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HOT GAS CLEANUP FOR MOLTEN CARBONATE FUEL CELLS
A ZINC OXIDE REACTOR MODEL
FINAL REPORT

By

George Steinfeld

September 1980

Prepared for

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, West Virginia

Under Contract No. DE-AT21-78MC08333

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FINAL REPORT
SEPTEMBER 16, 1980

By

George Steinfeld
Science Applications, Inc.

Prepared For

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, WV 26505

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Work performed for the U.S. Department of Energy under Contract No. DE-AT21-78MC08333

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EXECUTIVE SUMMARY

The utilization of coal gasifiers to provide clean fuel gas to power molten carbonate fuel cells in combined cycle schemes is an ongoing concern of both DOE and privately funded organizations. One of the primary areas of concern is desulfurization of high sulfur bearing gases derived from coal. Due to the sensitive nature of fuel cell electrode catalysts, the sulfur tolerance of fuel cells is considered to be 1 part per million in the feed gas stream. Since coal derived gases may contain several percent sulfur compounds, a system is required to remove large quantities of sulfur to sub ppm levels in an economic manner. This report addresses itself to the Hot Gas Cleanup option, and specifically to zinc oxide as part of an iron oxide/zinc oxide system.

Zinc oxide has been used commercially at relatively low temperatures as guard beds before hydrocarbon reformers to prevent sulfur poisoning of reformer catalyst. It is suggested that zinc oxide can be used in a similar manner at high temperatures to treat fuel gas from a coal gasifier to desulfurize coal derived gases, prior to consumption by molten carbonate fuel cells. An iron oxide unit would be required for bulk sulfur removal, the low level (less than 200 ppm) sulfur removal could be done by a zinc oxide reactor. In addition, a regenerable iron oxide/zinc oxide system would greatly improve the economics of such a system to the point that it may be preferable to low temperature desulfurization systems.

This report is provided as an analytical tool to assist in evaluation of performance parameters in systems studies of combined cycle power plants. It is a reactor model of a fixed bed of zinc oxide, and as such models a non-catalytic gas-solid reaction in a packed bed of sorbent. It is based on a mass-balance equation for a packed bed, where the reaction term is calculated by another model, the modified grain model for single particles, to provide concentration profiles in the reactor, and at the exit. In addition, the modified grain model which is based on kinetic and mass transport properties of the system, as well as physical properties of the sorbent, provides the rate of conversion of the solid sorbent to provide an indication of the utilization of the sorbent throughout the reactor. This model can be used

to assist in understanding the effect of various parameters on the overall system performance, and to test hypothetical operating conditions for suitability to other system constraints.

Test cases have been run at accelerated conditions, and documented in this report indicating that sub ppm levels in H_2S can be achieved at high temperatures, and further study is warranted in the evaluation of Hot Gas Cleanup systems. This model is currently operating on a DEC VAX-11 at the Morgantown Energy Technology Center in Morgantown, West Virginia. The packed bed model has been developed and written to support the system studies capabilities at METC and to assist in evaluation and development of Hot Gas Cleanup systems for coal derived gases. It provides a basic one dimensional simulation of a packed bed reactor as a function of operating conditions and physical properties of the sorbent. It is hoped that its use will lead to advances in the state of the art of Hot Gas Cleanup systems.

I. Introduction

A. Hot Gas Cleanup for Molten Carbonate Fuel Cells (MCFC)

Utilization of coal gasifiers to power MCFC, requires a cleanup system, to remove sulfur and particulates. Of the two near term options available for desulfurization of gasifier effluent, namely low temperature cleanup utilizing absorber/stripper technology, and hot gas cleanup utilizing metal oxides, there is a clear advantage to using hot gas cleanup. Since the MCFC will operate at 1200°F, and the gasifier effluent could be between 1200-1900°F, a hot gas cleanup system will require little or no change in process gas temperature, thereby contributing to a high overall system efficiency. The low temperature cleanup system, on the other hand, would require cooling the process stream to approximately 150°F utilizing heat exchangers which would also increase the complexity and cost of the system; and reheating back to 1200°F prior to consumption by MCFC. A hot gas cleanup system will consist of FeO for bulk H₂S removal and ZnO for reduction of H₂S to sub ppm levels. Hot gas cleanup systems at present are not available commercially, and therefore it is the objective of this project to model the components of the system in order to help bring this technology closer to commercialization, by providing simulated operating characteristics to aid in system design, and system simulations of gasifier/MCFC systems. This report covers the modeling of the ZnO reactor.

B. Choice of Models

1. Packed Bed Model

Gas-solid non-catalytic reactors can be one of the following configurations:

- Fixed Bed
- Moving Bed
- Fluid Bed

For the purpose of this model, the fixed bed configuration was chosen for several reasons. The fixed bed reactor is the simplest in terms

of the mechanics of the reaction, the equipment required, and ease of operation over a range of flows. In addition, minimum breakage and fines are obtained with minimum handling of the solid ZnO utilizing the fixed bed. For these reasons, commercial experience with ZnO has been in fixed beds.

In order to model the fixed bed reactor, the continuity equation is used for the gas phase. In order to simplify the solution to the continuity equation, several simplifying assumptions are made, all of which are considered valid. They are:

- Plug Flow
- No Axial or Longitudinal Dispersion
- Isothermal Conditions

The plug flow assumption incorporates the assumption of radial uniformity of velocity, concentration, and temperature. The elimination of axial and longitudinal dispersion effects simplify the solution by assuming radial and longitudinal diffusion of reactant to be negligible. The isothermal condition applies to the reaction at hand and is supported by experimental data by Gibson*.

The resulting equation is used to model the concentration profile in the reactor using numerical methods. Details of the procedure are described in Section III.

2. Single Particle Model

The primary reaction going on in the ZnO reactor is as follows:

This reaction is classified as a non-catalytic gas-solid reaction, and as such falls into a family of reactions having a variety of physical phenomena taking place in the reacting system depending on the reactants present and their properties. There are three well known gas-solid reaction models (with variations) each of which depicts different physical phenomena taking place in a gas-solid reacting system. They are:

1. The Shrinking Core Model
2. The Volumetric Model
3. The Grain Model

*This is an approximation, since the reaction is slightly exothermic.

Figure 1 Physical Representation of Each Model

Figure 1 depicts the physical representation of each model.

The unreacted shrinking core model theorizes a non-porous pellet reacting on the surface at first, and then forming a shell of product which is porous, thus allowing the reactant gas to penetrate the product layer. The reaction takes place at the sharply defined interface between the product layer and unreacted core, proceeding towards the center of the pellet, hence the name shrinking core. The shrinking core model is applicable when either the solid is non-porous or the intrinsic reaction rate is much faster than the internal diffusion rate (reaction is internal diffusion controlled). The unreacted-core model was one of the earliest developed and is the most widely used because of its simplicity. The resistances to the reaction usually considered by this model are the external and internal mass transfer resistances and the intrinsic reaction rate. These resistances are all in series. The shrinking core model has been used for both isothermal and non-isothermal reaction systems.

The volumetric model applies when the solid particle is very porous and the reactant gas can diffuse into the interior of the particle, so that the reaction occurs in a zone rather than at a sharply defined boundary as in the shrinking core model. In the volumetric model, the solid particle may be considered as an ensemble of much smaller particles of reactant distributed homogeneously throughout the solid phase. Reaction rates at different locations within the solid may vary depending upon gas concentration gradients induced by diffusional effects.

The grain model is a combination of the volumetric model, and the shrinking core model. In this model the solid particle is composed of small non-porous spherical grains, each of which reacts according to the shrinking core model. The reactant gas diffuses from the particle surface into the particle between the grains, then through a product layer on each grain, and reacts at the unreacted core surface. The product gas diffuses back through the product layer, between the grains to the surface of the particle, and into the bulk gas stream. The reaction rate inside the grain is controlled by both diffusion through the product layer and chemical reaction at the unreacted core surface. The grain model incorporates important structural properties such as particle and grain porosity, grain size, solid reactivity, and diffusivity in the solid-state and in the gas into the overall reaction description. As originally developed these properties were assumed constant

with time. This factor prevented the model from depicting incomplete conversion of solid after long reaction times (reaction "die-off"). Subsequently, a modification to the grain model by Ranade and Harrison was put forth to account for structural changes due to the combined effects of sintering and reaction.¹ This modified version does depict reaction "die-off".

In each case, an attempt is made to account for the series of events that determines the overall rate of reaction for a gas-solid reaction as follows:

1. Mass transfer of gaseous reactant from the bulk gas phase to the surface of the solid reactant.
2. Internal diffusion of the gaseous reactant through the porous solid reactant or product layer.
3. Chemical reaction between the gaseous and solid reactants.
4. Diffusion of the gaseous product from the reaction surface through the porous solid to the external surface of the solid.
5. Transport of gaseous products from the external surface of the solid to the bulk gas stream.

All three of the non-catalytic solid-gas reaction models are based on the simultaneous solution of the equations of continuity for the reactant gas and solid species. Difference in the models are depicted by the different manners in which the reaction term and the boundary conditions are applied. The major resistances which are incorporated into all three models are the diffusional resistance, both external and internal to the solid, and the intrinsic, or true chemical reaction rate.

A comparison of the three models on ZnO by Gibson⁴ indicates that the simpler unreacted core model described the reactions as well or better than the complex zone models. Presumably, this is because the reaction was diffusion controlled throughout most of the temperature range. However, only the grain model can depict incomplete conversion, as observed experimentally below 600°C⁴ and as experienced commercially below 400°C. The volumetric model was found to have the poorest "fit" to the data, and to be the most difficult and time consuming to solve. The modified grain model was therefore chosen to model the reaction of single pellets within a packed bed reactor of Zinc Oxide.

C. Overall Procedure

The ZnO reactor is divided into several equally spaced intervals for the purpose of solving the partial differential equation derived from a mass balance on a volume element for each interval. The modified grain model is used for single particles to calculate a global reaction rate for that interval. Having calculated a global reaction rate for each interval, the packed bed equation is solved, yielding a new concentration profile for the reactor. This new profile is then used to generate a new set of global reaction rates, which are used to generate an updated concentration profile. This procedure is continued until breakthrough or until a preset time is exceeded.

II. Modified Grain Model

A. Introduction

The advantage of the modified grain model over other non-catalytic reaction models is its ability to account for reaction "die off" or incomplete conversion of solid after long reaction times. Experimental and commercial experience with ZnO has shown that ZnO pellets are typically converted only 20% at temperatures up to 400°C. This, apparently is due to structural changes such as surface area, and porosity which change during reaction causing a gradual choking off of the reaction due to the increasing difficulty with which the gas can diffuse to the reaction surface, and the decreasing surface area available for reaction. The modified grain model continuously updates the surface area available by taking into account the sintering rate at the given temperature, and updates the effective diffusivity through the particle which is constantly decreasing.

B. Modified Grain Model

Consider a porous spherical particle composed initially of a large number of non-porous spherical grains as shown in Figure 2. The particle has a radius of r_p which is assumed to remain constant. The grains have an initial radius of r_g which may be determined from the measured initial specific surface area according to the following equation:

$$r_g = 2/A \rho$$

where A = specific surface area (area/mass)
 ρ = grain density (mass/volume)

This correlation was derived by Wen (2) by assuming that all grains are non-porous spheres having equal radius.

At the start of the reaction, specific surface area changes as a result of both sintering and conversion. The process is visualized as the combination of adjacent grains through the necking step shown in Figure 2(b). With the passage of time the large number of small grains is replaced by fewer grains of larger radius. The unreacted core initially at the center of each small

Figure 2 The Modified Grain Model

grain is required to remain at the center of the new larger grain. This restriction, while not necessarily representing physical reality, is needed for mathematical simplicity. Sintering alone will produce uniform grain growth across the particle radius. When coupled with reaction, the grain radius may become a function of radial position as shown in Figure 2(c). In the case pictured, the larger grains are located near the exterior of the particle indicating that the effects of sintering and conversion are additive in producing larger grains.

Initially (Figure 2a) the unreacted core radius is equal to the grain radius and is independent of radial position. With increasing time, the unreacted core radius may initially increase due to sintering as shown in Figure 2(b). The initial increase, after sufficient time, will be offset by the decrease associated with reaction. A radial variation in unreacted core radius will be established as a result of the radial variation in the extent of reaction, Figure 2(c). Near the exterior, the unreacted core radius is small indicating a high value of local conversion, and near the center the unreacted radius increases and approaches the grain radius.

The porosity of the pellet is important in determining the effective diffusivity of the gaseous reactant through the solid. The overall porosity consists of micropores within the grain and macropores between the grains. Sintering and reaction may result in the alteration of the pore structure and therefore cause the effective diffusivity to change. In this model the pellet porosity is assumed to be a linear function of overall conversion within the pellet and is based on the molar volume of solid reactant and product. Thus, the effective diffusivity is considered to vary with time but to be independent of the radial position at a fixed time.

The solid density, also important in determining the grain size, is a function of conversion and, therefore, is also dependent on radial position. The relation between solid density and conversion is assumed to be linear. For the calculation of grain size the solid density is based on the local fractional conversion level whereas the calculation of density for the purpose of estimation of pellet porosity uses overall conversion within the pellet. The assumption of linearity was made due to the absence of any correlation based on experimental data.

C. Mathematical Formulation of the Modified Grain Model

The mathematical development is based on the general gas solid reaction

where a_A and a_S are stoichiometric coefficients which are negative numbers for reactants.

The assumptions involved in the mathematics of the modified grain model are:

1. The pellet retains its spherical shape and initial size during the reaction.
2. The reaction is isothermal.
3. The pseudo steady-state approximation is valid.

The pseudo steady-state approximation ($\partial C_A / \partial t = 0$) is a good approximation for most of the solid-gas reaction systems except for systems with extremely high pressure and very low solid reactant concentration³. The physical significance of the pseudo steady-state approximation is that the volume of gaseous reactant within the pores at any given time is negligible compared with the volume required to bring the solid to complete conversion. Thus there is negligible accumulation of gaseous reactant within the solid⁴.

The equation of continuity for gaseous reactant A in spherical coordinates is,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{eA} r^2 \frac{\partial C_A}{\partial r} \right) + R_A = \epsilon \frac{\partial C_A}{\partial t} \quad (1)$$

where

r = radial position within the pellet through the particle

D_{eA} = effective diffusivity of gaseous reactant

R_A = rate of production of gaseous reactant A by chemical reaction per unit volume.

t = time

ϵ = pellet porosity

C_A = molar concentration of gaseous reactant A

The effective diffusivity is used here in place of the binary molecular diffusivity ordinarily used in the continuity equation in order to account for lower diffusion rates caused by the pore structure of the solid.

Equimolar counter diffusion is also assumed and is applicable for the reaction of ZnO with H₂S, since one mole of H₂S reacts and forms 1 mole of H₂O. The effective diffusivity includes both Knudsen and molecular diffusion and also accounts for the reduction in area for diffusion in a porous medium and the increase in distance which the diffusing specie must travel due to the tortuous nature of the pore channels.

The equation of continuity for the gas phase in the pores of the solid pellet reduces to the following after application of the pseudo steady-state approximation ($\partial C/\partial t = 0$).

$$\frac{1}{r^2} \frac{d}{dr} \left(D_{eA} r^2 \frac{dC_A}{dr} \right) + \bar{R}_A = 0 \quad (2)$$

where

r = radial position within the solid pellet

$\bar{R}_A$ = molar rate of reaction of gaseous reactant A by chemical reaction on a volume basis

D_{eA} = effective diffusivity

In the solid phase, where there is no molar flux of material, the equation of continuity as applied to the solid particle reduces to:

$$\frac{dC_S}{dt} = -\bar{R}_S \quad \text{where } \bar{R}_S = \text{rate of production of S by chemical reaction per unit volume of pellet} \quad (3)$$

The intrinsic rate expression is first order with respect to the gas, as supported by experimental data⁴. The rate expression is:

$$R_A = a_A K'_S C'_{S0} C'_{AC}$$

where the prime denotes grain properties.

K'_S = reaction rate constant based on the surface area of the unreacted core

C'_{S0} = initial bulk concentration of solid reactant

C'_{AC} = molar concentration of gaseous reactant A at unreacted core surface

a_A = stoichiometric coefficient for reactant A

The rate expression per unit volume is given by:

$$\bar{R}_A = \frac{4\pi r_C'^2}{\frac{4\pi r_G'^3}{3}} (1-\epsilon) a_A K_S' C_{So}' C_{AC}'$$

where

$$\frac{4\pi r_C'^2}{\frac{4\pi r_G'^3}{3}} = \text{surface area to volume ratio for a single grain}$$

$$(1-\epsilon) = \text{solid fraction per unit particle volume}$$

With this rate expression, equation (2) becomes

$$\frac{D_{eA}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) + 3a_A \frac{r_C'^2}{r_G'^3} (1-\epsilon) K_S' C_{So}' C_{AC}' = 0 \quad (4)$$

where D_{eA} the effective diffusivity in the particle is independent of the particle radius and is therefore removed from the radial derivative term.

The molar gas concentration at the unreacted surface of the grain, C_{AC}' is now obtained from the shrinking core model⁴:

$$\frac{C_{AC}'}{C_{Ao}} = \frac{1}{1 - \frac{a_A K_S' C_{So}' r_C'^2}{k_{mA} r_G'^2} - \frac{a_A K_S' C_{So}' r_C'}{D_{eA}} \left(1 - \frac{r_C'}{r_G'} \right)}$$

The resistance due to mass transfer to the grain surface, expressed by term

$$\frac{a_A K_S' C_{So}' r_C'^2}{k_{mA} r_G'^2}$$

where k_{mA} = mass transfer coefficient

is eliminated from this expression since mass transfer resistance is associated with the particle surface and not the grain surface. The shrinking core equation now reduces to:

$$\frac{C_{AC}'}{C_{Ao}} = \frac{1}{1 - \frac{a_A K_S' C_{So}' r_C'}{D_{eA}} \left(1 - \frac{r_C'}{r_G'} \right)}$$

where

C_{Ao} = molar concentration of gaseous reactant A at the grain surface

C_{Ao} is assumed to be the same as the concentration within the pores, C_A so that

$$C'_{AC} = \frac{C_A}{1 - \frac{a_A K'_S C'_{So} r'_C}{D'_{eA}} \left(1 - \frac{r'_C}{r'_G}\right)}$$

This expression for the gas concentration at the unreacted core surface can now be substituted in Equation (4), as well as C_{So} for $C'_{So} (1 - \epsilon)$ to yield:

$$\frac{D_{eA}}{r^2} \frac{d}{dr} r^2 \frac{dC_A}{dr} + 3 a_A \frac{r'^2_C}{r'^3_G} \left[\frac{K'_S C_{So} C_A}{1 - \frac{a_A K'_S C'_{So} r'_C}{D'_{eA}} \left(1 - \frac{r'_C}{r'_G}\right)} \right] = 0 \quad (5)$$

The boundary conditions are:

(1) At the surface of the pellet

$$D_{eA} \left(\frac{dC_A}{dr} \right)_{r=r_p} = k_{ma} (C_{Ao} - C_{AS})$$

where

C_{Ao} = gas concentration in the bulk gas

C_{AS} = gas concentration at the external surface of the pellet

k_{ma} = mass transfer coefficient from the bulk gas to the solid surface

(2) At the center of the pellet

$$\left. \frac{dC_A}{dr} \right|_{r=0} = 0$$

The solid phase material balance Equation (3), with the appropriate rate expression is as follows:

$$\frac{dC_S}{dt} = 3 a_S \frac{r'^2_C}{r'^3_G} \left[\frac{K'_S C'_{So} C_A}{1 - \frac{a_A K'_S C'_{So} r'_C}{D'_{eA}} \left(1 - \frac{r'_C}{r'_G}\right)} \right] \quad (6)$$

The solid concentration term, C_S , may be expressed in terms of conversion with the following substitutes:

$$\frac{dC_S}{dt} = \frac{d}{dt} [C_{S0} (1 - X)]$$

$$X = 1 - \frac{r_C'^3}{r_G'^3} = \text{local conversion}$$

Substituting these terms into Equation (6) yields:

$$\frac{dX}{dt} = \frac{-3 a_S (1 - X)^{2/3} K'_S C_A}{r_G' \left[1 - \frac{a_A C'_{S0} K'_S (1 - X)^{1/3} r_G'}{D'_{eA}} \left(1 - (1 - X^{1/3}) \right) \right]}$$

The initial condition is

$$X \Big|_{t=0} = 0$$

The overall fractional conversion for the pellet is then obtained by integrating over the volume of the pellet, so that:

$$\bar{X} = \frac{\int_0^V X dV}{V}$$

where

V = volume of the pellet

D. Evaluation of Physical Properties

The solution of the mathematical equations formulated earlier, requires numerical values of several physical properties. These properties are estimated using the procedures described in this section.

1. Effective Diffusivity -- Within the Particle

The effective diffusivity estimate is based on the random pore model of Wakao and Smith^{1,5}. A modification by Wen³, assuming that effective diffusivity is proportional to the porosity raised to the α power where α

is a positive constant between two and three, was incorporated to provide additional flexibility. The correlation is as follows:

$$D_{eA} = D_A \epsilon^\alpha \quad (7)$$

where

α = a constant with a value between two and three, usually two

ϵ = pellet porosity

D_A = combination of Knudsen and molecular diffusion coefficients defined as follows:

$$\frac{1}{D_A} = \frac{1}{D_K} + \frac{1}{D_M}$$

where

D_K = Knudsen diffusion coefficient through the solid (cm²/sec)

D_M = Molecular diffusivity of the gas pair through the pore (cm²/sec)

The Knudsen diffusion coefficient is estimated using the relationship^{1,6}:

$$D_K = 9.7 \times 10^3 r_{\text{pore}} \left(\frac{T}{M}\right)^{1/2}$$

where

r_{pore} = average pore radius (cm)

T = temperature (°K)

M = molecular weight of the gas

The average pore radius is given by⁷

$$r_{\text{pore}} = \frac{2 \epsilon \rho}{A_T \rho_s (1 - \epsilon_p)}$$

The molecular diffusivity (D_M) is independent of solid properties and may be estimated using the Chapman-Enskog formula⁶:

$$D_M = \frac{1.858 \times 10^{-3} T^{3/2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}{P_T \sigma_{G_1 G_2}^2 \Omega_{G_1 G_2}}$$

where

$M_1 M_2$ = molecular weights of gases G_1 and G_2 respectively

P_t = total pressure (ATM)

$\sigma_{G_1 G_2}$
 $\Omega_{G_1 G_2}$ = constants in the Lennard-Jones potential energy functions

2. Effective Diffusivity -- Within the Grain

The effective diffusivity for the grain is not calculated using the same procedure as for the pellet, which is based on the kinetic theory of gases, due to the relative insensitivity of the calculated value to temperature. Instead, an activation process is assumed for the solid state diffusion, therefore

$$D'_{eA} = D'_{eA_0} e^{-E_D/RT}$$

where

D'_{eA_0} = frequency factor for the grain coefficient (cm^2/sec)

E_D = activation energy for diffusion within the grain (cal/g mole)

R = gas constant (cal/g mole $^{\circ}\text{K}$)

T = temperature ($^{\circ}\text{K}$)

3. Total Surface Area

The total area available for reaction is required in order to calculate the grain radius. Experimental work by Ranade¹ in the sintering of ZnO and ZnS, and variation of surface area with conversion, has provided the following relationship for the total area:

$$A_T = A_2 + (A_1 - A_2) (1 - \bar{X})^a$$

where

A_1 = area of ZnO at any time and temperature

A_2 = area of ZnS at any time and temperature

A_T = total area of mixture of ZnO and ZnS at any time and temperature

$\bar{X}$ = fractional conversion of ZnO

a = experimental constant (equals three)

The area of ZnO and ZnS is a function of time and temperature due to sintering and can be expressed by the following relationship¹⁰.

$$A_1 = A_{1f} + (A_{1i} - A_{1f}) e^{-K_1 t}$$

$$A_2 = A_{2f} + (A_{2i} - A_{2f}) e^{-K_2 t}$$

where the sintering rate constants K_1 and K_2 are given by the Arrhenius equation:

$$K_1 = K_{10} e^{-E_1/RT} \quad \text{for ZnO}$$

$$K_2 = K_{20} e^{-E_2/RT} \quad \text{For ZnS}$$

The coefficients K_{10} , K_{20} , and activation energies E_1 , E_2 are determined experimentally, and have been determined by Ranade¹⁰ as follows:

ZnO	ZnS
$E_1 = 7183.0 \frac{\text{cal}}{\text{g mole}}$	$E_2 = 6027.0 \frac{\text{cal}}{\text{g mole}}$
$K_{10} = 25.07 \text{ HR}^{-1}$	$K_{20} = 23.41 \text{ HR}^{-1}$

Having the total area from these calculations, the grain radius can be calculated according to the equation previously mentioned

$$r'_G = \frac{3}{A_T \rho_s}$$

4. Solid Density

Solid density is assumed to be a linear function of local conversion

$$\rho_s = \rho_1 - (\rho_1 - \rho_2) X$$

where

ρ_1, ρ_2 = true densities of solid reactant and product respectively

X = local conversion

The true density of the solid for the purpose of estimating the pellet porosity is based on overall conversion, $\bar{X}$ within the pellet:

$$\rho_p = \rho_1 - (\rho_1 - \rho_2) \bar{X}$$

5. Pellet Porosity

Pellet porosity is assumed to be a linear function of overall conversion:

$$\epsilon_p(\bar{X}) = 1.0 - \frac{\frac{W_0}{M_{s1}} (1-\bar{X}) M_{s1} + \frac{a_{s2}}{a_{s1}} (\bar{X} M_{s2})}{\frac{4}{3} \pi r_p^3 \rho_p} \quad (8)$$

where

W_0 = initial pellet weight

M_{s1}, M_{s2} = molecular weights of solid reactant and product respectively

E. Rate of Reaction

The intrinsic reaction rate expression is considered to be

$$R_A = a_A K'_S C'_{so} C_{A_0}^N$$

where

N = order of the reaction

K'_S = reaction rate constant

C'_{SO} = molar concentration of solid

C_{A_0} = molar concentration of gas

a_A = stoichiometric coefficient

Experimental data on ZnO powder has been conducted by Gibson⁴, and it was determined that the reaction is first order with respect to the gas (H_2S).

The rate constant K'_S was found to obey the classical Arrhenius relationship:

$$K'_S = K_0 e^{-E_A/RT}$$

where

K_0 = frequency factor ($cm^4/g \text{ mole min}$)

E_A = activation energy ($cal/g \text{ mole}$)

R = gas constant ($1.987 \text{ cal/g mole } ^\circ K$)

T = absolute temperature ($^\circ K$)

Using data obtained from experiments carried out between $325^\circ C$ and $687^\circ C$ the frequency factor K_0 , and activation energy E_A , were determined by a non-linear least-square analysis of the data. Figure 3 depicts the data used and curve fit obtained. From the slope and the intercept of Figure the activation energy and frequency factor were obtained to yield

$$K'_S = 0.09458 e^{-7236/RT}$$

This rate expression is used in the modified grain model.

Figure 3 Arrhenius Dependence of Rate Constant for Reagent Grade ZnO Powders

F. Dimensionless Equations

For the purpose of numerical solution, it is convenient to write the equations described previously in dimensionless form. Thus, the gas phase material balance Equation 5 becomes:

$$\frac{d^2 c}{d\zeta^2} + \frac{2}{\zeta} \frac{dc}{d\zeta} = \frac{-3a_A (1-X)^{2/3} \phi_G r_p \frac{1}{D} c}{r'_{G_0} r'_{GD} \left[1 - a_A \phi'_G r'_{GD} (1-X)^{1/3} (1 - (1-X)^{1/3}) \right]} \quad (9)$$

with the boundary conditions

- 1) At the external surface of the pellet

$$\left. \frac{dc}{d\zeta} \right|_{\zeta=1} = -\frac{\beta}{D} (1-c) \quad (9A)$$

- 2) At the center of the pellet

$$\left. \frac{dc}{d\zeta} \right|_{\zeta=0} = 0 \quad (9B)$$

The solid phase material balance Equation 7 in dimensionless form becomes:

$$\frac{dX}{d\theta_G} = \frac{3a_s (1-X)^{2/3} c}{r'_{GD} \left[(1 - a_A \phi'_G (1-X)^{1/3} (1 - (1-X)^{1/3})) \right]} \quad (10)$$

with initial conditions

$$\left. \begin{array}{l} X \\ \theta_G \end{array} \right|_{\theta_G=0} = 0$$

and

$$\left. \begin{array}{l} r'_G \\ \theta_G \end{array} \right|_{\theta_G=0} = 1.0$$

The terms introduced in these dimensionless equations are:

$$r'_{G_0} = \text{initial grain radius} \quad 3/A_{1j} \rho_1$$

$$\zeta = \text{dimensionless radial coordinate for the pellet } r/r_p$$

$$r'_{GD} = \text{dimensionless grain radius} \quad \frac{r'_G}{r'_{G_0}}$$

$$C = \text{dimensionless gas concentration} \quad \frac{C_{A1}}{C_{A10}}$$

$$D = \text{dimensionless effective diffusivity within the pellet} \quad \frac{D_{eA}}{D_{eA_0}}$$

$$D_{eA_0} = \text{initial value of effective diffusivity within the pellet}$$

$$\phi_G = \text{Thiele modulus for the pellet} \quad \frac{K'_s C_{so} r_p}{D_{eA_0}}$$

$$\beta = \text{Biot number for mass transfer} \quad \frac{k_{ma} r_p}{D_{eA_0}}$$

$$\phi'_G = \text{Thiele modulus for the grain} \quad \frac{K'_s C'_{so} r'_{Go}}{D'_{eA}}$$

$$\theta_G = \text{dimensionless time} \quad \frac{K'_s C'_{so} r'_{Go}}{D'_{eA}}$$

G. Numerical Solution Procedure

The numerical solution used by Ranade¹ has been adopted for the use of this model.

The simplified block diagram of the procedure used is shown in Figure 4, and explained below:

- 1) The gas phase material balance Equation 9 with the boundary conditions (9A and 9B) is solved at initial conditions using finite difference approximations⁸. This provides the gas concentration profile at dimensionless time equals zero.

Figure 4 Simple Block Diagram of Numerical Procedure
for Modified Grain Model

- 2) The time step is advanced and the solid phase material balance, Equation 10 with initial conditions is solved using Hamming's predictor-corrector method with a fourth order Runge-Kutta initiator. This gives the local fractional conversion profile.
- 3) The value of the dimensionless grain radius is obtained at current time using conversion (X) from Step 2. Surface area and density needed to calculate the grain radius are obtained from the equations in sections D3 and D4.
- 4) The unreacted core radius profile is obtained using the value of the dimensionless grain radius r'_{GD} from Step 3 and the equation

$$\zeta' = r'_{GD} (1-X)^{1/3}$$

where

$$\zeta' = \text{dimensionless unreacted core radius} \quad \frac{r'_c}{r'_{Go}}$$

- 5) Overall fractional conversion is obtained by integrating the local conversion over the entire pellet volume:

$$\bar{X} = 3 \int_0^1 X \zeta'^2 d\zeta'$$

Simpson's rule of integration is used for this step.

- 6) If the desired overall conversion is not reached, updated values of effective diffusivity are obtained from Equation 7 and Equation 8 using the overall conversion from Step 5.
- 7) The gas phase material balance equation is solved using the dimensionless grain radius from Step 3, X from Step 2 and D from Step 6.

The procedure is repeated until the desired conversion is reached.

The numerical output of the modified grain model solution gives the gas concentration, the local fractional conversion, the grain radius, and the unreacted-core radius, each as a function of radial position within the pellet. Since the grain radius is a function of conversion (X), the value

of the grain radius at each new time is calculated using the values of X from the previous time. Also the value of overall fractional conversion at the previous time is used to calculate the effective diffusivity at each new time.

III. Packed Bed Model

A. Mass Balance Equation

Having chosen isothermal conditions as representative of the system plug flow, to simplify the flow profile and allow a one dimensional model, a mass balance on a volume element can be reduced to the following equation:

$$-u \frac{\partial (C_A)_B}{\partial z} = R_g + \epsilon_B \frac{\partial (C_A)_B}{\partial t} \quad (11)$$

where

$(C_A)_B$ - concentration of H_2S in the bulk gas

z = length of reactor (cm)

u = superficial velocity in direction of flow cm/min

ϵ_B = void fraction in bed

R_g = global reaction rate per unit volume of reactor

The boundary conditions are:

At the reactor inlet for all time

1) $C(0,t) = C_B$

The H_2S concentration is equal to the bulk gas concentration at the inlet.

At all other locations, other than the inlet, at time = 0.

2) $C(z,0) = 0$

The H_2S concentration is zero through the reactor at time = 0.

Equation 11 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 R_g , is calculated by obtaining the rate of conversion from the grain model for each space interval and at each time interval.

B. Global Reaction Rate

The global reaction rate needed in order to solve the partial differential equation for the packed bed cannot be obtained analytically due to its complexity. It was therefore chosen to calculate it for each space interval along the reactor at each time interval. The subroutine grain calculates the rate of conversion of solid dx/dt . This rate is used to calculate the global reaction rate per unit volume of reactor as follows:

$$R_g = \frac{c_{so}}{Rowp} \frac{dx}{dt} \frac{1 - \epsilon_B}{\frac{4}{3} \pi r_p^3} (W_o)$$

where

c_{so} = molar concentration of solid ZnO

$Rowp$ = density of ZnO particles

W_o = weight of ZnO particle initially

$$\frac{1 - \epsilon_B}{\frac{4}{3} \pi r_p^3} = \frac{\# \text{ of particles}}{\text{unit volume of reactor}}$$

$\frac{dx}{dt}$ = rate of change of conversion of solid ZnO

R_g = global reaction rate per unit reactor volume $\frac{\text{g mole}}{\text{MIN cm}^3}$

Since $\frac{dx}{dt}$ varies with space and time it is a variable that is calculated at each step. The resulting R_g is then used to solve for concentration C of H_2S in the gas stream at the space interval in question.

C. Numerical Procedure

The method used to solve the partial differential equation is the explicit form of the finite difference approximation⁸. This method requires that the derivatives be approximated by finite differences. For the equation at hand:

$$-u \frac{\partial (C_A)_B}{\partial z} = R_g + \epsilon_B \frac{\partial (C_A)_B}{\partial t} \quad (11)$$

B.C. 1) $C(0,t) = C_B$
 2) $C(z,0) = 0$

The derivatives in this equation are then approximated using the backward, and forward difference equation⁸, so that:

$$\frac{\partial C}{\partial z} = \frac{C_{i,j} - C_{i-1,j}}{\Delta z} \quad \text{Backward Difference}$$

$$\frac{\partial C}{\partial t} = \frac{C_{i,j+1} - C_{i,j}}{\Delta t} \quad \text{Forward Difference}$$

The subscripts used in these difference equations are determined by establishing a grid system with Δz as the X axis and Δt as the y axis. The subscript i denotes increments in space (Δz) and the subscript j denotes increments in time (Δt).

These approximations are now substituted in Equation 11 to yield:

$$-u \left(\frac{C_{i,j} - C_{i-1,j}}{\Delta z} \right) = R_g + \epsilon_B \left(\frac{C_{i,j+1} - C_{i,j}}{\Delta t} \right)$$

where R_g = the global reaction rate

Defining $\lambda = \frac{\Delta t}{\Delta z}$

and rearranging

$$C_{i,j+1} = \frac{u\lambda}{\epsilon_B} C_{i-1,j} + \left(1 - \frac{u\lambda}{\epsilon_B} \right) C_{i,j} - \frac{\Delta t}{\epsilon_B} R_g \quad (12)$$

Equation 12 enables $C_{i,j+1}$, the concentration at any space interval at the advanced point in time, to be calculated directly if all the $C_{i,j}$ at any time level t_j are known. Known initial and boundary conditions are required to initiate this procedure, and the boundary condition, and initial condition defined earlier are used.

Equation 12 therefore describes the concentration profile in the packed bed based on the initial conditions and the inlet conditions. The concentration at each point in the reactor is a function of the concentration in the previous interval and the present interval during the previous increment in time, and the global reaction rate, the time increment, the space increment, superficial velocity, and void fraction of the bed. The grid describing the relationship between newly calculated concentrations (shown by X) and previously known concentrations (shown by ●) is shown below:

In this manner it is possible to step through the reactor to calculate concentrations at an advanced point in time to obtain a new profile for the whole reactor. This procedure can be repeated indefinitely until predetermined conditions are met, in this case until a specified exit concentration is reached.

The stability of this method is limited to values of $\frac{u\lambda}{\epsilon_B} < 1$. This requirement puts a limitation on the time increment, given a space increment and a superficial velocity. To simulate long operating times of such a system an empirical correlation for R_g will be required based on shorter operating times. Such a correlation can be obtained for specific operating conditions by running the subroutine grain at various bulk gas concentrations, to generate a family of curves describing the rate of change of conversion at various locations along the reactor. An empirical correlation can be obtained from these curves and used in place of actually calculating R_g at each point in the reactor. This simplified version of the model is expected to consume less computer time and be usable for a systems study simulation.

FIGURE 5: Simple Block Diagram of Numerical Procedure for Packed Bed

IV. Model Output

A-1. Model Verification -- Single Particles

Verification of the ZnO Model has been divided into two sections. The first stage of verification was to verify the global reaction rate for single particles, by comparing experimental data on single particles with the output of subroutine grain which determines the rate of conversion of a single particle. The experimental data is by Gibson and Ranade, and although the data was obtained by using relatively high H_2S levels (1-4 mole %), it was used for lack of data at lower levels of H_2S .

Two temperatures were chosen in the range of expected operation; 1106°F and 1279°F. For each temperature, two levels of H_2S concentration were chosen between 1 mole % and 4 mole %. Figures 6 through 9 depict the experimental data and the model simulation generated by subroutine grain. Fractional conversion of the solid versus time is depicted in each case.

In each case depicted, the model duplicates the shape of the conversion curve, however, it does not reach the maximum conversion obtained experimentally. Figures 6 and 9 show the rapid rate of conversion obtained by using 4% H_2S . The model follows the experimental data initially, and levels off at a conversion of approximately 70%, whereas the experimental data indicates conversion reading 90%. Incomplete reaction, or reaction "die off" is depicted well in both cases. For the lower level of H_2S , 1% and 2.5%, it is seen that the rate is slower and spread out over a larger period of time, as shown in Figures 7 and 8. Here again, the model follows the initial experimental data, and levels off approximately 20% below the experimental data.

A possible explanation might be the effect of the isothermal assumption in the model. Since the reaction of ZnO and H_2S is exothermic, there may be a slight temperature rise of the pellet with time. This could raise the rate of reaction slightly to a higher value resulting in higher conversion. Calculations by Gibson, indicate that this temperature rise is negligible and is below 0.3%, so that isothermal conditions are justified, however this factor may explain partially the discrepancies between the model and the experimental data.

Other factors affecting the accuracy of the model are sintering rates, grain diffusivity, particle diffusion rates, initial surface area and reaction rates. All of these are obtained experimentally or calculated, and therefore there will be a margin of error.

Since the model is seen to predict a conservative conversion rate, and a good reaction die off, it is felt that it can be useful in future modeling efforts. Further validation is required at lower levels of H_2S in the range of 1-200 ppm, as expected in the operation of a ZnO reactor for fuel cell application.

A-2. Model Verification -- Packed Bed

In order to verify the packed bed simulation by this model two items are required: (1) experimental data for a packed bed of ZnO over relatively short periods of time and for various inlet concentrations of H_2S at several temperatures and flow rates, and (2) simulation of the packed bed reactor over a period of time corresponding to the experimental data. The experimental data is expected to range over a period on the order of tens of hours for a subscale reactor. Using the explicit method in this model, simulation of large period of time are not practical due to the computer time required. Therefore, in order to obtain an accurate validation of this model, the method used to solve the partial differential equation for the packed bed must be improved. Several implicit schemes have been tried based on the centered difference finite difference approximation,^{11,12} however these schemes resulted in unstable output to date. Therefore, the explicit form is presented at this time in order to expedite the documentation of this model, and improvements are planned as revisions to this original documentation.

FIGURE 6

MODIFIED GRAIN MODEL VALIDATION

MASS TRANSFER COEFFICIENT (CM/SEC)	0.15000E+06
BULK REACTIVE GAS CONCENTRATION (MG MOLE/CC)	0.51700E-03
STOICHIOMETRIC COEFFICIENT-GAS PHASE	-1.000
STOICHIOMETRIC COEFFICIENT-SOLID PHASE	-1.000
PARTICLE WEIGHT (GM)	0.04030
MOLECULAR WEIGHT ZNO	81.36000
MOLECULAR WEIGHT ZNS	97.43000
NUMBER OF DIVISIONS OF SOLID RADIUS	10
MAXIMUM NUMBER OF TIME STEPS	1800
TIME STEP SIZE (MIN)	0.0250
DESIRED FINAL CONVERSION	0.9500
TEMPERATURE (DEG K)	959.000
EQUILIBRIUM SURFACE AREA ZNO (CM**2/GM)	53216.473
EQUILIBRIUM SURFACE AREA ZNS (CM**2/GM)	43215.633
GRAIN RADIUS (CM)	0.29913E-05
SINTERING RATE CONSTANT ZNO (1/MIN)	0.217701E-03
SINTERING RATE CONSTANT ZNS (1/MIN)	0.217701E-03
REACTION RATE CONSTANT (CM**4/MG MOLE MIN)	0.21053E-02
PARTICLE POROSITY	0.66565
AVERAGE PORE RADIUS (CM)	0.39703E-05
KNUDSEN DIFFUSION COEFFICIENT	0.20429E+00
MOLECULAR DIFFUSION COEFFICIENT	0.13364E+01
COMBINED PORE DIFFUSION COEFFICIENT	0.17720E+00
PARTICLE THIELE MODULUS	0.1679E-02
GRAIN THIELE MODULUS	0.3005E+00
BIOT NUMBER	0.3295E+06
DIMENSIONLESS TIME	0.9097E-02
EFFECTIVE GRAIN DIFFUSIVITY	0.2275E-07

TABLE 1

MODIFIED GRAIN MODEL PARAMETERS - RUN 102

FIGURE 7

MODIFIED GRAIN MODEL VALIDATION

MASS TRANSFER COEFFICIENT (CM/SEC)	0.15000E+06
BULK REACTIVE GAS CONCENTRATION (MG MOLE/CC)	0.12500E-03
STOICHIOMETRIC COEFFICIENT-GAS PHASE	-1.000
STOICHIOMETRIC COEFFICIENT-SOLID PHASE	-1.000
PARTICLE WEIGHT (GM)	0.04400
MOLECULAR WEIGHT ZNO	81.36000
MOLECULAR WEIGHT ZNS	97.43000
NUMBER OF DIVISIONS OF SOLID RADIUS	10
MAXIMUM NUMBER OF TIME STEPS	4300
TIME STEP SIZE (MIN)	0.0250
DESIRED FINAL CONVERSION	0.9500
TEMPERATURE (DEG K)	966.000
EQUILIBRIUM SURFACE AREA ZNO (CM**2/GM)	51170.738
EQUILIBRIUM SURFACE AREA ZNS (CM**2/GM)	42169.715
GRAIN RADIUS (CM)	0.29913E-05
SINTERING RATE CONSTANT ZNO (1/MIN)	0.223109E-03
SINTERING RATE CONSTANT ZNS (1/MIN)	0.223109E-03
REACTION RATE CONSTANT (CM**4/MG MOLE MIN)	0.21641E-02
PARTICLE POROSITY	0.67871
AVERAGE PORE RADIUS (CM)	0.42127E-05
KNUDSEN DIFFUSION COEFFICIENT	0.21756E+00
MOLECULAR DIFFUSION COEFFICIENT	0.13511E+01
COMBINED PORE DIFFUSION COEFFICIENT	0.18738E+00
PARTICLE THIELE MODULUS	0.1570E-02
GRAIN THIELE MODULUS	0.2653E+00
BIOT NUMBER	0.3128E+06
DIMENSIONLESS TIME	0.2261E-02
EFFECTIVE GRAIN DIFFUSIVITY	0.2641E-07

TABLE 2

MODIFIED GRAIN MODEL PARAMETERS - RUN 155

FIGURE 8

MODIFIED GRAIN MODEL VALIDATION

MASS TRANSFER COEFFICIENT (CM/SEC)	0.15000E+06
BULK REACTIVE GAS CONCENTRATION (MG MOLE/CC)	0.34800E-03
STOICHIOMETRIC COEFFICIENT-GAS PHASE	-1.000
STOICHIOMETRIC COEFFICIENT-SOLID PHASE	-1.000
PARTICLE WEIGHT (GM)	0.04260
MOLECULAR WEIGHT ZNO	81.36000
MOLECULAR WEIGHT ZNS	97.43000
NUMBER OF DIVISIONS OF SOLID RADIUS	10
MAXIMUM NUMBER OF TIME STEPS	3000
TIME STEP SIZE (MIN)	0.0250
DESIRED FINAL CONVERSION	0.9500
TEMPERATURE (DEG K)	870.000
EQUILIBRIUM SURFACE AREA ZNO (CM**2/GM)	87598.859
EQUILIBRIUM SURFACE AREA ZNS (CM**2/GM)	59009.727
GRAIN RADIUS (CM)	0.29913E-05
SINTERING RATE CONSTANT ZNO (1/MIN)	0.154036E-03
SINTERING RATE CONSTANT ZNS (1/MIN)	0.154036E-03
REACTION RATE CONSTANT (CM**4/MG MOLE MIN)	0.14265E-02
PARTICLE POROSITY	0.65563
AVERAGE PORE RADIUS (CM)	0.37967E-05
KNUDSEN DIFFUSION COEFFICIENT	0.18608E+00
MOLECULAR DIFFUSION COEFFICIENT	0.11548E+01
COMBINED PORE DIFFUSION COEFFICIENT	0.16025E+00
PARTICLE THIELE MODULUS	0.1345E-02
GRAIN THIELE MODULUS	0.1672E+01
BIOT NUMBER	0.3739E+06
DIMENSIONLESS TIME	0.4149E-02
EFFECTIVE GRAIN DIFFUSIVITY	0.2757E-08

TABLE 3

MODIFIED GRAIN MODEL PARAMETERS - RUN 104

FIGURE 9

MODIFIED GRAIN MODEL VALIDATION

MASS TRANSFER COEFFICIENT (CM/SEC)	0.15000E+06
BULK REACTIVE GAS CONCENTRATION (MG MOLE/CC)	0.51700E-03
STOICHIOMETRIC COEFFICIENT-GAS PHASE	-1.000
STOICHIOMETRIC COEFFICIENT-SOLID PHASE	-1.000
PARTICLE WEIGHT (GM)	0.06290
MOLECULAR WEIGHT ZNO	81.36800
MOLECULAR WEIGHT ZNS	97.43000
NUMBER OF DIVISIONS OF SOLID RADIUS	10
MAXIMUM NUMBER OF TIME STEPS	2000
TIME STEP SIZE (MIN)	0.0250
DESIRED FINAL CONVERSION	0.9500
TEMPERATURE (DEG K)	870.000
EQUILIBRIUM SURFACE AREA ZNO (CM**2/GM)	87598.859
EQUILIBRIUM SURFACE AREA ZNS (CM**2/GM)	59009.727
GRAIN RADIUS (CM)	0.29913E-05
SINTERING RATE CONSTANT ZNO (1/MIN)	0.154036E-03
SINTERING RATE CONSTANT ZNS (1/MIN)	0.154036E-03
REACTION RATE CONSTANT (CM**4/MG MOLE MIN)	0.14265E-02
PARTICLE POROSITY	0.67015
AVERAGE PORE RADIUS (CM)	0.40515E-05
KNUDSEN DIFFUSION COEFFICIENT	0.19856E+00
MOLECULAR DIFFUSION COEFFICIENT	0.11548E+01
COMBINED PORE DIFFUSION COEFFICIENT	0.16943E+00
PARTICLE THIELE MODULUS	0.1347E-02
GRAIN THIELE MODULUS	0.1671E+01
BIOT NUMBER	0.3962E+06
DIMENSIONLESS TIME	0.6164E-02
EFFECTIVE GRAIN DIFFUSIVITY	0.2767E-08

TABLE 4

MODIFIED GRAIN MODEL PARAMETERS - RUN 105

B. Test Cases

Three test cases have been run to illustrate the output at accelerated conditions and hot gas cleanup temperatures. In order to minimize the time required for each simulation a very small reactor size was chosen with a very high gas flow rate, and a high H_2S concentration at the inlet. The parameters used for these test cases are shown below:

Reactor Length	=	5 cm
Superficial Velocity	=	386.6 cm/min
Space Velocity	=	8000 vol/vol hr
Inlet H_2S concentration	=	2000 ppm
Temperature	=	1000°F, 1200°F, 1400°F
Time	=	0.001 minute

The space velocity used is 20 times greater than the typical space velocity of 400 hr^{-1} that is normally used with a zinc oxide reactor. This was done to obtain the equivalent of a longer simulation in terms of volume of gas passed over the sorbent per volume of sorbent.

The H_2S concentration of 2000 ppm is 10 times the expected value in a hot gas cleanup system consisting of iron oxide for bulk H_2S removal and zinc oxide for low level sulfur removal.

Three temperatures were chosen in the hot gas cleanup range; 1000°F, 1200°F and 1400°F, and three these cases were simulated and plotted so that they could be compared. Figures 10, 11, and 12 are the resulting curves. Figure 10 shows the H_2S concentration profile in the reactor for each of the three temperatures, indicating a lower profile as temperature increases. This is an expected result since the rate of reaction and diffusion both increase with temperature, so that at least initially, higher temperatures would cause more H_2S to be consumed within the reactor. Figure 11 depicts the H_2S breakthrough curves for each temperature, and here too the higher temperatures result in lower H_2S levels at the reactor exit, for the same reasons as in Figure 10. Figure 12 refers to the solid ZnO pellets rather than the gas stream, and shows the percent conversion profile for each temperature. In this plot the percent conversion at higher temperatures was higher due to faster reaction kinetics and improved mass transfer within the pellets. The higher solid conversion figures result in the lower gas concentrations, as shown in Figure 10.

Tables 5, 6 and 7 show the output data in tabular form for each of the individual test cases, where temperature is shown in degrees Kelvin. These tables show the change with time of the gas concentration profile, as well as the conversion profile of the solid ZnO in percent shown at the end of the last time interval calculated. The operating parameters are also shown at the top of the table.

These three test cases are provided as an illustration only, and by no means exhaust the possibilities in sensitivity analysis of various parameters such as particle size, composition of the pellets, flow rates, bed porosity, inlet concentrations, and others. It is hoped that these will follow in the future.

C. Discussion

As pointed out earlier, validation runs for single particles using the modified grain model resulted in good similarities in the curves between experimental data and the model. However, final conversion figures were consistently off by approximately 20%. These results were investigated, and several parameter variations were tried in order to find a good match between experimental data and the model. It was found that temperature was the most effective parameter in matching the model to experimental data. Operating the model at 300-400 degrees Kelvin higher than the experimental data, produced very good fit to the experimental data. This result indicates that the temperature dependent parameters shown below;

- Rate of Reaction
- Sintering Rate
- Equilibrium Surface Area
- Molecular Diffusion (particle)
- Knudsen Diffusion (particle)
- Effective Grain Diffusivity

require modifications in their coefficients, and/or activation energies. As pointed out by Ranade¹⁰, in the development of the grain model, it was recommended that experimental values for effective diffusivity within the

FIGURE 10 - H₂S CONCENTRATION PROFILE

FIGURE 11 - BREAKTHROUGH CURVE

REACTOR LENGTH - DIMENSIONLESS
FIGURE 12 - ZNO CONVERSION PROFILE

TABLE 5

REACTION IN A PACKED BED OF ZNO WITH THE PARAMETERS

RADP = 0.1725

CSO = 21.7800

KMA = 150000.

ITER = 10

CB = 2000.0

PARU = 0.0403

TEMP = 1033.00

DTAU = .0001000

N = 10.

CMAX = 2000.0

LEN = 5.00

U = 386.60

EB = 0.4200

TIME

VALUES OF GAS CONCENTRATION AT ALL GRID POINTS

0.00000

2000.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.00010									

2000.0000	368.1305	67.7821	12.4784	2.2972	0.4223	0.4779	0.0143	0.0026	0.0005
0.00020									

2000.0000	501.2141	115.7600	26.0033	5.6170	1.1869	0.2466	0.0506	0.0103	0.0021
0.00030									

2000.0000	532.8127	136.2525	33.5560	8.0036	1.8586	0.4221	0.0941	0.0206	0.0045
0.00040									

2000.0000	544.3259	145.1316	37.7535	9.5764	2.3716	0.5746	0.1365	0.0319	0.0073
0.00050									

2000.0000	548.3455	148.9201	39.8752	10.4961	2.7124	0.6381	0.1714	0.0420	0.0101
0.00060									

2000.0000	549.7570	150.4867	40.8874	10.9037	2.9187	0.7640	0.1971	0.0501	0.0125
0.00070									

2000.0000	550.2554	151.1202	41.3506	11.2481	3.0362	0.8110	0.2143	0.0560	0.0144
0.00080									

2000.0000	550.4344	151.3727	41.5561	11.3726	3.0976	0.8383	0.2251	0.0600	0.0158
-----------	----------	----------	---------	---------	--------	--------	--------	--------	--------

TABLE 5
(Continued)

0.00000										
2000.0000	550.5008	151.4728	41.6452	11.4316	3.1297	0.8535	0.2316	0.0624	0.0167	
0.00100										
2000.0000	550.5287	151.5130	41.6833	11.4588	3.1456	0.8616	0.2352	0.0640	0.0173	
ICOUNT GREATER THAN ITER										
XBAR 0.00004854	0.00001154	0.00000302	0.00000079	0.00000020	0.00000005	0.00000001	0.00000000	0.00000000	0.00000000	0.00000000

TABLE 6

REACTION IN A PACKED BED OF ZNO WITH THE PARAMETERS

RADP = 0.1725

CSO = 21.7800

KMA = 150000.

ITER = 10

CB = 2000.0

PARU = 0.0403

TEMP = 921.00

DTAU = .0001000

M = 10.

CMAX = 2000.0

LEN = 5.00

U = 386.60

EB = 0.4200

TIME VALUES OF GAS CONCENTRATION AT ALL GRID POINTS

0.00000

2000.0000 0.00010	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
----------------------	--------	--------	--------	--------	--------	--------	--------	--------	--------

2000.0000 0.00020	368.1905	67.7821	12.4784	2.2972	0.4229	0.0779	0.0143	0.0026	0.0005
----------------------	----------	---------	---------	--------	--------	--------	--------	--------	--------

2000.0000 0.00030	545.3776	133.0207	30.4935	6.7192	1.4405	0.3027	0.0626	0.0128	0.0026
----------------------	----------	----------	---------	--------	--------	--------	--------	--------	--------

2000.0000 0.00040	617.1286	174.1611	45.5196	11.5036	2.7711	0.6473	0.1475	0.0330	0.0072
----------------------	----------	----------	---------	---------	--------	--------	--------	--------	--------

2000.0000 0.00050	650.8589	199.4341	57.6714	15.8601	4.1814	1.0642	0.2630	0.0634	0.0150
----------------------	----------	----------	---------	---------	--------	--------	--------	--------	--------

2000.0000 0.00060	666.6252	214.0540	65.7835	19.3559	5.4716	1.4925	0.3946	0.1015	0.0255
----------------------	----------	----------	---------	---------	--------	--------	--------	--------	--------

2000.0000 0.00070	673.8981	222.2006	71.0334	21.9331	6.5390	1.8855	0.5272	0.1433	0.0380
----------------------	----------	----------	---------	---------	--------	--------	--------	--------	--------

2000.0000 0.00080	677.4476	226.6231	74.2782	23.7200	7.3595	2.2171	0.6491	0.1850	0.0514
----------------------	----------	----------	---------	---------	--------	--------	--------	--------	--------

2000.0000	679.0630	228.9783	76.2160	24.9027	7.9556	2.4796	0.7534	0.2233	0.0646
-----------	----------	----------	---------	---------	--------	--------	--------	--------	--------

TABLE 6
(Continued)

0.00000										
2000.0000	679.8212	230.2145	77.3426	25.6574	8.3697	2.6767	0.8377	0.2564	0.0767	
0.00100										
2000.0000	680.1786	230.8563	77.9839	26.1250	8.6473	2.8188	0.9027	0.2836	0.0873	
ICOUNT GREATER THAN ITER										
XBAR 0.00003576	0.00001012	0.00000313	0.00000096	0.00000029	0.00000009	0.00000003	0.00000001	0.00000000	0.00000000	

TABLE 7

REACTION IN A PACKED BED OF ZNO WITH THE PARAMETERS

RADP = 0.1725	CSO = 21.7800	KMA = 150000.	ITER = 10
CB = 2000.0	PARL = 0.0403	TEMP = 810.00	
DTAU = .0001000	M = 10.	CMAK = 2000.0	
LEN = 5.00	U = 386.60	EB = 0.4200	

TIME VALUES OF GAS CONCENTRATION AT ALL GRID POINTS

0.00000										
0.00010	2000.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.00020	2000.0000	368.1905	67.7821	12.4784	2.2972	0.4229	0.0779	0.0143	0.0026	0.0005
0.00030	2000.0000	584.2878	147.3471	34.4497	7.6903	1.6640	0.3520	0.0732	0.0150	0.0031
0.00040	2000.0000	699.7195	212.2897	58.5803	15.1346	3.7271	0.8851	0.2043	0.0461	0.0102
0.00050	2000.0000	765.9705	261.5385	81.3744	23.5585	6.4482	1.6882	0.4264	0.1046	0.0250
0.00060	2000.0000	803.9467	296.6508	100.8229	31.9299	9.5352	2.7124	0.7410	0.1957	0.0502
0.00070	2000.0000	825.7169	320.7230	116.3447	39.5538	12.6944	3.8759	1.1338	0.3196	0.0873
0.00080	2000.0000	838.1879	336.7836	128.1590	46.0733	15.6828	5.0096	1.5804	0.4723	0.1364
	2000.0000	845.3548	347.2871	136.8382	51.3886	18.3793	6.2749	2.0528	0.6400	0.1984

TABLE 7
(Continued)

0.00000										
2000.0000	849.4597	354.0519	143.0414	55.5630	20.6789	7.3733	2.5236	0.8315	0.2645	
0.00100										
2000.0000	851.8151	358.3570	147.3785	58.7440	22.5758	8.3482	2.9712	1.0194	0.3379	
ICOUNT GREATER THAN ITER										
XBAR 0.00002470	0.00000833	0.00000304	0.00000108	0.00000037	0.00000013	0.00000004	0.00000001	0.00000000	0.00000000	

pellet and the grains be obtained rather than use calculated values as has been done.

The grain model is used to calculate the global reaction rate which is used in solving the packed bed mass balance equation. The discrepancy between experimental and model output should be kept in mind in using this model, however it is felt that for the purpose of systems studies the model will be useful, particularly since conservative predictions will be generated.

Test cases at greatly accelerated conditions as documented in Section IV.B. indicate that zinc oxide will be an effective desulfurization unit at high temperatures. This is due to improved reaction kinetics and improved diffusion of reactant and product to and away from the reaction zone. Longer simulations and cycling of several sorption/regeneration cycles will provide further indications of the expected performance of Zinc Oxide.

There are three limitations to this model, and they are as follows:

- H_2S inlet composition is assumed dry. (No H_2O). The H_2O/H_2S equilibrium will cause higher H_2S levels to be present in wet gas streams.
- Calculation of the global reaction rate by the modified grain model at each interval in space and time is relatively time consuming.
- The explicit finite difference method used is limited in time increment size, so that only relatively short periods of time can be simulated.

Recommendations for improvements are suggested to eliminate the limitations listed above in order to provide a model with greater flexibility and ability to simulate large scale reactors for longer periods of time.

- Incorporate an equilibrium calculation for the H_2O/H_2S equilibrium to adjust exit concentration to equilibrium levels with H_2O present.
- Map out the global reaction rate for various conditions over a range of time, and correlate mathematically. Use this expression to find the global reaction rate, rather than calculate it at each step. This will speed up the model greatly.
- Develop a stable implicit finite difference technique, or other method such as collocation to solve the partial differential equation. Such a method should be independent of time step size to allow long term simulations of large reactors.

In conclusion, a reactor model for sorption of H_2S on zinc oxide has been provided which uses the modified grain model for single pellets to calculate the global reaction rate based on kinetic and mass transport effects and physical properties of the solid pellets. Basic principles of kinetics and mass transport, along with experimental data available, were used to provide a rigorous mathematical simulation, by starting with mass balances around a single particle to provide global reaction rates, and ending with a mass balance around a whole reactor. The model is currently operational on the METC DEC VAX-11.

V. ZnO Properties

Zinc oxide is used commercially as an adsorbent for the desulfurization of process streams prior to catalytic operations. The major current application for zinc oxide is the desulfurization of hydrocarbon feedstocks prior to steam reforming to prevent poisoning of reformer catalyst. There are several commercial suppliers of ZnO adsorbents, among them are Katalco, Haldor Topsoe, and United Catalysts, Inc. For the purpose of this study United Catalysts, Inc. has been contacted to provide typical properties of two types of ZnO adsorbents, namely: G-72D and C7-2. The specifications sheets for these two adsorbents have been reproduced here for reference along with some general information provided by the manufacturer, showing sulfur loading as a function of temperature, effect of space velocity, and steam to gas ratio. Properties that are expected to be important in the analysis of ZnO for desulfurization are percent ZnO, surface area, pore volume, strength, and type of support.

Introduction

Zinc oxide adsorbents are gaining wider acceptance for the desulfurization of process streams prior to catalytic processing due to their superior ability to effect more complete removal of sulfur compounds on an un-interrupted basis. The major current application for zinc oxide is the desulfurization of hydrocarbon feedstocks to steam-hydrocarbon reforming units. Such units are capable of reducing the sulfur level continuously to <0.1 ppm thus enabling the steam hydrocarbon

reforming unit to achieve maximum efficiency. Satisfactory performance of a zinc oxide is dependent on its rate and capacity of sulfur pick-up as well as its resistance to physical degradation during use.

UCI offers a high surface area, high capacity, zinc oxide adsorbent designated as C7-2 for the economical desulfurization of various process streams, both wet and dry. Unique features offered by C7-2 when compared to other zinc oxides available are:

Sulfur capacities in excess of 25 weight percent.

High crush strength ($>$ two times that of spherical types).

Low attrition loss ($<50\%$ that of spherical type).

High resistance to strength loss by water contact.

C7-2 has been established through its wide-spread commercial use as an adsorbent capable of providing entirely trouble-free operations. It has been thoroughly proven by industry over several years of commercial operation.

Sulfur capacity of a zinc oxide is dependent on the surface area of the adsorbent and its density.

C7-2 is manufactured using zinc oxides specially precipitated to give the maximum surface area which is a criteria for maximizing sulfur adsorption capacity and rate of adsorption reaction. The method of forming the high surface area oxides results in a product having a high bulk density. This combination of properties renders to C7-2 an extremely high sulfur pick-up both in terms of weight percent sulfur adsorbed and the pounds of sulfur adsorbed per cubic foot of zinc oxide adsorbent. In Figures 6 and 7

we have plotted laboratory determinations of the sulfur capacity of C7-2 as compared to a spherical type of zinc oxide also available to the industry. As noted, the sulfur capacity of C7-2 expressed as a weight percent sulfur pick-up is approximately 10% higher than the spherical type. When the sulfur pick-up is expressed as pounds of sulfur adsorbed per cubic foot of adsorbent the C7-2 demonstrates almost a 20% higher capacity. This difference in performance characteristic is a result of the higher surface area of the C7-2 and the slightly higher bulk density of the product. Such higher sulfur capacity can be directly related

to the cost of desulfurization utilizing zinc oxide and the eventual savings, assuming identical purchase prices for zinc oxide adsorbent accordingly the cost should total approximately 20% less. Commercial applications utilizing C7-2 have verified this performance difference and several users have experienced sulfur pick-ups of 25 weight percent sulfur or higher in the lead zinc oxide bed position. The capacity of the zinc oxide does vary considerably with temperature and the higher capacity figures reported are for those operations in the neighborhood of 700°F (371°C).

Fig. 6 — Effect of temperature on weight % sulfur adsorbed by zinc oxide. (Laboratory Evaluation, 900 S.V., 1 atm.)

Fig. 7 — Zinc oxide sulfur capacity vs. temperature (Laboratory Evaluation, 900 S.V., 1 atm.)

Mechanical strength of a zinc oxide is dependent on the forming method used and the post-treatment of the material for developing strength. C7-2, being a pelletized product, experiences considerable compacting during forming which contributes to its higher mechanical strength. This is to be compared to a spherical product which experiences virtually no compacting during forming and depends solely on post-treatment for any strength development. As noted under Physical and Chemical Properties, the mechanical strength of the C7-2 is very satisfactory and more than twice as high as the spherical type product. The attrition resistance of a material is highly dependent on the mechanical strength and, as noted, the attrition loss of C7-2 is less than half of that of the spherical type product. The significance of mechanical strength is manifest in the ability of the adsorbent to hold up under adverse processing conditions. Should the adsorbent powder or disintegrate during operations the adsorbent is carried into subsequent processing units, sometimes with serious effects. Zinc oxide swept into reformer tubes can cause

physical fouling of the catalyst, decreased heat transfer characteristics, decreased activity characteristics, and an eventual increase in tube skin temperatures. In addition, powdered zinc oxide can migrate downstream and foul subsequent process equipment, such as waste heat boilers, with a resultant decrease in overall plant efficiency. Zinc oxide, when used as a guard for low temperature shift catalyst, must possess high mechanical strength in order to avoid the occurrence of fines fouling the LTS converter catalyst. Such fouling can cause channeling of the gas in the LTS converter and resultant decrease in performance characteristics. In addition, waste heat boilers upstream of the LTS converter frequently rupture tubes resulting in condensate carryover into the LTS converter. Such carryover must not disintegrate the zinc oxide as such disintegration eventually affects the LTS catalyst performance in a manner similar to that described above. C7-2, by virtue of its higher mechanical strength, possesses superior water resistance characteristics.

Other factors affecting the performance of zinc oxide to a

significant degree are the operating space velocity and the steam to gas ratio prevailing in the process gas. Figure 8 illustrates the effect of space velocity on weight percent sulfur pickup over the C7-2 as determined in the laboratory. Most commercial installations for front-end desulfurization of reformer feedstocks are designed for sulfur pick-ups in the neighborhood of 18 weight percent and at a relatively low limiting space velocity. It should be noted that the data contained in Figure 8 is less conservative than that data used as a design criteria for such systems. Figure 9 shows the effect of steam to gas ratio on the weight percent sulfur pick-up of zinc oxide at a relatively low space velocity. As noted, the effect of increasing steam content is significant as regards the capacity of the zinc oxide. Low temperature shift zinc oxide guard beds which operate at low temperatures (400°F) (204°C) and high steam to gas ratios demonstrate very low sulfur pick-ups due to the low operating temperature and the high interference caused by the steam present.

Fig. 8 — Weight % sulfur capacity as function of space velocity (Laboratory test condition @ 800°F) (427°C)

Fig. 9 — Effect of steam on sulfur capacity of C7-2 ZnO (Laboratory test @ 600°F (316°C) and 900 S.V.)

Application

The principal use of zinc oxide is the desulfurization of hydrocarbon feedstocks to steam hydrocarbon reforming units. Used either by itself or in

combination with other desulfurization systems, C7-2 zinc oxide is capable of providing effluent sulfur levels of less than 0.1 ppm. Such sulfur levels are considered essential for obtain-

ing satisfactory operation of high severity reformers. Some typical process schemes for the use of C7-2 on various hydrocarbon feedstocks are presented in Figures 1 thru 5.

Fig. 1 — Desulfurization using activated carbon followed by zinc oxide.

Fig. 2 — Desulfurization by hydro-desulfurization followed by zinc oxide.

Fig. 3 — Desulfurization using acid-gas scrubber, activated carbon and zinc oxide.

Fig. 4 — Desulfurization by hydro-desulfurization, acid gas scrubber and zinc oxide.

Fig. 5 — Desulfurization using two hydro-desulfurization units with a stripper in between followed by zinc oxide guard case.

C7-2 is also used as a guard adsorbent to remove sulfur from gas streams entering various other catalytic reactors which

are sensitive to sulfur. One such application is the protection of copper-zinc low temperature CO conversion catalysts which

are severely poisoned by relatively small quantities of sulfur.

Physical and Chemical Properties

The performance of any zinc oxide is measured primarily by its sulfur adsorption capacity and such capacity is a direct function of the physical and chemical properties of the material. UCI developed its C7-2 zinc oxide in 1966 after first

noting the deficiencies of the materials then being used and then developing a product which eventually overcame these deficiencies. The result was a product which demonstrates —

High sulfur capacities
Higher crush strength
Lower attrition loss
Good water resistance

when compared to other products available then and now.

A comparison of the typical physical and chemical properties of C7-2 with a spherical type material also used demonstrates the vast improvements which C7-2 makes available to the user:

Typical Physical and Chemical Properties

Identification:	C7-2	X
Size and Form:	$\frac{3}{16}$ " Pellets	$\frac{1}{4}$ " x $\frac{1}{8}$ " Spheres
Bulk Density, lbs./CF:	70	65
Wt. % ZnO:	80	80
Lbs. ZnO/CF:	56	52
Surface Area, M ² /g:	22	25
Crush Strength, lbs. D. W. L.:	15	6
Attrition Loss, wt. %	10	20

As will be noted, the C7-2 has a higher surface area and a higher loading of ZnO per unit volume of adsorbent. These

factors account for the higher sulfur adsorption capacity of the C7-2 as discussed under **Performance**. The critical

importance of the physical properties (crush strength and attrition are also discussed under **Performance**.

Performance

As discussed under **Application**, C7-2 is used for the removal of reactive sulfur compounds from hydrocarbon and synthesis gas streams. The

major factors affecting the life, performance, and eventual cost of a zinc oxide operation are:

Sulfur pickup (expressed as lbs. sulfur/CF zinc)
Mechanical strength (its

affect on pressure drop and downstream operations)

Either of these can be the eventual cause for change-out of the adsorbent.

Operations

Sulfur removal with zinc oxide is a chemical reaction in which the sulfur compounds are converted to H₂S and reacted with the zinc oxide to form ZnS. The catalyst, after reaching its adsorptive capacity, is not economically regenerable and should be discarded. Depending upon the quantity of sulfur adsorbed on the zinc, the catalyst may exhibit pyrophoric tendencies when exposed to air during the unloading operation. As a result, moderate care must be used to make sure that the used catalyst is not stored or unloaded in such location where the possible build-up

of heat from the auto oxidation is likely to present a hazard. Discharged catalyst may be wetted down with water to prevent such overheating.

The process conditions and normal operating parameters for zinc oxide in most applications are as follows:

Process Conditions and Normal Design Parameters

Operating Temperature Range	400-800°F (204-427°C)
Pressure	Not critical
Normal Effluent Purity	0.1 ppm sulfur
Design for Dry Gas Applications	18 wt. %
Design for LTS Guard Application	20,000 WGSV or 1.0 wt. % sulfur, whichever limits
Sulfur Compounds Removed	RSH, H ₂ S
Catalyst Poisons	No known poisons

Engineering and Technical Services

It is recommended that UCI be consulted on each desulfurization application to insure that the best operating conditions are utilized for each particular case. Specific recommendations will be given at no cost, by UCI's Engineering Service Department for any proposed application for zinc oxide. In addition, UCI provides, at no cost, the assistance of its Technical Service Engineers for catalyst handling, start up, operation and problem consultation.

Guarantees

UCI grants to the user process performance guarantees covering the performance of its zinc oxide for desulfurization applications. Before granting such performance guarantees, the design conditions and/or anticipated operating conditions must be evaluated and recommendations or confirmations given on the basis of UCI's design system.

Shipping Information

Shipments are made in steel drums of the following specifications:

- Capacity
7.50 Ft.³/drum (average)
- Dimensions
23" O.D. x 34" high
- Tare Weight
49 lbs.
- Cubage
11.5 cubic feet

Process Conditions and Normal Design Parameters

Operating Temperature Range	400-800°F (204-427°C)
Pressure	Not critical
Normal Effluent Purity	0.1 ppm sulfur
Design for Dry Gas	
Applications	18 wt. %
Design for LTS Guard	20,000 WGSV or 1.0 wt. %
Application	sulfur, whichever limits
Sulfur Compounds Removed	RSH, H ₂ S
Catalyst Poisons	No known poisons

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It is recommended that UCI be consulted on each desulfurization application to insure that the best operating conditions are utilized for each particular case. Specific recommendations will be given at no cost, by UCI's Engineering Service Department for any proposed application for zinc oxide. In addition, UCI provides, at no cost, the assistance of its Technical Service Engineers for catalyst handling, start up, operation and problem consultation.

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Shipments are made in steel drums of the following specifications:

Capacity
7.50 Ft. ³ /drum (average)
Dimensions
23" O.D. x 34" high
Tare Weight
49 lbs.
Cubage
11.5 cubic feet

United Catalysts Inc.

Zinc Oxide for Desulfurization of Gas Streams

Typical Chemical and Physical Properties

**Catalyst Type,
Form and Size** Catalyst Type C7-2-01
Form Pellets
Size: Diameter 3/16"

Effective 8/21/75
Supercedes: 4/22/75

Chemical Composition	Weight Percent		Trace Metal Impurities	Weight Percent
ZnO*	80.±5%		Pb	<0.15%
Carbon	<0.20%		Sn	<0.005%
Sulfur*	<0.15%		As	<0.005%
Chlorides	<0.05		Hg	<0.005%
SiO ₂	5 to 10%		Fe	<0.1%
Al ₂ O ₃	4 to 6%		Cd	<0.005%
Other Alkali Metals			LOI to constant weight at	
Ca and K	0.05-0.01%		250°F	0.2%
Other Heavy Metals			1000°F*	5.0%
Ni and Ti	0.01-0.02%			

**Physical
Properties** A. Bulk Density, lbs./cu. ft. 70 ± 5
B. Surface Area, m²/g* 22 (minimum)

Pre-treatment of catalyst for surface area determination consists of drying the catalyst in powder form (60-100 mesh) at 200°C.

C. Pore Volume, cc/g 0.20 to 0.28

The pore volume is obtained with the mercury porsimeter at 60,000 psia which corresponds to a total pore volume of pores greater than 29.2A diameter.

D. Attrition, wt. % loss 3.0

a) Attrition Test Method

Apparatus — Rotating horizontal steel cylinder with a single baffle.

Cylinder Diameter 6½"
Cylinder Length 7¼"
Number of baffles 1
Height of baffle 7"
Length of baffle 1"
Thickness of baffle 1/16"
Cylinder turns, RPM 60
Length of time for test 10 minutes
Sample quantity tested 100 grams
Screen used to separate
fines-mesh size 20

b) Calculation Method

$$\text{wt \% Attrition} = \frac{\text{weight in} - \text{weight out}}{\text{weight in}} \times 100$$

Physical Properties

- E. Crush Strength,* minimum average 15.0 lbs.

Apparatus — Hydraulic press with horizontal plates of which the top plate moves vertically. In series with the top plate is a pressure gauge which records the pressure exerted on the pellet.

Procedure — The pellet is placed on its side and the top plate is lowered to the pellet with zero pounds pressure on the gauge. Pressure is then increased on the top plate until the pellet crushes and the pressure at pellet breakage is recorded.

The crush on a minimum of ten pellets per sample is obtained and the average taken arithmetically.

To pretreat the sample, dry tablets at 250°F for three hours, allow to cool.

Crush Strength range on
individual pellets 10 to 30

- F. Particle Size

Normal Length $\frac{1}{2}$ "
Normal Diameter $\frac{3}{16}$ "

Form Variation:

Length $\pm \frac{1}{4}$ "
Diameter ± 0.005

*Properties normally measured by Quality Control.

**Typical
Pore Volume
Distribution Curve**

General

G-72D is used for the removal of H_2S and organic sulfur compounds from gases. It consists of zinc oxide/binder in the form of $\frac{3}{16}$ " (4.76mm) Extrusions. The bulk density is about 62 lbs./cu. ft.

It is used for the removal of small concentrations of hydrogen sulfide and organic sulfur compounds from gases before they come into contact with nickel catalysts such as United G-56 for steam reforming of hydrocarbons.

The catalyst is normally used in the temperature range 650-850°F (343-454°C) at a space velocity of 400 Hr⁻¹. It may be used at pressures ranging from atmospheric to over 50 atmospheres. The catalyst will absorb hydrogen sulfide at room temperature but has a longer lifetime when operating in the recommended temperature range.

When the catalyst is used as recommended, hydrogen sulfide and other non-refractory sulfur compounds are removed so that the exit gas contains less than 1 ppm total S. When sulfur breakthrough occurs while operating under the above conditions, we guarantee that the catalyst will contain an average of more than 18% w/w sulfur. Most of this is in the first half of the bed which will contain approximately 25% w/w sulfur. It is often convenient to split the catalyst into two beds so that when breakthrough occurs the catalyst in the first bed may be discharged, the

catalyst in the second bed used as first bed catalyst and fresh material charged to the second bed. If the gas flow through the desulfurization stage can be reversed, the original second bed catalyst need not be disturbed. By this method all the catalyst discharged will have an average of approximately 25% w/w sulfur. The following shows typical amounts as absorbed sulfur measured in single beds of United G-72D before the exit level of H_2S reached 1 ppm.

Space Velocity	700 Hr ⁻¹
Inlet H_2S	50 ppm
Exit H_2S below	1 ppm
Temperature °F (°C)	% w/w sulfur in G-72D
70 (21)	5.5
212 (100)	6.0
400 (204)	11.0
575 (302)	17.0
750 (399)	20.0

Low sulfur content gas streams

When the gas stream contains less than 10 ppm of non-refractory sulfur compounds, a higher space velocity up to 2,000 Hr⁻¹ may be used.

Low temperature use (70-212°F) (21-100°C)

United G-72D may be used at temperatures as low as 70°F (21°C) at a space velocity of 400 Hr⁻¹. Under these conditions it will absorb H_2S from gas streams until the catalyst contains more than 6% w/w sulfur.

Guard for low temperature shift catalyst

United G-72D may be used as a sulfur guard before a low temperature shift catalyst such as United catalyst G-66B. In this type of operation, normally at 400-480°F (204-249°C) with a sulfur content of the gas of the order of 1-2 ppm H_2S a much higher space velocity, 10,000 Hr⁻¹, may be used.

With gas containing up to 50% steam, i.e. a steam ratio of 1.0, the expected sulfur uptake in the catalyst is greater than 10% w/w before exit gas contains more than 0.1 ppm H_2S .

Catalyst in steam

At atmospheric pressure, above 212°F (100°C), steam has no effect on the strength of United G-72D. Contact with high pressure steam, however, can weaken the catalyst unless the temperature is more than 70°F (21°C) above the condensation temperature. The catalyst can be damaged if it is washed in hot water or condensate.

Sulfur removal in the presence of steam is generally carried out at temperatures below 575°F (302°C). Above this temperature efficiency can be limited because the gas reaches an equilibrium with the catalyst.

Operation —

Loading

The catalyst may be stored for several years with negligible deterioration in activity or strength. The drums should be kept under cover and clear of damp floors or walls. Before charging, United G-72D should be inspected, and fines, caused if rough handling occurs during transport, should be screened out. Treatment likely to damage the catalyst should be avoided and it should not undergo a free fall of more than 2 to 3 feet.

It is important that the catalyst packing should be even throughout the bed so that pressure drop variations and uneven gas flow are minimal. This is not achieved if the extrusions are poured from the drum on to a pile which is subsequently raked level. The extrusions may be charged directly from the drum by pouring them evenly around the converter. Alternatively, the drum may be emptied into a small hopper or funnel before being fed into the converter down a flexible chute, such as a rubber hose, which is moved around so as to direct the catalyst evenly to all parts of the bed.

Walking on the catalyst must be avoided since it causes uneven packing. If operators are needed inside the converter to assist in charging, they should be provided with boards arranged above the catalyst.

Start-up

The converter is heated to operating temperature during start-up. Heating can be carried out with an inert gas. After heating above the condensation point steam can be added. It may sometimes be convenient to keep the converter at atmospheric pressure so that steam can be employed as soon as the catalyst temperature exceeds 212°F (100°C). No special treatment is required before use and sulfur removal is commenced as soon as process gas can be added to the converter.

For further information contact our Sales Department.

Warranties And Liabilities

UCI warrants that the catalyst as sold does not infringe any U. S. patents which claim the catalyst's composition or its method of manufacture per se. In addition to such patents, there sometimes exist patents which claim the use of the catalyst in a specific process. Since, in such cases, the potential liability is related to the value of the material being processed and since the catalyst supplier cannot always be familiar with the process conditions, UCI cannot accept liability for infringement of such patents. The customer will, no doubt, find it advisable to make a patent search to determine the possibility of infringement. UCI can supply or make arrangements under which sufficient information can be supplied about the catalyst that such a search can be made.

As to process liability, UCI assumes no liability for time, material or product, or injury to personnel resulting from the use of this catalyst. In general UCI limits its liability to the value of the catalyst. However, UCI makes every effort to supply a catalyst that is produced from carefully selected raw materials and with close attention to quality control. Although the quality of the raw materials and the method of preparation often affect the activity of the catalyst, there are other factors, often beyond the control of the catalyst supplier that affect the performance. These factors are the operating conditions such as temperature, pressure, composition of process materials and the presence of trace impurities that constitute catalyst poisons. UCI provides process information to assist the customer in establishing the optimum operating conditions and indicates what known materials may be poisonous to the catalyst. UCI also provides field technical service without cost to the customer to assist in attaining the best possible performance from a catalyst.

United Catalysts Inc.

Zinc Oxide For Desulfurization Of Gas Streams

Typical Chemical and Physical Properties

Catalyst Type, Form and Size

Catalyst Type G72D
Form Pellets
Size $\frac{3}{16}$ "

Effective: 9/17/79
Supersedes: 8/27/79

Chemical Composition

	Weight Percent
ZnO*	$90.0 \pm 5\%$
Carbon	<0.20
Sulfur*	<0.15
Chlorides	<0.02
Al ₂ O ₃	3-7
CaO	0.5-3.0

Trace Metal Impurities

	Weight Percent
Pb	<0.15
Sn	<0.005
As	<0.005
Hg	<0.005
Fe	<0.1
Cd	<0.005

LOI to Constant Weight at:

	Weight Percent
250°F	0.2
1000°F*	5.0

Physical Properties

A. Bulk Density, lbs./cu. ft. 65 ± 5

B. Surface Area, m²/g* 35 minimum

The surface area is obtained by a modified BET method which consists of nitrogen adsorption by the sample. The sample is ground to a fine powder (60-100 mesh) and purged with nitrogen at 200°C to a constant weight.

C. Pore Volume, cc/g 0.25-0.35

The pore volume is obtained with the mercury porsimeter at 60,000 psig which corresponds to the total pore volume of pores greater than 29.2 Angstroms diameter.

D. Crush Strength, minimum average* 15

Apparatus — Hydraulic press with horizontal plates of which the top plate moves vertically. In series with the top plate is a pressure gauge which records the pressure exerted on the pellet.

Procedure — The pellet is placed on its side, and the top plate is lowered to the pellet with zero pounds pressure on the gauge. Pressure is then increased on the top plate until the pellet crushes and the pressure at pellet breakage is recorded.

The crush on a minimum of ten pellets per sample is obtained and the average taken arithmetically.

To pretreat the sample, dry tablets at 250°F for three hours, allow to cool.

**Physical
Properties**

Crush Strength Range on
Individual Pellets 12 to 30

E. Particle Size

Normal Length $\frac{1}{2}$ "
Normal Diameter $\frac{3}{16}$ "

Form Variation

Length 0.25-0.65"
Diameter 0.180-0.192"

*Properties normally measured by Quality Control.

**Typical
Pore Volume
Distribution Curve**

1

3

4

5

6

7

6034

199

321

300

1.

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ICOUNT = ICOUNT + 1
DO 5 K = 1,M
XBAR = LXBAR(K)
DIND(1) = LDIND(K)
I(2)
CONTINUE
CAO = C(K)
CALL GRAIN
CONTINUE
CALL TIMER(2,0)
PI=3.1415926
DO 6 I = 1,M
RG(I) = (CSO/ROW1)*DX(I)*PARU*3*((1-EB)/(4*PI*RADP*3.0))
RG(I) = 1000*RG(I)
CALL TIMER(3,0)
DO 7 I=2,M
C(I) = ((1-(UXRATIO/EB))*C(I)) + ((UXRATIO/EB)*C(I-1)) - (DTAU*RG
CALL TIMER(4,0)
CONTINUE
IF (ICOUNT .GT. ITER ) GOTO 300
IF (( ICOUNT/IFREQ)*IFREQ .NE. ICOUNT) GO TO 4
DO 199 I=1,M
C(I) =C(I)*22.4E6
WRITE (12,202) TAU,(C(I),I=1,M)
CLAST(ILAST) =C(M)
TAUTIME(ILAST) = TAU
ILAST=ILAST +1
DO 371 I = 1,M
C(I) = C(I)/22.4E6
IF ( C(M) .LT. CMAX) GOTO 4
FORMAT ( 10X,'REACTION IN A PACKED BED OF ZNO WITH THE PAR'
'ETERS',/,10X,'RADP = ',F8.4,T40,'CSO = ',
F8.4,T70,'KWA = ',F8.0,T100,'ITER = ',I5,/,10X,'CB = ',F8.
T40,'PARU = ',F8.4,T70,'TEMP = ',F8.2,/,
10X,'DTAU = ',F8.7,T40,'M = ',F8.0,T70,'CMAX = ',
F8.1,/,10X,'LEN = ',F8.2,T40,'U = ',F8.2,

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201 1 T70,'EB = ',F8.4)
    FORMAT(////,4X,'TIME',18X,'VALUES OF GAS CONCENTRATION ',
1    'AT ALL GRID POINTS',////)
    FORMAT(3X,F8.5////(8X,10(1X,F10.4)))
250 1    FORMAT(10(8X,F10.8//))
350 1    FORMAT(2X,'XBAR',10(2X,F10.8))
    GO TO 370
300 1    WRITE (12,2)'ICOUNT GREATER THAN ITER'
    GO TO 380
370 1    WRITE (12,2) 'C(M) GREATER THAN CMAX'
    WRITE (12,2) C(M),CMAX
380 1    DO 360 I=1,M
360 1    C(I)= C(I)*22.4E6
    CMAX = CMAX*22.4E6
    CONTINUE
390 1    WRITE(12,350) LXBAR
    DO 400 I = 2,M+1
    RL(I)=0.0
400 1    RL(I)=RL(I-1) + 1/M
    XMIN=0.0
    XMAX=1.0
    CALL BELL
    CALL ERASE
    CALL BINITT
    WRITE (47,2) M,M
    DO 786 I=2,M+1
    XPLOT(I)=RL(I-1)
    YPLOT(I)=C(I-1)
    WRITE (47,2) XPLOT(I),YPLOT(I)
786 1    CONTINUE
    XPLOT(1)=M
    YPLOT(1)=M
    CALL CHECK(XPLOT,YPLOT)
    CALL DISPLAY(XPLOT,YPLOT)
    OPEN(UNIT=99,NAME='ELCJLAB1.DAT',TYPE='OLD')
    CALL LABEL3
    IF (IND.EQ.1) GO TO 2005
    CALL HDCOPY
2005 1    CALL TINPUT(JKL)
    CALL ERASE
    CALL BINITT
    WRITE (47,2) ITER,ITER
    DO 787 I=2,ITER+1
    XPLOT(I)=TAUTIME(I-1)
    YPLOT(I)=CLAST(I-1)
    WRITE (47,2) XPLOT(I),YPLOT(I)
787 1    CONTINUE
    XPLOT(1)=ITER
    YPLOT(1)=ITER
    CALL CHECK(XPLOT,YPLOT)
    CALL DISPLAY(XPLOT,YPLOT)
    CLOSE(UNIT=99,DISPOSE='KEEP')
    OPEN(UNIT=99,NAME='ELCJLAB2.DAT',TYPE='OLD')
    CALL LABEL3
    IF (IND.EQ.1) GO TO 2006
    CALL HDCOPY
2006 1    CALL TINPUT(IJK)
    CALL ERASE
    CALL BINITT
    WRITE (47,2) M,M
    DO 788 I=2,M+1
    XPLOT(I)=RL(I-1)
    YPLOT(I)=LXBAR(I-1)

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788 1    WRITE (47,2) XPLOT(I),YPLOT(I)
    CONTINUE
    XPLOT(1)=M
    YPLOT(1)=M
    CALL CHECK(XPLOT,YPLOT)
    CALL DISPLAY(XPLOT,YPLOT)
    CLOSE(UNIT=99,DISPOSE='KEEP')
    OPEN(UNIT=99,NAME='ELCJLAB3.DAT',TYPE='OLD')
    CALL LABEL3
    IF (IND.EQ.1) GO TO 2007
    CALL HDCOPY
2007 1    CALL TINPUT(KLJ)
    CALL FINITT(0,700)
    XINCR=ITER*DTAU/10
    YMAX=LXBAR(1)
    CALL TIMER(5,0)
    CALL TIMER(1,1)
    STOP
END

```

8 -

C SUBROUTINE GRAIN
 MODIFIED GRAIN MODEL - FOR ONE REACTIVE GAS
 DIMENSION DTHETA(20)
 DIMENSION C(2,20),CTEMP(20),R(20),CNEU(20),X(20),
 1 TX(2,6),PROFL1(11,21),PROFL2(2,11,21),PROFL3(11,21),
 BPROFL4(11,21),STIME(11),SXBAR(11),DG(2),DEAP(2),
 3 BI(2),PHIP(2),PHIG(2),DEAPO(2),
 4 DK(2),DM(2),AI(20),RADG(20),ROMIX(20),
 5 DEAG(2)
 DIMENSION DX(20),LCNEU(20,15),LRADG(20,15),LXBAR(20),
 1 LDIND(20),LX(20,15),GAMMA(20),BETA(20),DIND(2)
 REAL KMA,K5(2),K10,K20,K1,K2,KBAR,M1,M2,M
 REAL LCNEU,LRADG,LXBAR,LDIND,LX
 COMMON/A11/N,NP1,ISTART
 COMMON/B11/RADP,RSO,M,M2
 COMMON/E11/TEMP,BETA,GAMMA,XBAR
 COMMON/F11/EPSP,CSO,BETAS,KMA,CAO
 COMMON/G11/AA,AS,DTIME,XFINAL,PARU,M1,M2,M
 COMMON/H11/K10,ES1,K20,ES2,A11,ROW1,A12,ROU2
 COMMON/I11/LCNEU,LRADG,LXBAR,LDIND,DX,LX,DIND,PHIP,PHIG,BI,DTHETA,
 COMMON/J11/L,NREACT,ITER,I,J,K,ICNT
 L = L + 1
 DO 4 I=1,NP1
 X(I) = LX(K,I)
 RADG(I) = LRADG(K,I)
 CNEU(I) = LCNEU(K,I)
 IF (L.GT.M) GO TO 45
 K1=K10*EXP(-(ES1)/(1.9872*TEMP))/60.
 K2=K20*EXP(-(ES2)/(1.9872*TEMP))/60.
 KBAR=(K1+K2)/2.
 K1=KBAR
 K2=KBAR
 A11=A11*10000.
 A12=A12*10000.
 A1=A11
 A2=A12
 AF1=34.9*EXP(-0.0056*(TEMP-623.16))
 AF2=14.0*EXP(-0.0035*(TEMP-623.16))
 AF1=AF1*10000.0
 AF2=AF2*10000.0
 RSO=(3.0)/(A11*ROW1)
 DO 375 I=1,NREACT
 KS(I)=0.09458*EXP(-3649./TEMP)
 375 CONTINUE
 EPSP=1.-(PARU)/(ROW1*4.1888*RD*23.)
 DO 725 I=1,NREACT
 DM(I)=0.000045*(TEMP)**(1.5)
 PORE=2.0*EPSP/(A11*(1.-EPSP)*ROW1)
 DK(I)=PORE*9700.0*(TEMP/34.08)**.5
 DG(I)=(DK(I)*DM(I))/(DK(I)+DM(I))
 725 CONTINUE
 CSOG=CSO/(1.-EPSP)
 DO 50 I=1,NREACT
 KS(I)=KS(I)*1000.
 DEAPO(I)=DG(I)*EPSP*BETAS
 DEAG(I)=20.0*EXP(-19750./TEMP)
 PHIP(I)=KS(I)*CSOG*RD/(DEAPO(I)*80.)
 PHIG(I)=(KS(I)*CSOG*RSO)/(DEAG(I)*80.0)
 BI(I)=KMA*RD/DEAPO(I)
 45 CAO=CAO/1000
 DTHETA(K)=KS(1)*CAO*DTIME/RSO
 IF (L.GT.M) GO TO 100
 DIND(I)=1.0

50 CONTINUE
 M=1./FLOAT(M)
 M2=M*M
 NP1=N+1
 NPRINT=N/10
 IX=0
 ICNT=0
 ISTART=0
 XSTEP1=0.0
 XSTEP2=0.5
 TIME=0.
 XBAR=0.
 DO 60 I=1,NP1
 X(I)=0.0
 R(I)=1.
 ROMIX(I)=ROW1
 RADG(I)=1.0
 AI(I)=A11
 DO 60 II=1,NREACT
 C(II,I)=((FLOAT(I)-1.)/FLOAT(N))*23.
 60 DO 70 II=1,NREACT
 70 C(II,I)=C(II,2)
 DO 90 II=1,NREACT
 DO 80 I=1,NP1
 80 CTEMP(I)=C(II,I)
 CALL GASBLN(X,CTEMP,CNEU,AA,PHIG(II),PHIP(II),
 1 BI(II),RADG,DIND(II))
 DO 90 I=1,NP1
 90 C(II,I)=CNEU(I)
 100 CONTINUE
 IX=0
 II=0
 DO 100 IWRITE=1,6
 ICNT=ICNT+1
 TX(1,IWRITE)=TIME
 TX(2,IWRITE)=XBAR
 IF(XBAR.LT.XSTEP1) GO TO 120
 I=0
 IX=IX+1
 DO 110 IKEEP=1,NP1,NPRINT
 I=I+1
 PROFL1(IX,I)=X(IKEEP)
 DO 110 II=1,NREACT
 110 PROFL2(II,IX,I)=C(II,IKEEP)
 SXBAR(IX)=XBAR
 STIME(IX)=TIME
 XSTEP1=XSTEP1+.1
 I=0
 DO 225 IKEEP=1,NP1,NPRINT
 I=I+1
 PROFL3(IX,I)=RADG(IKEEP)
 PROFL4(IX,I)=R(IKEEP)
 225 IF(NREACT.EQ.1) CALL SLDBL1(CNEU,AA,AS,
 120 PHIG(1),PHIP(1),BI(1),DTHETA,RADG,TIME,X,DIND(1))
 TIME=TIME+DTIME
 DO 130 I=1,NP1
 IF(R(I).LT.0.0) R(I)=0.0
 IF(X(I).LT.0.0) X(I)=0.0000
 IF(X(I).GE.1.) X(I)=1.
 A1=(AF1+(A11-AF1)*EXP(-(K1*TIME)))
 A2=(AF2+(A12-AF2)*EXP(-(K2*TIME)))
 AI(I)=A2+(A1-A2)*X(1.-X(I))*23.0

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      IF (AI(I).GT.A11) AI(I)=A11
      RONI(I)=RONI-(RONI-ROU2)X(I)
      RADG(I)=(3.0)/(AI(I)SRONI(I))
      RADG(I)=RADG(I)/ROU
      R(I)=RADG(I)X(1.-X(I))X(1./3.)
130  CONTINUE
      CALL SIRPS(X,XBAR)
      DO 550 I=1,NREACT
      ROUP=RONI-(RONI-ROU2)XBAR
      EPSP=1.0-(PARLI((1.-XBAR)XN1+XBARXN2))
1  / (R1XROUP+4.1555RADP+13.0)
      DEAP(I)=DG(I)XEPSP+13BETAS
      DIND(I)=DEAP(I)/DEAPO(I)
550  CONTINUE
      DO 160 II=1,NREACT
      DO 140 I=1,NP1
140  CTEMP(I)=C(II,I)
      CALL GASBLN(X,CTEMP,CHEU,AA,PHIG(II),PHIP(II),
1  BI(II),RADG,DIND(II))
      DO 150 I=1,NP1
150  C(II,I)=CHEU(I)
160  CONTINUE
      IF (XBAR.LT.XSTEP2) GO TO 170
      DTIME=2.XDTIME
      DO 7025 I=1,NP1
      DTHETA(I)=2.XDTHETA(I)
7025  CONTINUE
      XSTEP2=2.XXSTEP2
      ISTART=0
170  IF (XBAR.GE.XFINAL) GO TO 210
180  CONTINUE
      DX(K)=(TX(2,6)-TX(2,1))/(TX(1,6)-TX(1,1))
      LXBAR(K)=XBAR
      DO 9050 I=1,NP1
      LX(K,I)=X(I)
      LCHEU(K,I)=CHEU(I)
      LRADG(K,I)=RADG(I)
9050  CONTINUE
      LDIND(K)=DIND(I)
      IF (K.EQ.N) GOTO 210
      TIME=TIME+63DTIME
      IF (TIME.GE.0) GOTO 210
      TIME=0
210  TX(1,II)=TIME
      TX(1,II)=TIME
      TX(2,II)=XBAR
      IF (L.GT.N) GOTO 220
      A11=A11/10000
220  CONTINUE
      RETURN
      END

```

```

SUBROUTINE GASBLN(X,C,CNEU,AA,PHIG,PHIP,BI,RADG,DIND)
COMMON/A11/N,NP1,ISTART
COMMON/B11/RADP,R50,H,H2
DIMENSION C(20),CNEUC(20),D(20),U(20),RHS(20)
REAL L(20)
DIMENSION RADG(20),X(20)
DO 10 I=1,NP1
  IF(X(I).LT.0.0) X(I)=0.0
  IF(X(I).GE.1.) X(I)=1.
10  CNEU(I)=C(I)
  DO 20 I=2,NP1
    L(I)=FLOAT(I-2)/(FLOAT(I-1)*H2)
    U(I)=FLOAT(I)/(FLOAT(I-1)*H2)
    U(1)=2./H2
    L(NP1)=2./H2
    DO 40 I=1,NP1
      D(I)=(3.*AA*(1.-X(I))*X(2./3.)*PHIP/RADP/DIND)/(R50
1  XRADG(I)*X(1.-AA*PHIG/RADG(I))*X(1.-X(I))*X(1./3.)*X(1.-
1  (1.-X(I))*X(1./3.)))-2./H2
40  RHS(I)=0.
    RHS(NP1)=-2.*H2*D(I)/DIND
    D(NP1)=D(NP1)+RHS(NP1)
    CALL TRIDAG(1,NP1,L,D,U,RHS,CNEU)
    DO 50 I=1,NP1
50  IF(CNEU(I).LE.0) CNEU(I)=1.E-30
  RETURN
END

```

```

SUBROUTINE SLDBL1( C,AA,AS,PHIG,PHIP,
1 BI,DTMETHA ,RADG,TIME,X,DIND)
DIMENSION C(20),CTEMP(20),RADG(20),X(20),DTMETHA(20)
COMMON/111/N,NP1,ISTART
COMMON/112/RADP,R20,M,M2
COMMON/C11/K1,K2,K3,K4,VH1(20,20),VH2(20,20),VH3(20,20),F(20),FM1(20,20),FM2(20,20)
1 F(20,20)
COMMON/J11/L,MREACT,ITER,I,J,K,ICNT
REAL K1(20),K2(20),K3(20),K4(20,20)
FCT1(X1,X2,K3)=-(3.2ASDDB1(1.-X1)X2(2./3.))/
1 (X3(1.-ASPHIGXK3(1.-X1)X2(1./3.)X(1.-((1.-X1)X2(1./3.)
1 )))
DO 5 I=1,NP1
5 F(I)=FCT1(X(I),C(I),RADG(I))
IF(X(NP1).EQ.0.0) GO TO 7
IF(ISTART.GE.1) GO TO 20
7 DO 10 I=1,NP1
VH3(K,I)=0.
VH2(K,I)=0.
VH1(K,I)=0.
FV2(K,I)=0.
FM1(K,I)=0.
10 CONTINUE
IF(X(NP1).EQ.0.0) GO TO 25
IF(ISTART.GE.3) GO TO 100
20 DO 30 I=1,NP1
K1(I)=F(I)
30 DO 40 I=1,NP1
K2(I)=X(I)+.5XDTMETHA(K)XK1(I)
40 CALL GASBLN(K2,C,CTEMP,AA,PHIG,PHIP,BI,RADG,DIND)
DO 50 I=1,NP1
K2(I)=FCT1(K2(I),CTEMP(I),RADG(I))
50 DO 60 I=1,NP1
K3(I)=X(I)+.5XDTMETHA(K)XK2(I)
60 CALL GASBLN(K3,C,CTEMP,AA,PHIG,PHIP,BI,RADG,DIND)
DO 70 I=1,NP1
K3(I)=FCT1(K3(I),CTEMP(I),RADG(I))
70 DO 80 I=1,NP1
K4(K,I)=X(I)+DTMETHA(K)XK3(I)
80 CALL GASBLN(K4,C,CTEMP,AA,PHIG,PHIP,BI,RADG,DIND)
DO 90 I=1,NP1
K4(K,I)=FCT1(K4(K,I),CTEMP(I),RADG(I))
VH3(K,I)=VH2(K,I)
VH2(K,I)=VH1(K,I)
VH1(K,I)=X(I)
X(I)=X(I)+0.16666666XDTMETHA(K)X(K1(I)+2.XK2(I)+2.XK3(I)
1 +K4(K,I))
IF(X(I).GE.1.) X(I)=1.
FV2(K,I)=FM1(K,I)
FM1(K,I)=F(I)
90 ISTART=ISTART+1
RETURN
100 DO 110 I=1,NP1
K1(I)=VH3(K,I)+1.3333333XDTMETHA(K)X(2.XF(I)-FM1(K,I)+2.XFM2(K,I))
110 IF(ISTART.GT.3) GO TO 130
DO 120 I=1,NP1
K4(K,I)=0.
120 DO 140 I=1,NP1
K2(I)=K1(I)+0.92561983XK4(K,I)
140 CALL GASBLN(K2,C,CTEMP,AA,PHIG,PHIP,BI,RADG,DIND)
DO 150 I=1,NP1
K3(I)=6.125X(9.XX(I)-VH2(K,I)+3.XDTMETHA(K)X(FCT1(K2(I),CTEMP(I),
1 RADG(I))+2.XF(I)-FM1(K,I)))

```

```

K4(K,I)=K3(I)-K1(I)
VH3(K,I)=VH2(K,I)
VH2(K,I)=VH1(K,I)
VH1(K,I)=X(I)
X(I)=K3(I)-7.438016E-02XK4(K,I)
IF(X(I).GE.1.) X(I)=1.
IF(ISTART.GE.1) FM1(K,I)=F(I)
FM1(K,I)=F(I)
ISTART=ISTART+1
RETURN
END

```

```

SUBROUTINE TRIDAG(IF,L,A,B,C,D,U )
DIMENSION A(20),B(20),C(20),D(20),U(20),BETA(20),GAMMA(20)
COMMON/E11/TEMP,BETA,GAMMA,KBAR
BETA(IF)=B(IF)
GAMMA(IF)=D(IF)/BETA(IF)
IFP1=IF+1
DO 1 I=IFP1,L
  BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
  GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
  U(L)=GAMMA(L)
  LAST=L-IF
DO 2 K=1,LAST
  I=L-K
  U(I)=GAMMA(I)-C(I)*U(I+1)/BETA(I)
  RETURN
END
)

```



```

SUBROUTINE SIMPS(X,XBAR)
COMMON/ALL/N,NP1,ISTART
COMMON/BI1/RASP,R50,M,H2
DIMENSION F(20),X(20)
NCHECK=(NP1/2)22
IF(NCHECK.EQ.NP1) GO TO 30
NP1=N-1
DO 10 I=1,NP1
  F(I)=K(I)X(((FLOAT(I)-1.)2H)222)
  XBAR=F(1)+4.2F(2)+F(NP1)
DO 20 I=3,NP1,2
  XBAR=XBAR+2.2F(I)+4.2F(I+1)
  XBAR=H2XBAR
RETURN
30 WRITE(12,40)
40 FORMAT(///5X,'SIMPSONS RULE REQUIRES AN EVEN NUMBER OF INTERVALS')
STOP
END

```

VII. NOMENCLATURE

a_A	=	Stoichiometric coefficient for gas A
a_S	=	Stoichiometric coefficient for solid S
A_1	=	Surface area of ZnO
A_2	=	Surface area of ZnS
A_T	=	Total surface area of mixture ZnO and ZnS
C_A	=	Molar concentration of gas A
C'_{AC}	=	Molar concentration of gaseous reactant A at unreacted core surface
C_S	=	Molar concentration of solid reactant S
C'_{SO}	=	Initial bulk concentration of solid reactant
CSO	=	Molar concentration of solid ZnO in pellet
D	=	Dimensionless effective diffusivity within the pellet
D_{eA}	=	Effective diffusivity of gaseous reactant
E_A	=	Activation energy for reaction within the grain
E_D	=	Activation energy for diffusion within the grain
E_1	=	Activation energy for sintering of ZnO
E_2	=	Activation energy for sintering of ZnS
K'_S	=	Reaction rate constant based on the surface area of unreacted core
k_{ma}	=	Mass transfer coefficient
k_o	=	Frequency factor in rate of reaction
k_1	=	Sintering rate constant for ZnO
k_2	=	Sintering rate constant for ZnS
k_{10}	=	Sintering rate coefficient for ZnO
k_{20}	=	Sintering rate coefficient for ZnS
M_{s1}	=	Molecular weight ZnO
M_{s2}	=	Molecular weight ZnS

NOMENCLATURE
(Continued)

$\bar{R}_A$	=	Intrinsic reaction rate per unit volume
R_G	=	Global reaction rate
R_A	=	Intrinsic reaction rate per unit surface area
r'_{Go}	=	Initial grain radius
r	=	Radial coordinate in particle
r_{GD}	=	Dimensionless grain radius
r_p	=	Particle radius
r'_G	=	Grain radius
r'_c	=	Grain unreacted core radius
R	=	Gas constant (cal/g mole $^{\circ}K$)
T	=	Temperature ($^{\circ}K$)
t	=	Time
u	=	Superficial velocity in direction of flow
V	=	Volume of pellet
W_0	=	Initial pellet weight
X	=	Local extent of reaction
$\bar{X}$	=	Overall extent of reaction
Z	=	Length of reactor

NOMENCLATURE

(Continued)

Greek Letters

α	=	Effective diffusivity parameter, a positive constant with a value between 2.0 and 3.0
β	=	Biot number for mass transfer
ϵ	=	Pellet porosity
ϵ_B	=	Void fraction in packed bed
ζ	=	Dimensionless radial coordinate for pellet
θ_G	=	Dimensionless time
λ	=	A finite difference parameter
π	=	3.141592
ρ	=	Grain density
ρ_1	=	True density of solid reactant
ρ_2	=	True density of solid product
ρ_s	=	Solid density
ρ_p	=	Pellet density
σ_{G1G2}	=	Constant in Lennard-Jones potential energy functions
ϕ_G	=	Thiele modulus for pellet
ϕ'_G	=	Thiele modulus for grain
Ω_{G1G2}	=	Constant in Lennard-Jones potential energy function

VIII. User's Guide for Packed Bed Model

The data file for Packed is called PBED.DAT. A sample PBED.DAT file is shown below.

```

TY PBED.DAT
2000 80 2000 680 .42
1 .01 .1725 21.78 2.0
150000. -1 -1
10 10 9
959 .0001
.0403 81.37 97.43
.417 7183 .390 6027
17 89E4 5.75 0. 4.102 40
$

```

The parameters listed are described below in order of their appearance.

2000	CB	Gas Bulk Concentration (ppm)
80	M	Number of intervals for finite difference calculation
2000	CMAx	Maximum desired exit concentration ppm
680	μ	Superficial velocity, cm/min
0.42	ϵ_B	Void bed fraction (dimensionless)
1	NREACT	Number of reactive gas species
.01	EPSG	Grain porosity -- determines grain effective diffusivity
.1725	RADP	particle radius -- (cm)
21.78	CSO	Bulk solid concentration, mg mole/cc
2.0	BETAS (α)	Constant used in the determination of effective diffusivity -- usually 2.0
150,000	KMA	Mass transfer constant (cm/sec)
-1	AA	Stoichiometric coefficient -- gas phase
-1	AS	Stoichiometric coefficient -- solid phase
10	N	Number of intervals the solid radius will be divided into for integration
10	ITER	Maximum number of time steps
.9	Xfinal	Desired final conversion
959	Temp	Temperature ($^{\circ}\text{K}$)
.0001	DTAU	Time Step -- (min)

.0403	PARW	Particle weight, initial (gm)
81.37	M1	Molecular weight of solid reactant
97.43	M2	Molecular weight of solid product
.417	K ₁₀	Frequency factor for sintering rate constant of reactant solid S ₁ (ZnO)
7183	E _{S1}	Activation energy of sintering of reactant solid S ₁ (ZnO)
.390	K ₂₀	Frequency factor for sintering rate constant of product solid S ₂ (ZnS)
6027	E _{S2}	Activation energy of sintering rate constant product solid S ₂ (ZnS)
17.89E4	AI1	Initial area of reactant S ₁ (ZnO)
5.75	Row1	Density of pure solid S ₁ (gm/cc)
0	AI2	Initial area of product S ₂
4.102	Row2	Density of pure solid S ₂ (gm/cc)
40	LEN	Reactor length (cm)

After PBED.DAT is adjusted to the desired parameters type
 ASSIGN PBED.DAT for 009
 RUN PACKED

An option is provided for automatic hardcopying of the graphical output. When prompted type in the desired answer.

At the start of execution the main parameters will be printed and copied if automatic copying was chosen. When the run is completed three graphs are displayed labelled Fig. 1, Fig. 2, Fig. 3 showing H₂S concentration profile, breakthrough curve, and solid conversion profile, respectively. In addition, the same output is typed out in table form into a file called GRG.DAT. to access this file type TY GRG.DAT. A sample output is attached.

TABLE 8

REACTION IN A PACKED BED OF ZNO WITH THE PARAMETERS

RADP = 0.1725

CSO = 21.7880

KMA = 150000.

ITER = 10

CB = 2000.0

PARU = 0.0403

TEMP = 810.00

DTAU = .0001000

M = 10.

CMAK = 2000.0

LEN = 5.00

U = 386.60

EB = 0.4200

REACTOR LENGTH - DIMENSIONLESS
FIGURE 1 - H₂S CONCENTRATION PROFILE

(Section VIII.)

FIGURE 2 - BREAKTHROUGH CURVE
(Section VIII.)

REACTOR LENGTH - DIMENSIONLESS
FIGURE 3 - ZNO CONVERSION PROFILE

(Section VIII.)

TABLE 9

REACTION IN A PACKED BED OF ZNO WITH THE PARAMETERS

RADP = 0.1725

CSO = 21.7800

KMA = 150000.

ITER = 10

CB = 2000.0

PARU = 0.0403

TEMP = 810.00

STAU = .0001000

M = 10.

CMAX = 2000.0

LEN = 5.00

U = 386.60

EB = 0.4200

TIME

VALUES OF GAS CONCENTRATION AT ALL GRID POINTS

0.00000

2000.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.00010									

2000.0000	368.1905	67.7821	12.4784	2.2972	0.4229	0.0779	0.0143	0.0026	0.0005
0.00020									

2000.0000	584.2878	147.3471	34.4497	7.6903	1.6640	0.3520	0.0732	0.0150	0.0031
0.00030									

2000.0000	699.7195	212.2897	58.5903	15.1346	3.7271	0.8851	0.2043	0.0461	0.0102
0.00040									

2000.0000	765.9705	261.5385	81.3744	23.5595	6.4482	1.6882	0.4264	0.1046	0.0250
0.00050									

2000.0000	803.9467	296.6508	100.8220	31.9299	9.5352	2.7124	0.7410	0.1957	0.0502
0.00060									

2000.0000	825.7160	320.7230	116.3447	39.5538	12.6044	3.8750	1.1338	0.3196	0.0873
0.00070									

2000.0000	838.1979	336.7836	128.1590	46.0733	15.6028	5.0896	1.5804	0.4723	0.1384
0.00080									

2000.0000	845.3542	347.8271	136.8382	51.3886	18.3793	6.2740	2.0528	0.6460	0.1984
-----------	----------	----------	----------	---------	---------	--------	--------	--------	--------

0.00000

2000.0000 849.4597 354.0519 143.0414 55.5630 20.6789 7.3733 2.5236 0.8315 0.2645
0.00100

2000.0000 851.8151 358.3570 147.3785 58.7440 22.5758 8.3482 2.9712 1.0194 0.3379
ICOUNT GREATER THAN ITER
XBAR 0.00002470 0.00000833 0.00000304 0.00000108 0.00000037 0.00000013 0.00000004 0.00000001 0.00000000 0.00000000

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