes the capacity of the sorbent pellets to absorb hydrogen sulfide which monotonically increases with t_p . t_r represents the reactivity of the sorbent which increases as t_r decreases. Both t_r and t_p are determined from the experimental data. The model has been assessed against somewhat limited experimental data and is found to be adequate to represent the hydrogen sulfide breakthrough characteristics. The latter is more sensitive to the values of t_p than t_r . More detailed examination of experimental data on the basis of this model is essential for the proper appraisal of the model and its specific deficiencies.

Steinfeld developed a mathematical model for hydrogen sulfide sorption in a fixed bed in which the heterogeneous gas-solid reaction is simulated on the basis of a modified grain model. The overall reactor model is based on the mass balance for the gas phase and the solid phase on a volume element of an interval. The bed is regarded to be composed of several equally spaced intervals. The continuity equations, which are partial differential equations, are thus derived under well defined approximations and are solved by the explicit form of the finite difference approximation. Verification of the

model was conducted in two stages. First, the global reaction rate for single particles is examined by comparing the experimental and calculated conversion rates for single particles. For zinc oxide, it is found that while the shape of the experimental conversion - time curves is reproduced by the theoretical calculations, the magnitude of the maximum is not reproduced. The theoretical values agree with the initial experimental data but then the curve levels off approximately twenty percent below the experimental data. Numerical computational difficulties did not permit an adequate check of the reactor performance.

In the light of limited success of these models in their present form to represent the experimental data, a relative assessment of their appropriateness is given in the last section of this report along with some recommendations for future work.

I. Introduction

Many gasification schemes have been developed for the production of a fuel gas from coal which can be piped for direct use. In case coal contains sulfur the fuel gas will have sulfur bearing compounds and these must be removed before fuel gas can be utilized. For scrubbing these sulfur compounds, which are mostly hydrogen sulfide and traces of such gases as carbonyl sulfide, carbon disulfide, thiophene etc., several metal oxides have been proposed. To accomplish this goal commonly referred to as the desulfurization process of the low - Btu fuel gas, Westmoreland, Gibson and Harrison¹ undertook a systematic investigation and recommended a set of eleven metal oxides. These are oxides of Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu and W. These workers have reported equilibrium fractional desulfurization for these metal oxides as a function of temperature in the range 633-1773K and at pressures up to 20 atmospheres. Another comprehensive review effort is that of Attar² dealing with the thermodynamics and chemical kinetics of reactions of sulfur in coal-gasification gases. Many recent works have concentrated on the use of iron oxide-fly ash and these will be discussed and evaluated in this report in detail with particular reference to the success achieved in mathematically modeling the desulfurization and regeneration process. The latter refers to restoring the sulfided iron in the fly ash back to the oxide state so that the process of desulfurization and regeneration may be repeated in a continuous fashion in an industrial gas scrubbing cleanup plant. A successful mathematical model for these processes will provide a reliable basis for engineering design and scale-up of coal fuel gas cleaning plants.

In the present report recent theoretical modeling efforts will be examined as to their appropriateness for successfully representing the sulfidation and regeneration processes for the iron oxide either naturally present in the fly ash and/or added to it. The basis of such a formulation rests on the proper recognition involved in the mechanism of gas-solid heterogeneous reactions and related processes. Many idealized models have been developed^{3,4} to mimic such reactions involving two different phases viz., gas and solid. We will, therefore, review those models first which have been used with some success to represent the sulfidation and regeneration processes and then evaluate them by comparing their relative merits of representing the experimental data. This will lead us to develop and conclude the success possible on the basis of existing models and the direction in which the theoretical and experimental effort must be directed to achieve the above outlined goal.

II. Models For Noncatalytic Gas-Solid Reactions

In the analysis of a chemical reactor involving heterogeneous reactions, a comprehensive study of the primary single nonisothermal noncatalytic reaction can assist in the substantial simplification of the overall formulation. For simplicity we shall consider a single spherical pellet. The results derived for the single pellet can then be used to predict the behavior of a fixed bed⁵ or to analyze the operation of a fluidized bed.⁶ Heterogeneous gas-solid reactions involving a moving boundary occur frequently in chemical and metallurgical industrial processes including combustion and gasification of solid fuels, reduction of metallic oxides, roasting of sulfides and the regeneration of carbon deposited catalysts and hence have been extensively studied⁶⁻²⁸.

A gas-solid reaction involves heat and mass transfer processes and chemical kinetics. Many models for the reactions taking place on a single particle of the solid reactant have been postulated. In general, the gas-solid reactions have been broadly treated in two categories. One category

assumes that the solid reactant is nonporous to the reacting gas and the reaction takes place only at the surface of the solid reactant. The other category assumes that the particle of the solid reactant is porous and the gas-solid reaction takes place throughout the pores. The porous particle has been further treated to account for the microscopic structures of the solid pellet by several idealized schemes. A brief description of the various models is presented below.

1. Shrinking Core Model

When the porosity of the solid reactant is very small so that the solid is practically impervious to the gaseous reactants, the reactions between the gas and the solid will occur at the surface of the solid or at the interface between unreacted solid and the porous solid product. As illustrated in Figure 1, we consider a spherical particle having an initial radius R_0 being reacted with gaseous reactant A. At first, the reaction takes place at the outside surface of the particle, but as the reaction proceeds, the surface of the reaction will move to the interior of the solid leaving behind a porous solid product. During this process, the reaction surface moves inward forming an unreacted core which shrinks with time. The external radius of the particle may change. For the gaseous reactant to reach the surface of the core, it has to move through various layers of the resistances in series, namely, the fluid film around the surface of the particle, the porous ash layer and the reaction surface at the core. Figure 1 illustrates the resistances in series as well as the concentration profiles within the particle. The shrinking core model holds particularly true when the chemical reaction rate is very rapid and the diffusion is sufficiently slow. Under such conditions, the zone of reaction is narrowly confined at the interface between the unreacted solid reactant and the product.

2. Zone Reaction Models

Difficulties arise when the shrinking core model is applied to the reactions in a porous solid because the gaseous reactant can easily diffuse

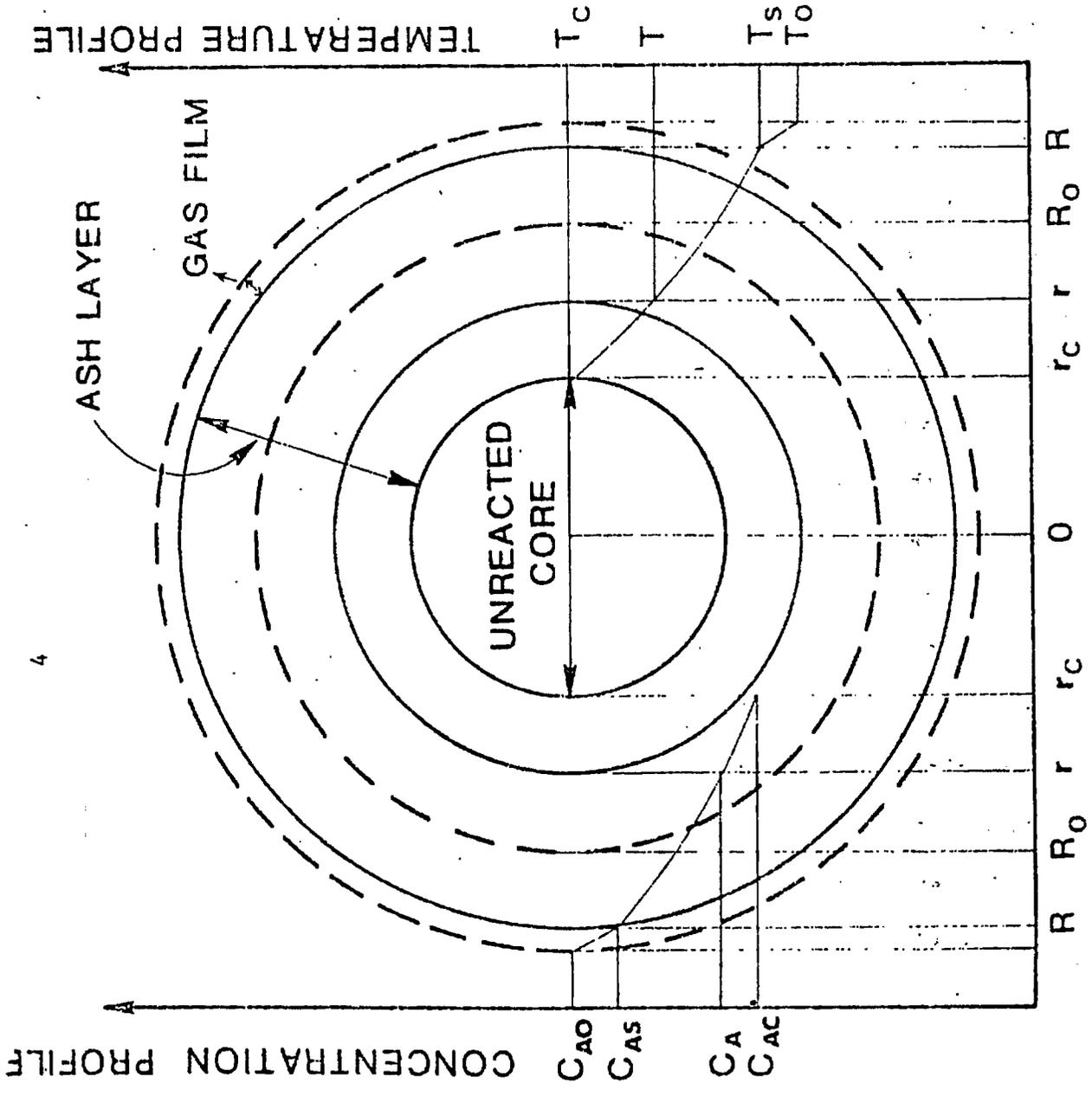


Figure 1. Gas Solid reaction of a growing particle: the concentration and temperature profiles.

beyond the interface and spread the reaction throughout the particle producing a gradual variation in the solid reactant concentration in all parts of the particle. The reaction models for the porous solid reactant and the gas can be subdivided to include the structural assumption of the particles. The following models have been widely used.

a. Homogeneous Model (Also referred to as the Volumetric Reaction Model)

In many cases, the solids contain enough voidage to permit the flow of gaseous reactant freely into the pores. The diffusivity of the gaseous reactant through the solid pores is large and invariant during the reaction. The solid is considered to be an ensemble of small lumps of reactant distributed evenly throughout the solid phase. In this case it is reasonable to consider that the reaction between the gas and the solid components is occurring homogeneously throughout the solid phase.

b. Grain Model

The pellet is considered to consist of uniformly sized spherical particles. The gaseous reactant diffuses through the interstices and then reacts with the spherical particles according to the shrinking core model. The reacted zones progressively form increasing concentric shells through which the reactant gas has to diffuse.

c. Pore Model

This model assumes that the reaction takes place at the surface of the uniform cylindrical pores contained in the particle. The reactant gas diffuses into the pores and reacts with the solid surface. Initially this reaction occurs at the pore walls but subsequently it will take place at a front which moves inward in the lateral direction. The process will then require the lateral diffusion of gaseous reactant through the solid product layer.

The concentration of solid and gaseous reactants for the zone reaction

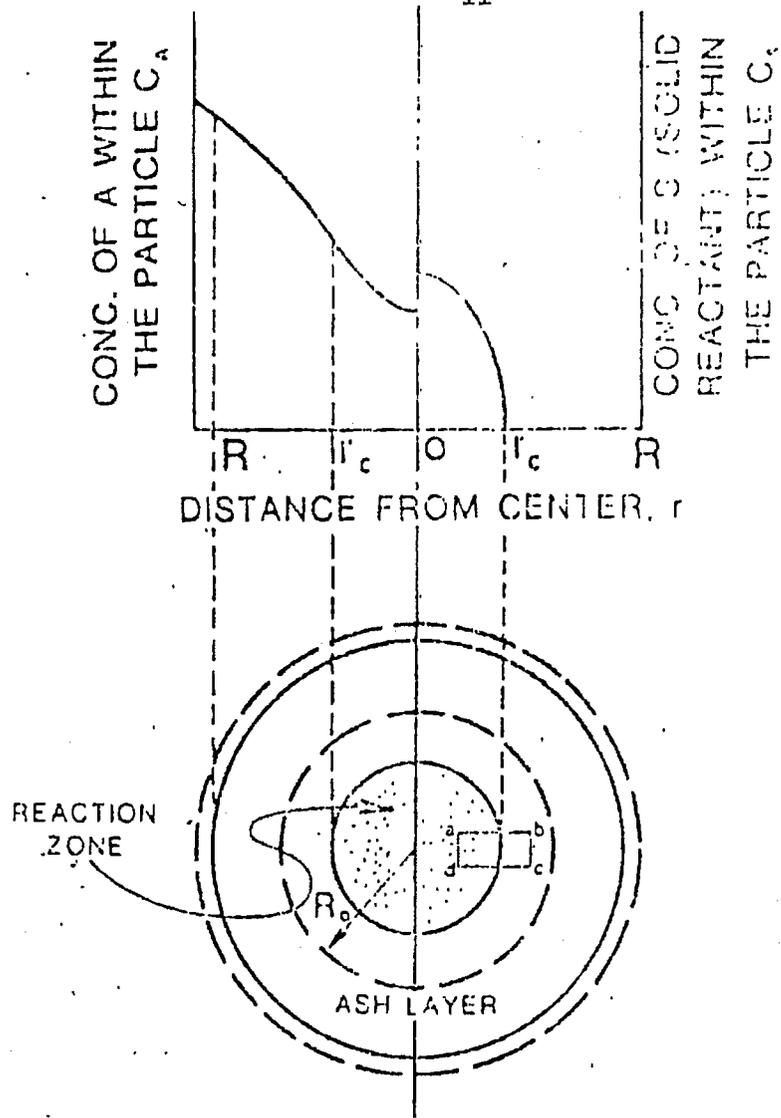
models are illustrated in Figure 2(a). The Figure 2(b) also illustrates the reaction mechanism proposed for homogenous, grain and the pore models.

The gas-solid reaction taking place on the surface of either a macroscopic particle or a micrograin depends on its chemical adsorption of the gaseous reactant. A gas-solid reaction can be considered to consist of the following steps:

- (i) diffusion of the gas across the gas film surrounding the solid,
- (ii) diffusion of the gas through the porous ash layer,
- (iii) adsorption of the gas at the solid surface,
- (iv) chemical reaction with the solid surface,
- (v) desorption of the gaseous products from the solid reaction surface, and
- (vi) diffusion of the product gases away from the reaction surface through the porous ash layer and the gas film surrounding the pellet.

These steps take place consecutively and the slowest becomes the rate controlling step. However, many reactions are influenced simultaneously by more than one step. In general, for the sake of mathematical simplicity, the process is viewed to consist of steps (i), (ii), and (iv) with the assumption that the remaining steps are relatively fast and do not influence the rate. These processes are further complicated by the heat of reaction, fluid flow, size, shape and the configuration of the solid particles. In view of these complications, many investigators, have attempted to analyze the problem by introducing simplifying assumptions such as neglecting some of the reaction resistances, or by using a simple form for reaction rate expression or by restricting the system to isothermal conditions only. Some works have accounted for three resistances simultaneously and included expressions for the rate of reaction in terms of the parameters defining the interphase mass transfer, intraparticle diffusion and chemical reaction rate constants.

Rehmat and Saxena^{29,30} employed the shrinking core model to describe



CROSS SECTIONAL VIEW OF abcd (from fig. 2a)

- i) HOMOGENOUS MODEL
- ii) GRAIN MODEL
- iii) PORE MODEL
FREE SURFACE

Figure 2. Concentration profile and reaction mechanism for zone reaction model.

the heterogeneous gas-solid reactions taking place on the surface of a spherical solid pellet whose size changes as the reaction proceeds. They considered all the above mentioned three resistances and also assumed the temperature of the unreacted core to be dependent on the degree of solid reacted as a result of the production of heat of reaction. The other models have also been employed to describe the kinetics of sulfidation and regeneration of metal oxides and these will now be discussed in reference to individual efforts.

III. Mathematical Models Due to Schrodtt³¹

Schrodtt³¹ proposed and developed two mathematical models for fixed-bed reactors on the basis of physical reasoning. The first model describes the behavior of a fixed bed when gaseous reactant diffuses through a stagnant film surrounding the particles and becomes uniformly distributed in the solid reactant where the chemical reaction takes place. This is somewhat similar to the above mentioned chemical reaction controlled, grain model where the particle grains react in a spatially uniform way with a uniform concentration of gaseous reactant. The second model describes the behavior of a fixed bed when the gaseous reactant first diffuses through a stagnant film surrounding the particles and then diffuses through the pores of reacted solid to reach a receding narrow boundary between the reacted and unreacted solid where the reaction occurs instantly. This is the above mentioned pore diffusion controlled model where the reactant gas diffuses through the interstices of the particle and reacts rapidly at a sharp solid-product - reactant interface limited by the diffusion of reactant through the pores. The results obtained for these two models and the assumptions under which they have been derived will be enumerated as given by Schrodtt³¹.

While applying the first model (the grain model) to the sorption of gaseous reactant by the solid particles in a fixed-bed reactor, the following

assumptions were made³¹,

1. gas flow in the reactor is characteristic of plug flow,
2. chemical reaction is irreversible,
3. particles and bed are in pseudosteady state,
4. during the course of reaction particle temperature remains constant,
5. particles are always exposed to a uniform gas composition,
6. solid reactant is approximated to be a flat plate and is surrounded by a porous solid product shell.

The rate, Rate (I), at which the gaseous reactant or sorbate reaches the surface of the particles is:

$$\text{Rate (I)} = k_m \rho_m a_p (y_b - y_p), \quad (1)$$

where

$$a_p = \frac{3(1-\epsilon)}{\phi_s r_p} \quad (2)$$

Here a_p is the surface area of particles per unit volume of packed reactor, k_m is the gas phase mass transfer coefficient, y_b is the bulk gas phase sorbate mole fraction, y_p is the particle interface sorbate mole fraction, r_p is the particle radius, ρ_m is the bulk gas phase molar density, ϵ is the void fraction or bed porosity, and ϕ_s is the particle sphericity factor.

The rate, Rate (II), of uniform chemical reaction within the particles is

$$\text{Rate (II)} = k_k \rho_m y_p (1-\epsilon) X \alpha M_o, \quad (3)$$

where k_k is the specific reaction rate constant, X is the fraction of solid available for reaction, α is the mole of reactant solid per mole of sorbate, and M_o is the sulfur concentration in the solid.

Since these two processes occur in series, their rates must be equal at the steady state. The resulting relation may then be solved to give the gaseous reactant concentration at the particle interface in terms of known quantities, i.e.,

$$y_p = \frac{k_{m p} a y_b}{k_{m p} a + k_k X (1 - \epsilon) \alpha M_o} \quad (4)$$

Substituting y_p from equation (4) in equation (1), the following expressions for the Global Rate of reactant consumption is obtained,

$$\text{Global Rate} = \frac{\rho_m y_b X (G/V)}{\frac{(G/V)}{k_k (1 - \epsilon) \alpha M_o} + \frac{X (G/V)}{k_{m p} a}} \quad (5)$$

Here G is the volumetric gas flow rate, and V is the packed bed volume.

It is customary to express rate expression in terms of a dimensionless number. We, therefore, define the film diffusion number, N_F , as

$$N_F \equiv \frac{k_{m p} a}{(G/V)} \quad (6)$$

and the kinetic sorption number, N_k , as

$$N_k \equiv k_k \frac{(1 - \epsilon) \alpha M_o}{(G/V)} \quad (7)$$

The relation of equation (5) then becomes:

$$\text{Global Rate} = \frac{\rho_m y_b X (G/V)}{(1/N_k) + (X/N_F)} \quad (8)$$

The reactant mass balance for an element δZ within the packed bed is given by:

$$G \rho_m \frac{\partial y_b}{\partial Z} = - \frac{\rho_m y_b X (G/V)}{(1/N_k) + (X/N_F)} \quad (9)$$

Let us define the following dimensionless quantities:

$$\bar{Y} \equiv \frac{y_b}{y_o} \quad (10)$$

and

$$\bar{Z} \equiv \frac{Z}{L} = \frac{Z \cdot A'}{V} \quad (11)$$

Here G is the volumetric gas flow rate, y_o is the inlet bulk gas phase reactant mole fraction, \bar{Y} is the dimensionless reactant concentration, Z is the position in packed bed, \bar{Z} is the dimensionless position in packed bed, L is the packed bed length, A' is cross-sectional area of packed bed reactor, and V is the packed bed volume. With equations (10) and (11) equation (9) becomes:

$$\frac{\partial \bar{Y}}{\partial \bar{Z}} = - \frac{\bar{Y} X}{\frac{1}{N_k} + \frac{X}{N_F}} \quad (12)$$

A solid phase mass balance for the sorbed gas in an element δZ of the bed leads to the following relation:

$$M_o (1 - \epsilon) \frac{\partial X}{\partial t} = \frac{\rho_m y_b X (G/V)}{(1/N_k) + (X/N_F)} \quad (13)$$

M_o is the ash sulfur capacity and ϵ is the bed voidage. Let us introduce the following dimensionless terms:

$$\beta \equiv \frac{M_o (1 - \epsilon)}{\rho_m y_o} \quad (14)$$

$$\tau \equiv \frac{t (G/V)}{\beta} \quad (15)$$

and

$$\bar{X} \equiv 1 - X \quad (16)$$

where \bar{X} is the dimensionless fraction of reacted solid and corresponds to the amount of sulfur absorbed when the stoichiometric ratio of iron/sulfur is one. The gas and solid phase mass balance equations (12) and (13) with equations (14) - (16) become:

$$\frac{\partial \bar{Y}}{\partial \bar{Z}} = - \frac{\bar{Y} (1 - \bar{X})}{\frac{1}{N} + \frac{(1 - \bar{X})}{N_F}} \quad (17)$$

and

$$\frac{\partial \bar{X}}{\partial \tau} = \frac{\bar{Y} (1 - \bar{X})}{\frac{1}{N_k} + \frac{1 - \bar{X}}{N_F}} \quad (18)$$

The solution of these two partial differential equations gives the dynamic behavior of a fixed-bed reactor.

Equations (16) and (17) were solved by Schrodt³¹ following the method of Bischoff³² under the following boundary conditions:

$$\begin{aligned} \bar{Y} &= 0 \text{ for } \bar{Z} > 0, \tau = 0 \quad , \\ \bar{Y} &= 1 \text{ for } \bar{Z} = 0, \tau \geq 0 \quad , \\ \bar{X} &= 0 \text{ for } \bar{Z} \geq 0, \tau = 0 \quad . \end{aligned} \quad (19)$$

The solution is:

$$\tau = \frac{1}{N_F} \frac{1 - \lambda}{1 - \lambda \bar{Y}} - \frac{1}{N_k} \ln \frac{\lambda (1 - \bar{Y})}{1 - \lambda \bar{Y}} \quad , \quad (20)$$

where

$$\lambda = \frac{\exp(-N_k \bar{Z})}{\bar{Y} [1 + (N_k/N_F)]} \quad . \quad (21)$$

Equations (20) and (21) may be used to predict the bed efficiency, τ , for a specified concentration of reactant, \bar{Y} , at $\bar{Z} = 1.0$.

For irreversible reactions,³³ $\bar{X} = \bar{Y}$ and equation (18) then can be integrated to yield the following result:

$$\tau = \frac{1}{N_k} \ln \frac{\bar{Y}}{1 - \bar{Y}} + \frac{1}{N_F} \ln \bar{Y} + \text{constant} \quad . \quad (22)$$

For a sorbent bed which is long enough for the sorbate concentration wave to be fully developed before breakthrough, Schrodt³¹ comments that the bed efficiency can be closely approximated by equation (22) if the basic model is correct and N_k and N_F are known. Alternatively, equation (22) can be used to obtain the dimensionless numbers N_k and N_F from experimental breakthrough data. The values thus obtained can then be correlated with the operating parameters of the system through equations (6) and (7). Another approach proposed by Schrodt³¹ is to compute k_m from the packed bed mass transfer correlation of Carberry,³⁴ viz.:

$$k_m = \left(1.15 \frac{U_o}{\epsilon} \right) \left(\frac{2 r_p U_o}{v \epsilon} \right)^{-0.5} \left(\frac{v}{D_m} \right)^{-0.667} \quad (23)$$

Here U_o is the superficial gas velocity, v is the kinematic viscosity coefficient, and D_m is the gas phase diffusivity. The reaction rate constant k_k may be correlated by the following Arrhenius type expression. i.e.,

$$k_k = S \exp (-E/RT)$$

Here the pre-exponential coefficient S and the activation energy E are obtained from the experimental data, R is the gas constant and T is the temperature.

Now a parallel mathematical treatment for the above mentioned second model (the pore diffusion model) will be presented for the sorption of

gaseous reactant by the solid particles of the fixed-bed reactor. Schrod³¹ made the following simplifying assumptions:

1. gases are in plug flow in the reactor,
2. chemical reaction occurs irreversibly,
3. reactant concentration at the particle boundary is zero,
4. reactant solid is confined in a flat plate of thickness $r_p - r_o$,
5. pore diffusivities are temperature dependent,
6. pseudo-steady state conditions prevail.

The rate at which the reactant reaches the surface of the particles, Rate (I), is again given by equation (1). The reactant pore diffusion rate, Rate (III), is

$$\text{Rate (III)} = \frac{3\alpha_p D_p (1 - \epsilon)}{\phi_s (r_p - r_o) r_p \cdot (G/V)} \frac{\rho_m y_p (G/V)}{1 - X}, \quad (25)$$

where

$$X \equiv (r_i - r_o)/(r_p - r_o). \quad (26)$$

The dimensionless ratio X gives the fraction of solid available for reaction and the length of the diffusion path is given by $(r_p - r_i)$. α_p is the particle porosity in particle shell, D_p is pore diffusivity, and the rest of the quantities are the same as defined before and in the nomenclature. A dimensionless pore diffusion number, N_p , is defined such that

$$N_p = \frac{3\alpha_p D_p (1 - \epsilon)}{\phi_s (r_p - r_o) r_p (G/V)} \quad (27)$$

Since the processes whose rates are Rate (I) and Rate (III) occur in series, they are equal and the resulting equation can be solved for the unknown gaseous reactant concentration, y_p , such that

$$y_p = \frac{k_m a_p y_b}{k_m a_p + [N_p / (1 - X)] (G/V)} \quad (28)$$

Substituting for y_p from equation (28) in equation (1), the Global Rate for gaseous reactant consumption is obtained, viz.,

$$\text{Global Rate} = \frac{\rho_m y_b (G/V)}{\frac{(G/V)}{N_F} + \frac{(1 - X)}{N_P}} \quad (29)$$

We can now write the above derived gas and solid phase material balance equations in the dimensionless form:

$$\frac{\partial \bar{X}}{\partial \tau} = \frac{\bar{Y}}{\frac{1}{N_F} + \frac{\bar{X}}{N_P}}, \quad (30)$$

and

$$\frac{\partial \bar{Y}}{\partial Z} = - \frac{\bar{Y}}{\frac{1}{N_F} + \frac{\bar{X}}{N_P}} \quad (31)$$

These two partial differential equations give the dynamic behavior of a fixed bed reactor when the gas-solid reactions are represented by the pore model with the above listed six assumptions.

The method of Bischoff³² under the following boundary conditions,

$$\begin{aligned}\bar{Y} &= 0 \text{ for } Z > 0, \tau = 0, \\ \bar{Y} &= 1 \text{ for } Z = 0, \tau \geq 0, \\ \bar{X} &= 0 \text{ for } Z \geq 0, \tau = 0,\end{aligned}\tag{32}$$

leads to the following solution of equations (30) and (31):

$$\tau = \frac{N_P^2 \bar{Z}^2 + (2 N_P^2 / N_F) (\bar{Z} \ln \bar{Y}) + (N_P^2 / N_F^2) (\ln \bar{Y})^2}{2 N_P (1 - \bar{Y})^2} + \frac{N_P \bar{Z} + (N_P / N_F) \ln \bar{Y}}{N_F (1 - \bar{Y})}\tag{33}$$

Schrodt³¹ employed equation (33) to predict bed efficiency, τ , for a specified concentration of the reactant, \bar{Y} , at $\bar{Z} = 1.0$.

For constant pattern solution to equations (30) and (31), one puts $\bar{X} = \bar{Y}$. With this equality, equation (30) can be integrated to yield.

$$\tau = \frac{\bar{Y}}{N_P} + \frac{\ln \bar{Y}}{N_F} + \text{constant}\tag{34}$$

If the concentration profile develops fully before breakthrough occurs, the bed efficiency can be well approximated by equation (34). N_F can be computed from equations (23) and (6), and N_p is obtained through analysis of the experimental data.

Equations (20) and (33), and the equations (22) and (34) were used by Schrodt³¹ to predict dimensionless time for exact and constant pattern solutions for the two models and for selected values of the dimensionless rate parameters N_F , N_p and N_k . These results indicated that the model simulation is not sensitive to the values of N_F above fifty. As the test experimental conditions correspond to N_F values much larger than fifty, it is apparent that the bulk gas phase diffusion is not a controlling factor. Further, as expected when N_p and N_k become infinite, a condition corresponding to instantaneous reaction rate, perfect sorption is predicted; i.e., all reactant or sorbate introduced to the reactor bed reacts instantly with all the available solid reactant before breakthrough occurs.

It was found that neither of the two models could adequately reproduce the experimental data over the entire concentration range. The SEM-EDAX analyses showed that iron oxide was concentrated near the surface of the particles in a highly porous spongy structure, while some iron oxide remained in the deep core of the particles. As a result, the film-kinetic model fits the data quite well for the mole-fraction range 0.0 to ~ 0.8 , and the film-pore diffusion model fits the remainder of the concentration range data; i.e., ~ 0.8 to 1.0. The

film-kinetic model was found to fit the data for concentrations up to $\bar{Y} = 0.74$ for 1000°F , $\bar{Y} = 0.80$ for 1200°F , and $\bar{Y} = 0.86$ for 1400°F .

N_k is expressed as

$$N_k = \frac{S [\exp (-E/RT)] (1 - \epsilon) \alpha M_o}{(G/V)_o (T/530) (1/P)} \quad (35)$$

or alternatively in the form

$$\ln \frac{N_k (G/V)_o T}{M_o P} = -\frac{E}{RT} + \ln [530 S \alpha (1 - \epsilon)]. \quad (36)$$

A plot of the left side of equation (36) versus $(1/T)$ is a straight line, the slope of which gives $(-E/R)$ and hence E , while the intercept gives S . The values k_k and E thus obtained by Schrod³¹ are found to be in good agreement with the values reported by other investigators.

The upper portion of the breakthrough curves, $\bar{Y} = 0.8$ to 1.0 , is adequately represented by the film-pore diffusion model. Schrod³¹ evaluated the pore diffusion number, N_p , from the analysis of his experimental data and the relation of equation (34) obtained on the constant pattern solution for this model. Equation (27) was then utilized to estimate the pore diffusivity coefficient, D_p . This was found to be of the order of 10^{-3} to 10^{-4} ft^2/hr , which is characteristic of the Knudsen diffusivity coefficient. Substituting the variation of G with temperature (T) and pressure (P), and recalling that $D_p \propto \sqrt{T}$, equation

(27) transforms to

$$N_p = \frac{3 D_p \alpha_p (1 - \epsilon) \sqrt{T/530} \cdot P}{(G/V)_o \cdot (r_p - r_o) \cdot r_p \cdot \phi_s \cdot (T/530)} \quad (37)$$

Schrodt³¹ has introduced a constant, ξ , defined as follows and which is found to be independent of temperature and pressure on the basis of experimental data,

$$N_p = \xi \frac{P}{(G/V)_o T} \quad (38)$$

The average value of ξ is 244.5 with the standard deviation of 26.5.

Equation (38) thus leads to N_p values which are accurate to within $\pm 11\%$.

Each ash will have a different value of ξ as D_p , ϕ_s , r_p , $(r_p - r_o)$ and α_p are different for different ashes.

Schrodt³¹ employed the film-kinetic model to represent his oxygen breakthrough curves for the regeneration process. Here in a fixed bed of solid reactant (FeS), the gaseous reactant (oxygen) diffuses through a stagnant film surrounding the particles and becomes uniformly distributed in solid reactant where the reaction occurs uniformly. Equation (7) again defines the kinetic sorption number for this regeneration reaction, where α has a value of 4/5 and is the ratio of reactant iron to molecular oxygen, and M_o is the ash's oxygen capacity, lb-mol/ft³ solid. The constant pattern solution for this case obtained by setting $\bar{X} = \bar{Y}$ is given by equation (22). A series of regeneration runs conducted using

fully sulfided ash at 1000° and 1200°F, a pressure of one atmosphere and a space velocity of 86.2 hr⁻¹ with a gas stream containing 5 mole percent oxygen in nitrogen were analysed on the basis of equation (22). Values of N_F were calculated using the known experimental operating conditions and the correlation of equation (23) for mass transfer in packed beds. Average values of N_k were then calculated by a linear regression analysis of equation (22). Regeneration reactions rates were found to be only weakly dependent on temperature.

Because the thermal and reaction zones are congruent, it is appropriate to employ the peak temperature in correlating the regeneration reaction rate constant. Schrod³¹ found the following Arrhenius form for k_k :

$$k_k = 1.75 \times 10^5 \exp [-1440/RT] \quad (39)$$

In the regeneration of sulfided ash a considerable amount of heat is released and so in fixed-bed reactors, the temperature is controlled by using relatively dilute streams of oxygen. Another approach to resolve this problem would be to employ fluidized-bed instead of fixed-bed reactors and Schrod³⁵ has investigated this alternative also. As the heat dispersal in and removal rates³⁶ from fluidized-bed reactors are much larger than from fixed-bed reactors, the problem of temperature excursion is not a serious one. It may be noted that the desulfurization reactions are only mildly exothermic with a ΔH value of about 8 kcal/mole-H₂S. We will now summarize the salient features of

this latter work of Schrodt,³⁵ particularly in reference to the mathematical models employed by him to represent his desulfurization and regeneration data as taken in a fluidized bed reactor. As in the earlier work,³¹ here also Schrodt³⁵ considers the breakthrough curves which involve the plot of C_A/C_{AO} versus dimensionless time, τ . τ is defined as the ratio of the cumulative moles of A passed through the reactor at time τ , to the total moles of A needed to saturate the bed.

If the sorption rate is infinite, all the reactant gas that can be absorbed will be absorbed at the instant of breakthrough. This corresponds to $C_A/C_{AO} = 1$ and $\tau = 1$. In practice, however, the breakthrough starts before all the solid reactant is consumed; i.e., when $\tau < 1$. One may, therefore, define a sorption efficiency as the value of τ at which C_A/C_{AO} is equal to a specified value. Schrodt arbitrarily selected a value of 0.1 for C_A/C_{AO} .

Schrodt³⁵ has considered the shrinking-core model and has derived the necessary equations which can be solved to generate the breakthrough curves. He has considered two limiting simplified cases of this general model. In the first case, chemical reaction rate is controlling and both the diffusion resistances through the gas film and through the product ash layer are negligibly small. In the second case, the diffusion through the product layer limits the reaction rate and the resistances due to gas film diffusion and reaction are relatively small. The theoretically computed curves of C_A/C_{AO} versus τ for the first case were found to be qualitatively different from the experimental curves, and

even for the second case the disagreement between theory and experiment was quite pronounced. He found that even the general shrinking core model with all the three resistances was inadequate to represent experimental data and, hence, he concluded that the shrinking core model is an unrealistic model to simulate desulfurization and regeneration processes.

Schrodt,³⁵ therefore, attempted to correlate his data using a model more appropriate for a porous particle and considered the homogeneous model where the reaction may be considered to occur in a pseudo-homogeneous fashion throughout the particle. The following assumptions were made in the analysis:³⁵

1. There are no diffusional resistances and the reactant diffuses readily to the reaction sites; i.e., no intraparticle concentration gradient exists.
2. The particle temperature and the reactor temperature are constant and the same throughout.
3. Reaction rate is first order with respect to the concentration of the reacting gas.
4. Superficial linear gas velocity is constant throughout the reactor during the course of the reaction.
5. The solids in the reactor are perfectly mixed.
6. Axial gas dispersion is negligible.
7. The gas is in plug flow.
8. The particles are spherical and their properties do not change as the reaction proceeds.

Numerical calculations performed with $m = 1$ in the first-order rate equation; viz.,

$$-r_A = k C_{AS} W^m, \quad (40)$$

yielded results which, though much better than with the shrinking models, were still not quite satisfactory. The value of m was then arbitrarily changed to 1.5, 1.75, 2.0, 2.5 and 3.0, and the predicted breakthrough curves were compared with the experimental ones. This comparison suggested a value of 2 for m . The comparison of experimental and simulated curves was also employed to back up the value of the kinetic parameter m and was found to vary with the nature of the coal ash.

In summary, it is reasonable to conclude that the shrinking core model is found to be inadequate to simulate the gas-solid kinetics of chemical reactions in fluidized beds, while the homogeneous model is relatively more successful. As in fixed-bed work, this work also suggests that the coal ash particles must be regarded as porous and the use of grain model or pore model for fixed beds is consistent with the use of homogeneous model in fluidized beds to simulate the heterogeneous gas-solid reactions.

IV. Nomenclature for Section III

a_p	surface area of particles per unit volume of packed bed reactor,
A	gaseous reactant,
A'	cross-sectional area of packed bed reactor,
C_A	concentration of the gas component,
C_{AC}	concentration of A at the core of the particle,
C_{AO}	concentration of A in the bulk phase,
C_{AS}	concentration of A at the surface of the particle,
D_m	bulk gas phase diffusivity,
D_p	pore diffusivity,
E	reaction activation energy,
G	volumetric gas flow rate,
k	rate constant
k_k	specific reaction rate constant,
k_m	gas phase mass transfer coefficient,
L	packed bed length,
m	reaction order with respect to solid,
M_o	sulfur concentration (or capacity) of the ash,
N_F	dimensionless film diffusion number,
N_k	dimensionless kinetic number,
N_p	dimensionless pore diffusion number,
P	total pressure,
r	radial distance from the center of the spherical particle,
$-r_a$	reaction rate per particle,
r_c	radius of the unreacted core,
r_i	radial boundary separating solid
r_o	original radial boundary of solid reactant,

r_p	particle radius,
R	spherical particle radius,
R'	perfect gas law constant,
R_o	initial radius of the spherical solid particle,
S	Arrhenius frequency factor,
T	temperature,
T_c	temperature of the unreacted core surface,
T_o	temperature of the bulk gas phase,
T_s	temperature of the outer surface of the particle,
U_o	superficial gas velocity,
W	solid reactant concentration,
X	dimensionless fraction of available reactant solid,
\bar{X}	dimensionless fraction of reacted solid,
y_b	bulk gas phase sorbate mole fraction,
y_o	inlet bulk gas phase sorbate mole fraction
y_p	particle interface sorbate mole fraction,
\bar{Y}	dimensionless sorbate concentration,
Z	position in packed bed,
\bar{Z}	dimensionless position in packed bed,

Greek Letters

α	moles of reactant solid per mole of sorbate,
α_p	particle porosity in particle shell,
β	dimensionless group number defined by equation (14),
ϵ	bed porosity,
ΔH	heat of reaction
ν	kinematic viscosity,
ρ_m	bulk gas phase molar density,
τ	dimensionless time defined by equation (15)
ϕ_s	sphericity of the particle,
λ	group defined by equation (21).

V. Mathematical Models Due to Joshi, et al.

A team of researchers led by Joshi, et al.³⁷⁻³⁹ at Air Products and Chemicals developed and examined three mathematical models to simulate desulfurization and regeneration processes in relation to the production of hot, low Btu (100-140 Btu/scf) producer gas with iron oxide sorbents in a fixed bed at 1200°F and 150 psig. This APCI effort, which was rather broad-based and included both experimental and theoretical aspects, was essentially in support of the development efforts in progress at Morgantown Energy Technology Center, West Virginia. The APCI experimental program, results, and their comparison with theoretical models is given by Joshi and Leuenberger.³⁷ A later report³⁸ gives the design details of the experimental unit and mathematical details associated with the development of desulfurization and regeneration models. Joshi, et al.³⁹ deal with the economic analysis of the process and further assess the APCI model on the basis of regeneration data produced at Morgantown Energy Technology Center previously known as Morgantown Energy Research Center. Consistent with the scope of our present report, we will consider here only the mathematical simulation models given in these reports.³⁷⁻³⁹

The shrinking core, the film, and the film-kinetic models were developed at APCI to mimic the desulfurization of producer gas and regeneration of sulfided iron oxide. These models will be described here briefly and only representative working equations will be reproduced.

1. The Shrinking Core Model

This model was employed in its simplest form to describe the absorption of hydrogen sulfide by iron oxide. The latter was

assumed to be present in the form of a spherical particle and consists of two distinct solid phases: the outer shell phase, which has reacted 100%, and the inner core that is 100% unreacted. The gas-solid reaction takes place at the boundary of these two phases. The following assumptions were implicit in the model's development:

- (i) The gas-solid reaction rate is infinitely fast.
- (ii) The concentration of hydrogen sulfide is zero at the interface due to the fast reaction rate.
- (iii) The reaction is not equilibrium limited.
- (iv) Mass transfer resistance in the bulk phase exterior to the particle is negligible.
- (v) Gas flow through the sorbent bed is plug flow.
- (vi) The product of pore diffusivity and gas concentration is constant; i.e., pore diffusivity is inversely proportional to temperature.

The overall mass balance for the sorbate in the gas phase of the unreacted shell is

$$\frac{\partial}{\partial r} \left(-4\pi r^2 p D_k f \frac{\partial x}{\partial r} \right) dr = 0 \quad (41)$$

Here r is the radial distance from the center of the sorbent particle, p is the sorbent porosity, D_k is the Knudsen diffusivity of hydrogen sulfide within porous particle, f is the gas molar density and x is the sorbate mole fraction. The solution of this equation (41) with the boundary conditions; viz.,

$$\text{at } r = a, x = Y, \text{ and} \quad (42)$$

$$r = z, x = 0, \quad (43)$$

where a is the radius of the sorbent particle, Y is the bulk phase mole fraction of the hydrogen sulfide sorbate, and z is the distance of the reaction zone from the particle center, is

$$x = \frac{Ya}{r} \cdot \frac{(r - z)}{(a - z)} \quad (44)$$

The overall particle mass balance for the sorbate is:

$$-N_{Ab}^D \frac{\partial Z}{\partial \tau} = \frac{F}{Z(1 - Z)} \quad (45)$$

Here N_{Ab}^D is the dimensionless absorption or regeneration number, Z is the dimensionless radial distance of reaction zone, τ is the dimensionless time, and F is the dimensionless mole fraction of the sorbate. The defining relations for these quantities are:

$$-N_{Ab}^D = \frac{a^2 V}{(1 - \epsilon) D_k L_p} \quad (46)$$

$$Z = (z/a) \quad (47)$$

$$\tau = \frac{Y^0 f V t}{(1 - \epsilon) L M_0} \quad \text{, and} \quad (48)$$

$$F = (Y/Y^0) \quad (49)$$

Here V is the superficial gas linear velocity, ϵ is the bed porosity, L is the sorbent bed height, Y^0 is the feed hydrogen sulfide

bulk fluid phase mole fraction, t is the onstream time, and M_0 is the fresh sorbent sulfur capacity.

Equation (45) represents the unsteady state behavior of a single spherical particle in terms of the dimensionless groups N_{Ab}^D and τ . τ is the ratio of amount of feed gas sorbate processed to the amount required to saturate the sorbent bed. Thus, τ is a measure of the chemical efficiency of the bed at any time.

In the sorbent bed the mass balance for a gas phase sorbate gives:

$$- N_{Ab}^D \frac{\partial F}{\partial X} = \frac{3FZ}{(1-Z)}, \quad (50)$$

Equations (45) and (50) may be solved with the following boundary conditions:

$$\text{At } \tau = 0, Z = 1, \text{ and } F = 0; \quad (51)$$

and

$$\text{at } X = 0, F = 1. \quad (52)$$

Further, the shell or diffusional sorption number may be expressed in terms of the process variables by the relation:

$$N_{Ab}^D = \left[\frac{1}{pD_{kb}(1-\epsilon)} \right] (\text{GHSV}) \frac{a^2 \sqrt{T}}{P}, \quad (53)$$

$$= C_0 (\text{GHSV}) \frac{a^2 \sqrt{T}}{P}, \quad (54)$$

C_0 is an empirical constant and is dependent on the structure of the sorbent, D_{kb} is the value of D_k at the base conditions of 492°R and 1 atm, GHSV is the gas hourly space velocity at 1 atm and 492°R, T is the dimensionless absolute temperature and is the ratio of $T_B/492$ where T_B is the absolute bed temperature in °R, and P is the system pressure. These calculations yielded³⁸ the breakthrough curves between chemical or sorption efficiencies of zero and one for sorption numbers of zero to thirteen.

In the shrinking core model, the internal diffusion controls the overall reaction rate. If the sorption process (desulfurization) is efficient, that is, the sorption number $\left(N_{Ab}^D\right)$ is small, the breakthrough curves can be represented by simple constant pattern solution to the model differential equation. For the isothermal shrinking core model, the constant pattern solution is given by³⁷

$$\tau = 1 - \frac{N_{Ab}^D}{15} \left[\ln(1 - F) + 1 \right], \quad (55)$$

$$\text{for } 0 \leq N_{Ab}^D < 6, \text{ and } 0 \leq F \leq 1.$$

This is a rough approximation for a complicated set of equations describing the model solution when the sorption number is less than 6. If the constant pattern solution leads to dimensionless

times of less than zero for a given fractional breakthrough, then the sorption efficiency for that particular sulfur breakthrough is zero. The capability of this model to predict the shape of the experimentally observed breakthrough curves can be established by checking the linearity of the plot of $\ln(1 - F)$ versus τ . The slope of this linear plot is proportional to the rate of sorption and is inversely proportional to the sorption number.

2. The Fluid Film-Kinetic Sorption Model

In the above discussed shrinking core model, the slowest step of the sorption mechanism is the Knudsen diffusion of the hydrogen sulfide from the pellet surface to a sorption site within the pellet interior; i.e., intraparticle diffusion resistance. In the fluid film model, the external diffusion of hydrogen sulfide from the bulk of the producer gas to the surface of the sorbent pellet is the slowest step. In the case of the kinetic model, the chemical reaction of the hydrogen sulfide with iron oxide at the sorption site is the rate controlling step. In the following, the film and the kinetic models are derived simultaneously and can be considered as special cases of the resultant film-kinetic model. The assumptions which are implicit in this derivation are:

- (i) Mass transfer resistance within the solid particle is negligible.
- (ii) As a result of assumption (i) the interstitial concentration

of hydrogen sulfide does not vary with radial distance within the particle.

- (iii) Sorbent saturation level is not influenced by temperature or concentration changes; i.e., the reaction is not equilibrium limited.
- (iv) The reaction is isothermal.
- (v) The gas flow through the sorbent bed is plugflow.

Joshi and Leuenberger,³⁸ on the basis of mass balance around a single particle, have shown that:

$$-\frac{\partial W}{\partial \tau} = \frac{FW}{N_{Ab}^K + N_{Ab}^F W} \quad (56)$$

Here, the dimensionless solid iron oxide concentration is $W = I/\alpha M_o$, where I is the sorbent iron oxide concentration, α is moles of iron oxide per mole of sorbent sulfur capacity, N_{Ab}^K is the dimensionless kinetic sorption number defined as:

$$N_{Ab}^K = \frac{V}{(1 - \epsilon)k_L \alpha M_o} \quad (57)$$

and N_{Ab}^F is the dimensionless fluid film sorption number defined as:

$$N_{Ab}^F = \frac{Va}{3(1 - \epsilon)k^F L} \quad (58)$$

k^K , the kinetic rate constant, is given by

$$k^K = A \exp(-\beta/T), \quad (59)$$

where A is the kinetic pre-exponential factor and β is the dimensionless activation energy. Similarly, k^F is given by

$$k^F = \frac{2.06}{\epsilon} \left(\frac{\rho}{\mu}\right)^{\frac{1}{6}} \left(\frac{v}{a}\right)^{0.5} D^{0.67} \quad (60)$$

Here ρ is the gas mass density, μ is the gas viscosity, and D is the diffusivity of hydrogen sulfide in the fluid phase. They³⁸ also show that the sulfur balance in the bed yields:

$$-\frac{\partial F}{\partial X} = \frac{FW}{N_{Ab}^K + N_{Ab}^F W}, \quad (61)$$

where $X = (\ell/L)$ is the dimensionless bed length, and ℓ is the axial distance from bed inlet.

The fluid film-kinetic sorption equations derived above are valid if the sorption reaction is essentially isothermal. For such an isothermal case, these equations can be solved by adopting the method of Bischoff³² and the appropriate boundary conditions. Joshi and Leuenberger³⁸ have given these solutions and these are reproduced below. Equation (61), with the boundary condition that at the bed inlet conditions $X = 0$,

the inlet gas contains a constant mole fraction of sorbate; i.e., $F = 1$; and equation (56), with the boundary condition that at initial time $\tau = 0$, the bed is unsaturated $W = 1$, and there is no sorbate in the gas phase of the bed; i.e., $F = 0$; are solved to give:

$$\tau = 1 + N_{Ab}^F \frac{\frac{N_{Ab}^F}{N_{Ab}^K} + 1}{\frac{N_{Ab}^F}{N_{Ab}^K} + 1} \frac{-e^{-1/N_{Ab}^K}}{-F e^{-1/N_{Ab}^K}} + N_{Ab}^K \ln \left[\frac{\frac{N_{Ab}^F}{N_{Ab}^K} + 1 - F e^{-1/N_{Ab}^K}}{1 - F} \right], \quad (62)$$

$$\text{for: } \exp \left(\frac{-1}{N_{Ab}^F + N_{Ab}^K} \right) \leq F \leq 1,$$

$$\text{and: } \tau = 0, \quad (63)$$

$$\text{for: } 0 \leq F \leq \exp \left(\frac{-1}{N_{Ab}^F + N_{Ab}^K} \right).$$

The solution of equation (62) is particularly simple for the special case of fully developed or constant pattern breakthrough. N_{Ab}^K is then quite small so that all $\exp \left(-1/N_{Ab}^K \right)$ terms

in equation (62) are negligibly small, and the simplified result is

$$\tau = 1 + N_{Ab}^F (1 + \ln F) + N_{Ab}^K \ln \left(\frac{F}{1-F} \right), \quad (64)$$

for small N_{Ab}^K and

$$\exp \left(\frac{-1}{N_{Ab}^F + N_{Ab}^K} \right) \leq F \leq 1. \quad (65)$$

Equation (65) is found accurate as long as the predicted efficiency is larger than the negative reciprocal of the \ln of F :

$$\tau > -(\ln F)^{-1}. \quad (66)$$

Equation (64) can be expressed in terms of design variables to yield:³⁸

$$\tau = 1 + C_1 \frac{(GHSV)_a^{1.5} T^{0.17}}{\sqrt{PV}} (1 + \ln F) + C_2$$

$$\frac{(GHSV)_T e^{\beta/T}}{P(\alpha M_o)} \ln \frac{F}{1-F}. \quad (67)$$

Empirical constants C_1 and C_2 should be determined from experi-

mental sorption dynamics data.

The fluid film-kinetic model discussed above can be degenerated into two distinct models where either the fluid-film or the chemical reaction is the predominant rate controlling step. Joshi and Leuenberger³⁷ have discussed these models and their results for the constant pattern solution corresponding to the general result of equation (64) and are reproduced below. For the film model when $0 \leq N_{Ab}^F < 0.3$, and $e^{-N_{Ab}^{F-1}} \leq F \leq 1$,

$$\tau = 1 + N_{Ab}^F (\ln F + 1), \quad (68)$$

and for the kinetic model when $0 \leq N_{Ab}^K < 0.3$, and

$$e^{-N_{Ab}^{K-1}} \leq \frac{F}{1-F} < \infty,$$

$$\tau = 1 + N_{Ab}^K \ln \left(\frac{F}{1-F} \right). \quad (69)$$

Further, for the case where the sorption process is controlled by all the three mechanisms of intermolecular (film) diffusion, intraparticle diffusion, and kinetic reaction resistance, the solution may be expressed as:

$$\tau = 1 + \left(N_{Ab}^F + N_{Ab}^K \right) (\ln F + 1) - \left(\frac{N_{Ab}}{15} + N_{Ab}^K \right) [\ln (1 - F) + 1], \quad (70)$$

when:

$$0 \leq N_{Ab}^F + N_{Ab}^K + N_{Ab}^D < 0.3$$

for all F such that $\tau \geq 0$.

All the three fundamental models describing the process of isothermal sorption reported above were tested by Joshi and Leuenberger³⁷ for their ability to predict the shape of the breakthrough curves and their ability to predict sorption efficiency at 10% breakthrough; i.e., when the hydrogen sulfide concentration in the effluent reached 10% of the inlet concentration. None of these models, nor their combinations, satisfied both the criteria reasonably well. A semi-empirical model of the following type between sorption efficiency and fractional breakthrough,

$$\tau = 1 + \left(A_1 N_{Ab}^F + A_2 N_{Ab}^K \right) \ln \left[\frac{F}{(1 - F)^2} \right], \quad (71)$$

was found to satisfy both of the above-mentioned criteria reasonably well. The empirical formula of equation (71) was derived

by a slight modification of the expression for the film-kinetic model. The isothermal sorption models were adapted for regeneration by incorporating the large adiabatic heat effect accompanying regeneration. The kinetic model was found to be most satisfactory.

In a later effort, Joshi, et al.³⁹ further developed the most successful of their models, the kinetic-film model, to allow for the different values of the temperatures for the gas and solid. The model contains three parameters, N_{Ab}^F , N_{Ab}^K and γ , and is quite flexible. However, because of the lack of experimental data, a crucial check of the model could not be made. All simulation models are found to be defective to some degree. This is not very surprising, for even the most general case of the shrinking core model, which takes into account all the three resistances (two diffusion and one reaction), is found to be inadequate to simulate the behavior of gas-solid reaction in porous solid particles.

There is an apparent similarity between the film-kinetic sorption model³⁸ outlined above and the pore diffusion model of Schrod³¹ described earlier in this report. However, there are differences in the formulation and the details adopted in solving the governing equations. It would, therefore, be interesting to employ these models to represent the same set of experimental data, say the one being generated at METC. A close examination of these model predictions in relation to experimental data will provide not only the relative absolute appropriateness of these models but also what features of model simplification are more crucial than the other. Obviously this will provide a firm basis for the development of a more comprehensive and generally valid model.

VI. Nomenclature for Section V

a	sorbent pellet radius,
A	kinetic pre-exponential factor,
D	hydrogen sulfide diffusivity in the fluid phase,
D_k	Knudsen diffusivity of hydrogen sulfide within porous pellet,
D_{kb}	value of D_k at the base conditions of 492°R and one atmosphere,
f	gas molar density,
F	dimensionless mole fraction of the sorbate defined by equation (49),
GHSV	gas hourly space velocity at standard temperature and pressure,
I	sorbent iron oxide concentration,
k^F	film transfer constant defined by equation (60),
k^K	kinetic rate constant defined by equation (59),
z	axial distance from bed inlet,
L	sorbent bed length,
M_o	fresh sorbent sulfur capacity,
N_{Ab}^D	diffusion sorption number defined by equation (53),
N_{Ab}^F	fluid film sorption number defined by equation (58),
N_{Ab}^K	kinetic sorption number defined by equation (57),

p	sorbent porosity,
P	system pressure,
r	distance from sorbent pellet center,
R_G	gas constant,
t	onstream time,
T	dimensionless absolute temperature,
T_B	absolute bed temperature,
T_{ref}	reference temperature,
V	superficial gas linear velocity,
W	dimensionless solid iron oxide concentration,
x	sorbate hydrogen sulfide mole fraction within fluid particle,
X	dimensionless bed length,
Y	dimensionless sorbate hydrogen sulfide bulk fluid phase mole fraction,
Y^0	feed hydrogen sulfide bulk fluid phase mole fraction,
z	distance of reaction zone from pellet center,
Z	dimensionless distance of reaction zone from pellet center.

Greek Letters

α	moles of iron oxide per mole of sorbent sulfur capacity,
β	dimensionless activation energy,
γ	activation energy group, $\left(-\Delta E/R_G T_{ref} \right)$,
ϵ	bed porosity,
μ	gas viscosity,

ρ gas mass density,

τ dimensionless time; it is a measure of the chemical efficiency of the bed at any time,

ΔE reaction activation energy.

VII. Mathematical Model Developed at Giner, Inc.

Jalan⁴⁰ has examined the problem of cleanup of gases from coal gasification plants from another application viewpoint; viz., as feed stock for molten carbonate fuel cell power plants. In this service the sulfur content of the gas must be reduced to the level of about 1 ppm of hydrogen sulfide to protect the molten carbonate fuel cell. Typical effluents from iron oxide/silica sorbent contain about 200-300 ppm of hydrogen sulfide. Many sorbents for this purpose have been investigated at Giner, Inc. However, their experimental effort will not be reviewed here. Instead, a detailed mention will be made of the salient features of their theoretical effort dealing with the mathematical modeling of the desulfurization process. In this formulation, such factors as hydrogen sulfide inlet concentration, the gas residence time, the temperature, particle size and porosity of the sorbent pellets, type of sorbent, etc., are considered so that adequate design of process plants may be developed for commercial applications.

The workers have clearly realized the difficulty involved in the mathematical development of a model, taking into account detailed chemical reaction and gas diffusion phenomena occurring in a single sorbent pellet and then incorporating it into a reactor model where fluid dynamics of the bed involving gas and solid flow rates and simultaneous heat and mass transfer operations seriously control the overall performance. The difficulty is further compounded because of the nonlinear

character of the particle gas-solid reaction models and the distributions which characterize the bed sorbent particle sizes and their residence times. While discussing the use of zinc oxide for desulfurization, and noting that zinc sulfide has much larger molar volume than zinc oxide, it is concluded that the porosity of the pellet will decrease dramatically and will cause pore plugging. Several models have been proposed from time to time to describe the reaction rate change with time. Some of these are due to Szekeley, et al.,⁴¹ Ramachandran and Smith,⁴² Chrostowski and Georgakis,⁴³ Georgakis, et al.,⁴⁴ Lee and Georgakis,⁴⁵ Wen and Ishida,⁴⁶ Rande and Harrison,⁴⁷ and Steinfeld.⁴⁸ However, Giner, Inc.,⁴⁰ in their formulation, have employed a simplified semianalytical model for the overall reaction rate of the desulfurization reaction in a sorbent pellet of a fixed size in a packed bed reactor. The model is motivated by the nature of the conversion versus time plots of experimental data and the details of the pore-plugging models proposed by Georgakis and co-workers.⁴²⁻⁴⁴ This model, which relates the exit and inlet hydrogen sulfide concentrations as a function of time, will not be described here.

As mentioned above, during the process of desulfurization, the porosity of pellets in general decreases and the decrease is greater near the surface of the particles, and, finally, the pores get plugged. As a result, the inner part of the reactant solid cannot react and the solids conversion is less than 100%. Let us consider a solid reactant with uniform pores of initial porosity ϵ_p . For complete pore plugging,

$$V_P(1 - \epsilon_\rho) = V_R \quad (72)$$

Here, V_P and V_R are the molar volumes of product and reactant solids respectively. The critical particle porosity, ϵ_ρ^* , is

$$\epsilon_\rho^* = 1 - \left(V_R / V_P \right) \quad (73)$$

The initial particle porosity has to be smaller than ϵ_ρ^* in order for the porosity at the surface of the pellet to become zero before complete conversion is attained. Calculations⁴⁰ for the zinc oxide/zinc sulfide system give for the critical porosity, ϵ_ρ^* , as 41%. Zinc oxide pellets must, therefore, have a porosity of greater than 41%.

It is assumed that the reactor is at pseudo-steady state during the time period of the gas residence time and the exit concentration changes very slowly, so that the corresponding time constant is much larger than the gas residence time in the reactor. If there are N sorbent particles in the bed of an average particle radius r_ρ , the weight of the particles, W , is given by

$$W = (4/3) \pi r_\rho^3 \rho_p N \quad (74)$$

ρ_p is the particle density. The external particle surface area, S , available for reaction is

$$S = 4 \pi r_\rho^2 N \quad (75)$$

N is determined from Equation (74). The total volume, V_p , occupied by the particle is

$$V_p = (W/\rho_p) = (4/3) \pi N r_p^3 \quad (76)$$

The total volume of the reaction zone V is

$$V = A H \quad (77)$$

The cross-sectional area of the reactor is A , and H is its height.

The bed voidage is

$$\epsilon = (V - V_p) / V_p \quad (78)$$

The local linear gas velocity is

$$v_e = v / \epsilon \quad (79)$$

The variation of hydrogen sulfide concentration, y , along the bed height is given by

$$\frac{\partial y}{\partial \zeta} = - Da (y - y_e) \quad (80)$$

where $\zeta = Z/H$, y_e is the equilibrium hydrogen sulfide concentration, and Da is the Damkohler number, defined as

$$Da = \frac{3 W/\rho}{v A r_p} k_1 \quad (81)$$

Here k_1 is the forward reaction rate constant. Also

$$Da = \frac{1 - \epsilon}{\epsilon} \frac{\theta}{t_R} \quad (82)$$

θ is the gas residence time and is equal to $\epsilon V/q$, where q is the volume flow rate through the reactor and is equal to the product of the superficial gas velocity (v) and the cross-sectional area of the reactor (A). t_R is the characteristic reaction time defined as:

$$t_R = \left(\frac{4}{3} \pi r_p^3 \right) / \left(4 \pi r_p^2 k_1 \right) = r_p / 3 k_1 \quad (83)$$

The local sorbent conversion, α , can be calculated by the following relation:

$$\frac{\partial \alpha}{\partial t} = m Q \frac{1}{t_R} (y - y_e) \quad (84)$$

with the initial condition $\alpha(0) = 0$. (85)

Here m is the moles of sorbent reacting with one mole of hydrogen sulfide, and Q is given by

$$Q = \frac{C_T}{M(0) / \left\{ (4/3) \pi r_p^3 \right\}} \quad (86)$$

Here C_T is the total molar concentration of the gas mixture, and $M(0)$ represents the total moles of sorbent per particle.

The reaction rate constant, k , depends on the sorbent conversion, α , which is a function of both location in the reactor and time. As a result, Da is a function of ξ and t , and the integration of Equation (80) is not possible until the dependence of k_1 on t and α is established. This is possible in principle by adopting the gas-solid reaction models available in the literature.^{43,44} In order to avoid mathematical complications, Giner, Inc. researchers⁴⁰ assumed that the reaction rate decreases exponentially with time, such that

$$k_1 = k_0 \exp(-t / t_p) \quad (87)$$

Here k_0 is the reaction rate when the sorbent is fresh and t_p is a time constant that indicates how fast or slow the sorbent will become inactive, either due to saturation or due to plugging at the pores at the external particle surface. The time constant, t_p , is an unknown and its value was determined⁴⁰ by matching the experimental data and model predictions.

Further, to simplify the formulation, it is assumed⁴⁰ that only the average bed conversion is followed and, consequently, Da will be only a function of time and Equation (80) can be integrated to yield the concentration profile as a function of time; viz.,

$$\frac{y(\xi) - y_e}{y(0) - y_e} = \exp(-Da \xi) \cdot \quad (88)$$

We can write that

$$Da = Da^0 \exp(-t / t_p) \cdot \quad (89)$$

Here, Da^0 corresponds to k_0 at initial time conditions. Equation (88) at exit conditions gives

$$\frac{y(1) - y_e}{y(0) - y_e} = \exp \left[-Da^0 \exp(-t / t_p) \right] \cdot \quad (90)$$

Alternatively, Equation (90) can be written as:

$$\ln \left[\frac{-1}{Da^0} \ln \left\{ \frac{y(1) - y_e}{y(0) - y_e} \right\} \right] = -t / t_p \cdot \quad (91)$$

Equation (91) is used⁴⁰ to estimate the values for Da and t_p from experimental data.

The average sorbent conversion in the bed is calculated⁴⁰ from Equation (84) and is compared with the conversion values obtained from input-output hydrogen-sulfide concentration data by the relation

$$\alpha = \frac{mF}{NM(0)} \int_0^t \{ y(0) - y(1) \} dt \cdot \quad (92)$$

Here m is the number of moles of sorbent reacting with one mole of hydrogen sulfide, $M(0)$ is the moles of sorbent per particle initially in the bed, and F is the molar flow of the inlet stream. Further,

$$NM(0) = N (4/3) \pi r_p^3 \rho_p (\Psi / M_s) = W\Psi / M_s \quad (93)$$

Here Ψ is the weight fractional constant of the pellets in the sorbent material, and M_s is the molecular weight of the active sorbent.

In this model, there are two unknown parameters; viz., the pore plugging time constant, t_p , and the reaction time constant, t_R . t_p characterizes the capacity of the sorbent pellets to absorb hydrogen sulfide, which monotonically increases with t_p . The second unknown, t_R , indicates the reactivity of the sorbent which increases as t_R decreases. t_R occurs in Equation (82). To determine t_R and t_p from the exit hydrogen sulfide versus time experimental data, Equation (91) is employed. A starting value of Da^0 is assumed and by linear regression the best fit is obtained when the mean square error is minimum, and these are the best fit values of Da^0 and t_p . Using these values of Da^0 and t_p , the exit hydrogen sulfide concentration versus time curve is computed on the basis of Equation (90), and then these are compared with the experimental values.

Somewhat limited comparison⁴⁰ with the experimental data has validated the general appropriateness of the model. It is found that the hydrogen sulfide breakthrough curve is reproduced by Equation (90).

The breakthrough characteristics are governed by both parameters: the reaction parameter (Da^0) and the pore plugging time constant (t_p). The latter parameter has relatively more influence on the breakthrough curve than the former. The other predictions of the model, such as the concentration profile of the hydrogen sulfide in the reactor as a function of time, bed void volume, gas residence time, sorbent particle size, reaction time constant (t_R), etc., on the hydrogen sulfide breakthrough are found to be in qualitative agreement with the general expected trends. Nevertheless, neither enough experimental data nor experimental data of the right nature have been taken to subject the model to an appropriate or crucial check. A carefully planned experimental program will not only provide the proper appraisal of the model in its present form, but will also suggest the directions in which it should be developed.

VIII. Nomenclature for Section VII

A	cross-sectional area of the reactor,
C_T	total molar concentration of the gas mixture,
Da	Damkohler number defined by Equation (81),
Da^0	value of Da at time zero,
F	molar flow of the inlet gas stream,
H	total height of the bed,
k_0	reaction rate constant of the fresh sorbent,
k_1	reaction rate constant,
m	number of moles of sorbent reacting with one mole of hydrogen sulfide,
$M(0)$	moles of sorbent per particle initially in the bed,
M_s	molecular weight of the active sorbent,
N	number of sorbent particles in the reactor bed,
q	volume flow rate through the reactor,
Q	defined by Equation (86),
r_p	average radius of the particle,
S	external particle surface area,
t	time,
t_p	pore plugging time constant,
t_R	reaction time constant,
v	superficial linear gas velocity,

v_e	local linear gas velocity
V	total volume of the bed,
V_P	molar volume of the product solid,
V_R	molar volume of the reactant solid,
W	weight of the particles,
y	hydrogen sulfide concentration,
y_e	equilibrium hydrogen sulfide concentration,
$y(0)$	value of y at the reactor inlet,
$y(1)$	value of y at the reactor exit,
z	bed height.

Greek Letters

ϵ	bed voidage,
ϵ_ρ	initial particle porosity,
ϵ^*	critical particle porosity,
ρ	density of sorbent particles,
ρ_p	apparent density of sorbent particles = $\rho(1 - \epsilon_\rho)$,
θ	gas residence time,
Ψ	weight fractional constant of the sorbent pellets,
ξ	reduced bed height.

IX. Mathematical Model Due to Steinfeld⁴⁸

Steinfeld⁴⁸ developed a mathematical framework for a packed bed of sorbent (zinc oxide) in which the heterogeneous noncatalytic gas-solid reaction is modeled on the basis of a modified grain model. The latter is based on the chemical kinetic and mass transport properties of the system and physical properties of the sorbent. This analysis yields the rate of conversion of the solid sorbent and, thereby, the utilization of the sorbent throughout the reactor. The overall reactor model is based on the mass balance system for a packed bed under well-defined approximations and enables determination of the concentration profiles in the reactor and at the exit. This model forms the basis for the understanding of the effect of various system parameters on the overall system performance. The salient features of this model development will now be briefly described.

Several simplifying assumptions have been made to facilitate the solution of the continuity equation for the reactant gas and solid species. These are: the gas is in plug flow, no axial or longitudinal dispersion, and the reactor temperature is uniform. The events which control the rate of reaction are:⁴⁸

1. mass transfer of gaseous reactant from the bulk gas phase to the surface of the solid reactant,
2. diffusion of the gaseous reactant through the porous solid product layer,

3. chemical reaction between the gaseous and solid reactants at the reaction interface,
4. diffusion of the gaseous products from the reaction interface through the porous solid to the external surface of the solid,
5. transport of the gaseous products from the external surface of the solid to the bulk gas system.

The calculation strategy involves dividing the reactor into several equally spaced intervals for the purpose of solving the partial differential equation representing the mass balance on a volume element for each interval. The modified grain model is used for single particles to compute a global reaction rate for that interval. The solution of the packed bed equation leads to a concentration profile for the reactor. The process is iterated until breakthrough or until a preset time is exceeded.

In writing the continuity equations, it is further assumed that the pellet is spherical and it retains its spherical shape and size during reaction when the isothermal conditions prevail. Under the pseudo-steady-state approximation, the gas phase material balance in the dimensionless form is

$$\frac{d^2 C_A}{d\xi^2} + \frac{2}{\xi} \frac{dC_A}{d\xi} = \frac{-3a_A (1-X)^{2/3} \phi_G r_p C_A}{r'_{G_0} r'_{GD} D \left[1 - a_A \phi'_G r'_{GD} (1-X)^{1/3} \{1 - (1-X)^{1/3}\} \right]} \quad (94)$$

with the boundary conditions:

at the external surface of the pellet,

$$\left. \frac{dC_A}{d\xi} \right|_{\xi=1} = \frac{B}{D} (1-C_A), \quad (95)$$

and at the center of the pellet

$$\left. \frac{dC_A}{d\xi} \right|_{\xi=0} = 0 \quad (96)$$

The solid phase material balance in the dimensionless form is

$$\frac{dX}{d\theta_G} = \frac{3a_s (1-X)^{2/3} C_A}{r'_{GD} \left[1 - a_A \phi'_G (1-X)^{1/3} \{1 - (1-X)^{1/3}\} \right]} \quad (97)$$

with the initial conditions

$$X \Big|_{\theta_G=0} = 0, \quad (98)$$

and

$$r'_G \Big|_{\theta_G=0} = 1.0 \quad (99)$$

The mass balance on a volume element is of the following form:

$$-u \frac{\partial (C_A)_B}{\partial Z} = R_g + \epsilon_B \frac{\partial (C_A)_B}{\partial t} \quad (100)$$

with the boundary conditions:

at the reactor inlet for all time

$$C_A(0, t) = (C_A)_B \quad (101)$$

The hydrogen sulfide concentration is equal to the bulk gas concentration

at the inlet. At all other locations, at time zero

$$C_A(Z, 0) = 0 \quad (102)$$

The hydrogen sulfide concentration is zero through the reactor at time zero.

Equation (100) is a partial differential equation correlating the concentration gradient in the reactor with the global reaction rate, superficial velocity and bed void fraction. The global reaction rate is calculated by obtaining the rate of conversion from the grain model for each space interval and at each time interval on the basis of the following expression:

$$R_g = \frac{CSO}{ROW_p} \frac{dX}{dt} \frac{1 - \epsilon_B}{(4\pi/3)r_p^3} W_o \quad (103)$$

The numerical procedure to solve the partial differential equation adopted by Steinfeld is outlined⁴⁸ in detail and is the explicit form of the finite difference approximation⁴⁹. In this method the derivatives are approximated by finite differences. The stability of this method is found to be limited to values of $(U\lambda/\epsilon_B) < 1$. For a given space increment and a superficial velocity, this requirement puts a limitation on the time increment. To simulate long operating times it is proposed⁴⁸ that an empirical correlation for R_g may be employed.

Verification of the model was conducted into two stages. First, the global reaction rate for single particles was examined by comparing the experimental and calculated conversion rates for single particles. Four different curves of zinc oxide conversion versus time were considered at 1106 and 1279^oF and for two levels of hydrogen sulfide concentration between 1 and 4 mole percent. In each case, the model duplicates the shape of the conversion - time curve but could not reproduce the maximum conversion obtained experimentally. The model follows the initial experimental data and levels off approximately twenty percent below the experimental data. The slight exothermic nature of the reaction cannot explain this discrepancy between the model predictions and experimental data.

Secondly, to check the ability of the model to simulate the packed bed behavior, it is found by Steinfeld⁴⁸ that the numerical computational difficulties warrant model validation for relatively short periods of time only. Using the explicit method, simulation for large periods of time are not found practical due to the large computer times required. A successful implicit scheme to accomplish this goal is still in the planning stage. The computer simulations of three test cases at hot gas cleanup temperatures, at accelerated conditions, and for reactor geometry to minimize the computer time yielded results which are found to be qualitatively appropriate. On

the basis of these results, it has been proposed by Steinfeld⁴⁸ to update the model in several respects and also to develop the more sophisticated computational scheme for correct appraisal of the model.

X. Nomenclature for Section IX

a_A	stoichiometric coefficient for gas A,
a_S	stoichiometric coefficient for solid S,
C_A	molar concentration for gas A,
$(C_A)_B$	molar concentration for gas A in the bulk gas,
CSO	molar concentration of solid zinc oxide in pellet,
D	dimensionless effective diffusivity within the pellet,
r_p	particle radius,
r'_G	grain radius,
r'_{GD}	dimensionless grain radius,
r'_{GO}	initial grain radius,
R_g	global reaction rate,
ROW_p	density of zinc oxide particles,
t	time,
u	superficial velocity in direction of flow,
W_o	initial pellet weight,
X	local extent of reaction,
Z	length of reactor.

Greek Letters

β	Biot number for mass transfer,
ϵ_B	void fraction in packed bed,
ξ	dimensionless radial coordinate for pellet,

- θ_G dimensionless time,
- λ a finite difference parameter,
- ϕ_G Thiele modulus for pellet,
- θ'_G Thiele modulus for grain.

XI. Concluding Remarks and Recommendations for Future Work

Having given the review of the noncatalytic gas-solid chemical reaction models employed to simulate the heterogeneous reactions in Section II, the four explicit models employed for the desulfurization of the fuel gas from coal gasification plants and in some cases for the regeneration of the sulfided metal oxides are detailed in Sections III, V, VII and IX of this report. All the relevant details about these models including the extent to which they have been tested and with what degree of success are given in these sections and will not be reproduced here. General conclusions emerging from these studies and the type of investigations which should be conducted in the future so that the design and operation of reactor may be accomplished with a greater degree of efficiency and reliability will be discussed in this section.

All investigations point to the difficulty and inability of the shrinking core model to represent these processes with any degree of success. This common inference besides being valuable is quite logical in as much as the experimental evidence has pointed out clearly that these metal oxides are porous and their treatment in the reactor as regards to temperature and pressure does not change this particular character. However, sulfidation does decrease the average porosity of the pellets and it is conceivable that the pore openings at the surface get plugged before all the metal oxide is consumed in the interior of the particles. This mechanism a priori suggests that a certain amount of metal oxide might never react and 100% conversion will never be accomplished. This will also imply that for reliable conversion predictions not only the pore structure of the particle but also the distribution of metal oxide in the particle be known together with its sintering and other bulk physical and thermal properties. Such detailed information is seldom likely to be available and consequently the prediction process is going to be that much uncertain.

In the light of the above remarks it is not difficult to appreciate the limited degree of success which is accomplished by Schrodt in correlating the experimental data by his somewhat over simplified model. It would appear that the approximations made by him to simplify the particle kinetics are more serious than those involved in describing the bed hydrodynamics. This result is tentative in the sense that the comparisons made by him of the model predictions with the experiments are quite limited. The numerical accuracy of the methods adopted by him in solving the differential equations is implicitly assumed in arriving at the above conclusion to be reasonable. The inference that the grain model fits the data in the concentration range 0 to ~ 0.8 , and the pore diffusion model for the range ~ 0.8 to 1.0 is somewhat artificial and premature. To get a more definitive picture, it would be logical to test this model in greater detail over a larger variety of experimental data. This is possible on the basis of available data from Morgantown Energy Technology Center and their continuing effort to generate desulfurization data using iron and zinc oxides and for a variety of operating conditions. Two possibilities can be conjectured.

First, if there is a reasonable agreement between theory and experiment it may just be a fortuitous coincidence. It may just imply that for the range of experimental conditions involved the calculation procedure provides a reasonable base and at least modest extrapolations will be reliable and in order. More ambitious extrapolations may involve greater uncertainties and this balance between the extent of extrapolation and degree of uncertainty will have to be decided by the designer for himself and consistent with his goal. The moral behind all this is clear, the complicated reactor kinetics and dynamics is described by a rather simple model and with the increasing degree of extrapolation the whole act is becoming more of an art rather than a science.

Secondly, if the agreement between the model predictions and experimental data is not satisfactory, the basic picture of the model does not accord with the mechanistic process details. In this situation a careful probing of the nature of experimental data and of the degree and nature of disagreement between theory and experiment will have to be carefully examined with the view point to identify the model's specific weaknesses. It is likely that the grain model is not appropriate for the process description and a pure pore diffusion model will have to be developed with adequate accounting for the variation of particle porosity which may be assumed to remain constant or may vary with time till surface plugging occurs. In this respect the concept of constant particle porosity employed by Schrodt in his work will have to be abandoned and the approach developed by Giner Inc., will appear in the consideration. Other approaches such as the modified grain model used by Steinfeld⁴⁸ may also be considered

Here once again, it appears quite logical to examine the model for Giner Inc., in its original form in the first instance. To the extent that it was not done before because of the lack of experimental data, and as stated above such data are available now, a detailed examination and assessment of the model is in order. Several simplifying assumptions have been made in this model and the degree to which these are valid and how sensitively these control the model predictions is an important piece of study which must be completed on some priority. The weaknesses of the model and in what directions refinements should be made will automatically follow from a critical study of the type mentioned above.

In view of the magnitude of numerical computation involved in the approach initiated by Steinfeld, it would be appropriate to delay this line of attack for a while. However, if neither of the above two models nor their simple modifications work, there will be no alternative left but to get involved in an ambitious effort. At that time, the work of Steinfeld will be an excellent starting point to draw a comprehensive program of mathematical modeling for the desulfurization and regeneration processes.

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