

**Paper Number:**

DOE/MC/31206-97/C0747

**Title:**

Reactivity of Metal Oxide Sorbents for Removal of H<sub>2</sub>S

**Authors:**

K.C. Kwon

E.R. Crowe

**Contractor:**

Tuskegee University

Chemical Engineering Department

School of Engineering and Architecture

Tuskegee, AL 36088

**Contract Number:**

DE-FG21-94MC31206

**Conference:**

Advanced Coal-Fired Power Systems '96 Review Meeting

**Conference Location:**

Morgantown, West Virginia

**Conference Dates:**

July 16-18, 1996

**Conference Sponsor:**

U.S. DOE, Morgantown Energy Technology Center

## **Disclaimer**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

# Reactivity of Metal Oxide Sorbents for Removal of H<sub>2</sub>S

Kyung C. Kwon (kwonk@acd.tusk.edu; (334)-727-8976)  
Edward R. Crowe (ecrowe@acd.tusk.edu; (334)-727-8975)  
Chemical Engineering Department, School of Engineering and Architecture,  
Tuskegee University, Tuskegee, Alabama 36088

Research sponsored by the U.S. Department of Energy's Morgantown Energy Technology Center, under Contract DE-FG21-94MC31206 with Tuskegee University, Tuskegee, AL 36088; telephone: (334) 727-8976/(334) 724-4528; fax: (334) 727-8976/ (334) 724-4188

## *Introduction*

Removal of hydrogen sulfide contained in hot coal gases produced from integrated gasification combined cycle power generation systems is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compounds from hot coal gas products is investigated by using various metal oxide sorbents and membrane separation methods. The main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles. In this research, durable metal oxide sorbents were formulated. Reactivity of the formulated metal oxide sorbents with simulated coal gas mixtures was examined to search for an ideal sorbent formulation with a high-sulfur-loading capacity suitable for removal of hydrogen sulfide from coal gases.

## *Objectives*

The main objectives of this research are to formulate durable metal oxide sorbents with high-sulfur-loading capacity by a physical mixing method, to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperature and pressure, to study reaction kinetics on the regeneration of sulfided sorbents, to identify effects of hydrogen partial pressures and moisture on equilibrium/dynamic absorption of hydrogen sulfide into formulated metal oxide sorbents as well as initial reaction rates of H<sub>2</sub>S with formulated metal oxide sorbents, and to evaluate intraparticulate diffusivity of H<sub>2</sub>S into formulated sorbents at various reaction conditions.

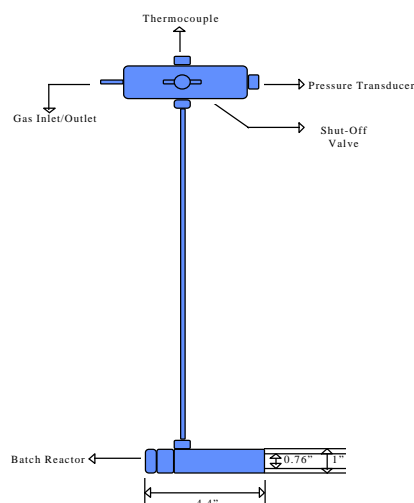
## *Experimental Approach*

Fresh metal oxide sorbent particles with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a 35 cm<sup>3</sup> 316 stainless steel batch reactor (see FIGURE 1). The batch reactor, loaded with a fresh sorbent and a simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the chosen heterogeneous reaction system at a desired reaction temperature<sup>1</sup>. Fine metal oxide sorbents are used to minimize effects of

intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles for the evaluation of initial reaction rates of H<sub>2</sub>S with formulated metal oxide sorbents. The batch reactor, loaded with a mixture of the fresh sorbent and the simulated coal gas mixture, is shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to the sorbent particles. The sulfidation reaction is terminated at a desired reaction duration. Conversions of the sorbent are analyzed with a gas chromatograph.

The metal oxide sorbents such as TU-1, TU-19, TU-24, TU-25 and TU-28 were formulated with zinc oxide powder as an active sorbent ingredient, bentonite as a binding material and titanium oxide as a supporting metal oxide. This pasty mixture was extruded 1-mm cylindrical rods. The viscosity of the pasty mixture appeared to be sensitive to the amount of water as well as the amount of bentonite added to the powder mixture at room temperature. Homogeneous mixing of these pasty slurry mixtures seemed to be very important in producing duplicate formulations of sorbents. The formulated metal oxide sorbents were calcined for 2 hours at 800 - 900 °C. The ingredients and some physical properties of the formulated sorbents were presented in TABLE 1.

FIGURE1. Batch Reactor Assembly



The fresh formulated metal oxide sorbents in the form of 1-mm cylindrical rod were crushed to obtain 100- 200 mesh particles and minus 200-mesh particles to evaluate initial intrinsic sulfidation kinetics as well as dynamic absorption of H<sub>2</sub>S into sorbents. Metal oxide sorbents with 100-200 mesh particles were reacted with simulated coal gases containing hydrogen sulfide in the 35 cm<sup>3</sup> 316 stainless steel batch reactor for 30-150 seconds at 500°C (see Table 2).

The formulated metal oxide sorbents in the form of 1-mm cylindrical rod were used in evaluating intraparticle diffusivity of H<sub>2</sub>S into the metal oxide matrices. Concentrations of hydrogen sulfide were analyzed with a gas chromatograph at various reaction durations to evaluate reaction rates of H<sub>2</sub>S as well as equilibrium/dynamic absorption of H<sub>2</sub>S into the sorbents.

TABLE 1. Formulation of metal oxide sorbents.

	TU-1	TU-19	TU-24	TU-25	TU-28
ZnO, g	1	1	1.8	0.5	1
TiO <sub>2</sub> , g	2	2	1.2	2.5	2
Bentonite, g	0.1	0.15	0.15	0.15	0.1
Calcination Temperature, °C	850	800	800	830	830
Calcination Duration, min	120	100	100	100	100
Density of Sorbent, g/cm <sup>3</sup>	1.73	1.73	1.73		
Specific Pore Volume, cm <sup>3</sup> /g	0.36	0.36	0.36		

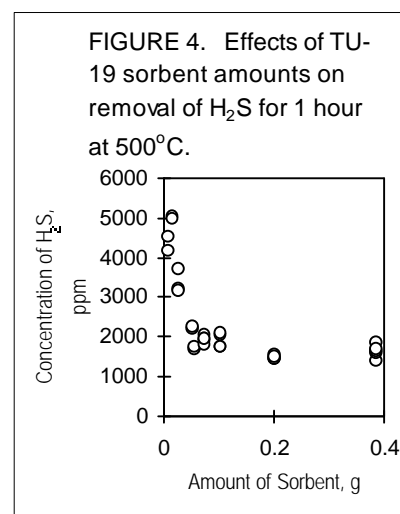
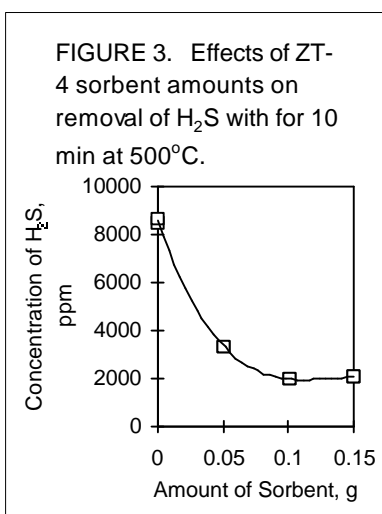
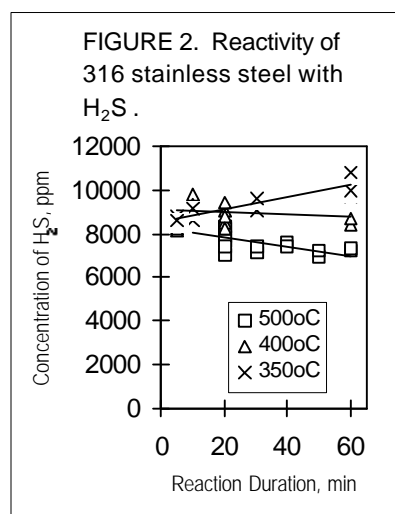
TABLE 2. Experimental conditions for the reaction of H<sub>2</sub>S with sorbents.

Reactor Volume, cm <sup>3</sup>	35
Temperature, °C	350 - 550
Reaction Time, min	0.5 - 60
Particle Size	100 - 200 mesh, <200 mesh, 200 μm, 1 mm cylindrical rod
Amount of Sorbent, g	0.015 - 0.4
Initial Partial Pressure of Hydrogen at 25 °C, psia	14.7 -24.7
Initial Amount of Water, g	0.085 - 0.120
Initial Concentration of H <sub>2</sub> S, ppm	8000 - 8700
Initial Partial Pressure of Nitrogen at 25 °C, psia	140 -150
Initial Total Pressure of Reaction Mixture at 25°C, psia	164.7

## Results

Experimental data of H<sub>2</sub>S concentrations at various reaction durations were obtained by reacting H<sub>2</sub>S with the sorbents formulated at our laboratory as well as the ZT-4 sorbent formulated at the Research Triangle Institute. Several blank experimental runs were made to evaluate absorption of H<sub>2</sub>S into the 316 stainless steel reactor wall at various temperatures. These experimental data were used in evaluating equilibrium/dynamic absorption of H<sub>2</sub>S into metal oxide sorbents as well as reaction rates of H<sub>2</sub>S with metal oxide sorbents. Experiments on reactivity of hydrogen sulfide contained in a simulated coal gas mixture with the 316 SS batch reactor wall were performed at various reaction temperatures to evaluate effects of reaction temperatures on its reactivity with the wall. The simulated coal gas mixture consists of 9107-ppm hydrogen sulfide (0.005 g; 1 w%), 0.085-g water (15.84 -17.08 w%), 0.0029-g hydrogen (0.58 w%), and 0.4046-g nitrogen (81.34 w%). Absorption of hydrogen sulfide on the reactor wall increases with absorption temperatures. Absorption of H<sub>2</sub>S into the 316 SS wall increases with absorption durations above 400°C. However, absorption of H<sub>2</sub>S into the 316 SS wall does not take place at 350°C and previously-absorbed H<sub>2</sub>S appears to be released from the 316 SS wall at 350°C<sup>2,3</sup> (see FIGURE 2).

A series of experiments on effects of ZT-4 sorbent quantities on removal of H<sub>2</sub>S were carried out in the presence of initial 8700-ppm H<sub>2</sub>S and 0.085-g moisture for 10 min at 500°C (see FIGURE 3). Removal of H<sub>2</sub>S increases with amounts of the sorbent, but appears to level off above 0.1-g sorbent. These data may suggest that equilibrium concentration of H<sub>2</sub>S in the reaction with the sorbent is reachable within 10-min reaction duration. A series of experiments were carried out in the presence of initial 8700-ppm H<sub>2</sub>S and 0.085-g moisture for 60 min at 500°C to investigate effects of varying the amount of TU-19 sorbent in the form of 1-mm cylindrical rod on the removal of H<sub>2</sub>S (see FIGURE 4). The removal of H<sub>2</sub>S

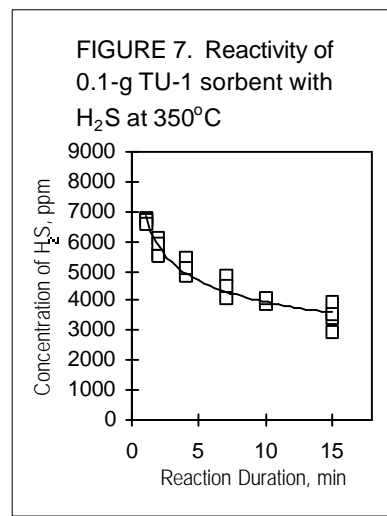
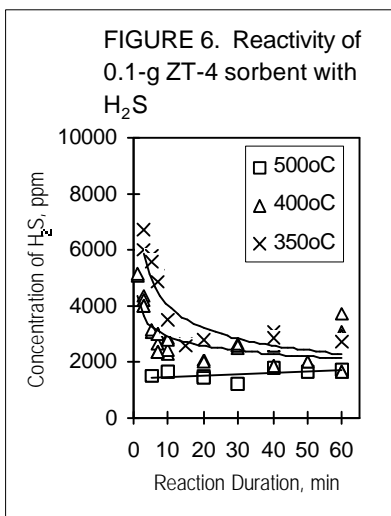
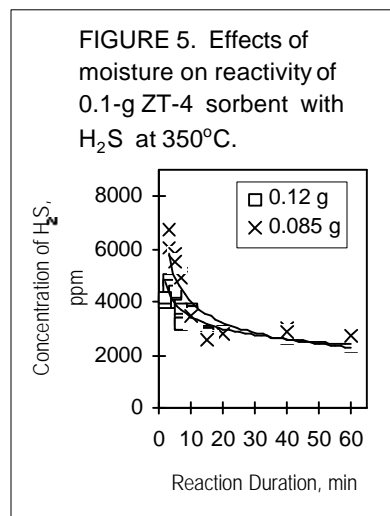


increases with amounts of the sorbent, but appears to level off above 0.05-g sorbent. These observations may suggest that equilibrium concentrations of H<sub>2</sub>S are independent of sorbent quantities above 0.05-g sorbent.

Effects of moisture on reactivity of 200- $\mu\text{m}$  ZT-4 sorbent with initial 9107-ppm  $\text{H}_2\text{S}$  were investigated at 350°C (see FIGURE 5). Increased moisture increases removal of  $\text{H}_2\text{S}$  below equilibrium absorption. This observation may suggest that dynamic absorption of  $\text{H}_2\text{S}$  into the sorbent is dependent on moisture quantities at 350°C. Equilibrium absorption of  $\text{H}_2\text{S}$  appears to be independent of moisture amounts. This fact may indicate that moisture does not affect equilibrium absorption of  $\text{H}_2\text{S}$  into the sorbent at 350°C.

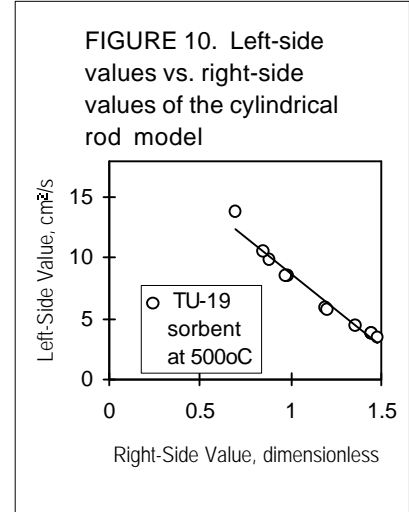
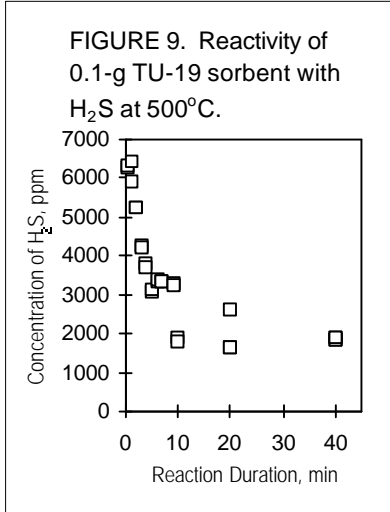
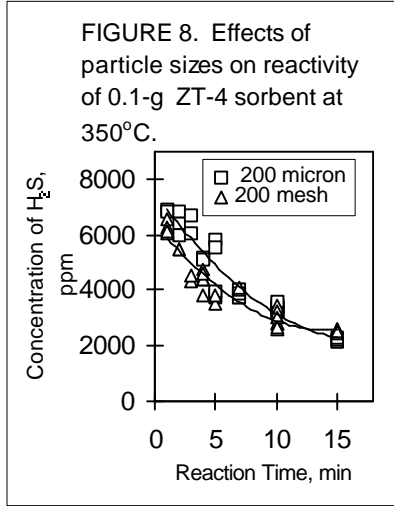
Reactivity of 200- $\mu\text{m}$  ZT-4 sorbent with initial 9107-ppm  $\text{H}_2\text{S}$  was examined in the presence of 0.085-g moisture at various reaction temperatures (FIGURE 6). Reactivity of the sorbent with  $\text{H}_2\text{S}$  increases with reaction temperatures. Equilibrium removal of  $\text{H}_2\text{S}$  increases with reaction temperature and requires longer reaction durations with lower reaction temperatures. Absorption of  $\text{H}_2\text{S}$  into the sorbent increases with absorption durations below equilibrium absorption.

Reactivity of TU-1 sorbent in the form of 1-mm cylindrical-rod with initial 9107-ppm  $\text{H}_2\text{S}$ , the first sorbent formulated at our laboratory, was examined in the presence of 0.085-g moisture at 350°C (see FIGURE 7). Absorption of  $\text{H}_2\text{S}$  into the sorbent also increases with absorption durations below equilibrium absorption, as observed from the experimental data of the ZT-4 sorbent.



Effects of particle sizes of the ZT-4 sorbent on the removal of  $\text{H}_2\text{S}$  were examined in the presence of initial 9107-ppm  $\text{H}_2\text{S}$  and 0.085-g moisture at 350°C as shown in FIGURE 8. The minus-127- $\mu\text{m}$  (micron) ZT-4 sorbent removes more  $\text{H}_2\text{S}$  than the 200- $\mu\text{m}$  (micron) sorbent below equilibrium absorption. Equilibrium absorption of  $\text{H}_2\text{S}$  is not affected by particle sizes. These observations may suggest that the intraparticle mass transfer of  $\text{H}_2\text{S}$  into pores of the sorbent is a limiting step for absorption of  $\text{H}_2\text{S}$  into the sorbent at 350°C. These experimental data may indicate that reaction rates of  $\text{H}_2\text{S}$  with the sorbent increases with decreased particle sizes.

Reactivity of TU-19 sorbent in the form of 0.1-g 1-mm cylindrical rod was investigated in the presence of the initial concentration 8700-ppm H<sub>2</sub>S and 0.085-g moisture at 500°C and various reaction durations (see FIGURE 9). These experimental data showed that most absorption of H<sub>2</sub>S into the sorbent occurs during the first 5-min reaction duration. These experimental data were utilized in evaluating intraparticle diffusivity of H<sub>2</sub>S through the TU-19 sorbent matrix, using a developed cylindrical rod model.



Intraparticle diffusivity of H<sub>2</sub>S through the TU-19 sorbent in the form of 1-mm cylindrical rods was evaluated at 500°C, using the following cylindrical rod model. The model<sup>4,5</sup> was developed with the unreacted core assumption and the quasi steady state assumption. Left-side values of Equation (1) were plotted against the right-side values (see FIGURE 10). Intraparticle diffusivity was determined from the slope of this plot. The intraparticle diffusivity of H<sub>2</sub>S into the TU-19 sorbent was found to be 2.018x10<sup>-3</sup> cm<sup>2</sup>/s at 500°C.

$$\ln\left(\frac{r}{R}\right)r \frac{dr}{dt} = D_e \left(\frac{B}{b}\right)(1 + Ar^2) + \text{constant} \quad (1)$$

$$r = \left(R^2 - \left(\frac{C_{A0} - C_A}{b\rho L r_B}\right)V\right)^{0.5} \quad (2)$$

$$B = \frac{C_{A0}}{r_B} - \frac{bV_B}{V} \quad (3)$$

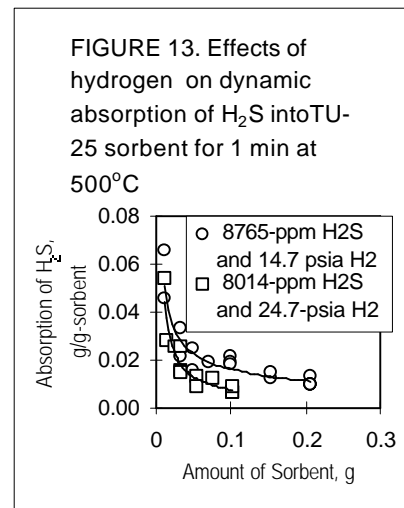
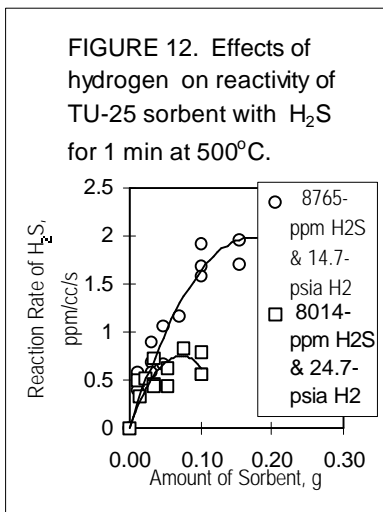
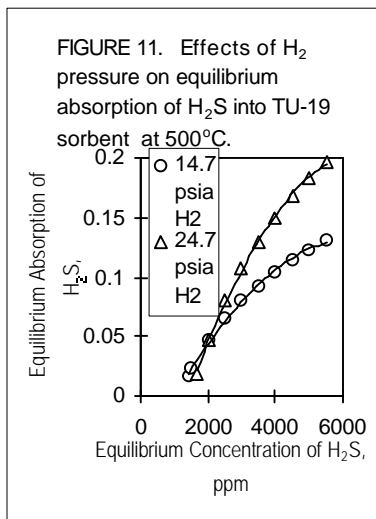
$$A = \frac{b\rho L}{BV} \quad (4)$$

where

- r: radius of an unreacted core
- R: radius of a cylindrical-rod sorbent
- t: reaction time
- V<sub>B</sub>: volume of a cylindrical-rod sorbent
- L: Length of a cylindrical-rod sorbent
- ρ<sub>B</sub>: density of a cylindrical-rod sorbent
- D<sub>e</sub>: intraparticle diffusivity

V: reactor volume  
 b: equilibrium absorption  
 $C_{AO}$ : initial concentration of  $H_2S$   
 $C_A$ : concentration of  $H_2S$

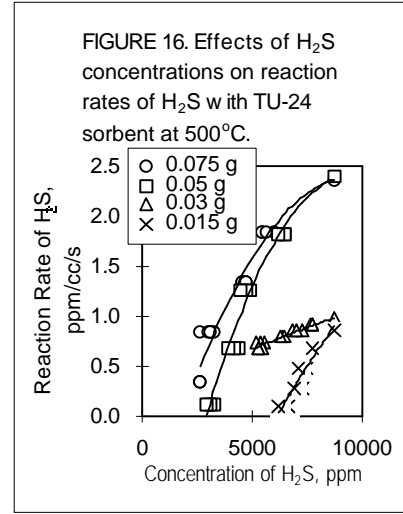
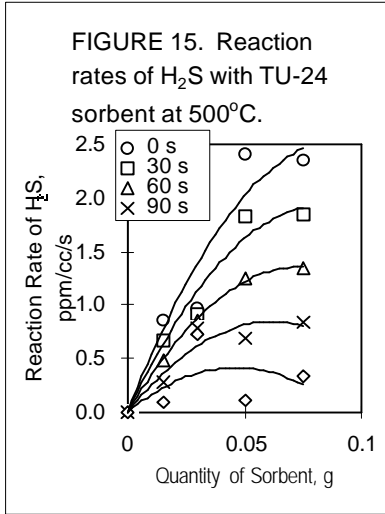
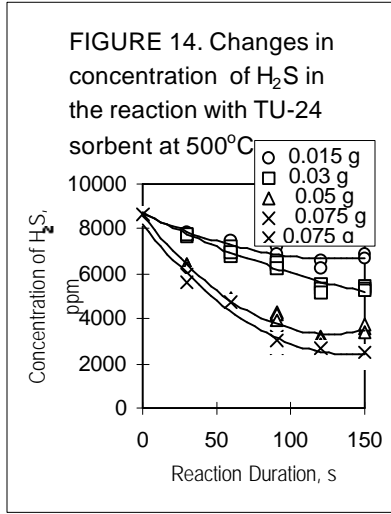
Equilibrium absorption of the TU-19 sorbent in the presence of the initial 24.7-psia  $H_2$  is compared with that in the presence of the initial 14.7-psia  $H_2$ . Equilibrium absorption of the TU-19 sorbent in the presence of the initial 24.7-psia  $H_2$  is higher than that in the presence of the initial 14.7-psia  $H_2$  (see FIGURE 11). This observation may indicate that partial pressure of hydrogen appears to affect significantly equilibrium absorption of  $H_2S$  into the sorbent. Effects of hydrogen partial pressures on reactivity of the 100-200 mesh TU-25 sorbent as well as dynamic absorption of  $H_2S$  into the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at 500°C, as shown in FIGURE 12. Reactivity of  $H_2S$  with the TU-25 sorbent in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen, and reaction rates of  $H_2S$  with the sorbent increases with quantities of the sorbent (see FIGURE 12). Dynamic absorption of  $H_2S$  into the TU-25 sorbent in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen, and dynamic absorption of  $H_2S$  into the TU-25 sorbent decreases with increased quantities of the sorbent (see FIGURE 13).



The TU-24 sorbent was reacted with the 8700-ppm initial concentration  $H_2S$  in the presence of initial 14.7-psia  $H_2$  and 0.085-g moisture for 30 -150 seconds at 500°C, as shown in FIGURE 14. Concentrations of  $H_2S$  decrease with increased reaction durations as well as increased amounts of the sorbent. These experimental data of  $H_2S$  concentrations at various reaction durations were used in evaluating reaction rates of  $H_2S$  with the TU-24 sorbent as well as dynamic absorption of  $H_2S$  into the sorbent at 500°C. FIGURE 15 shows that reaction rates of  $H_2S$  with the TU-24 sorbent increase with increased quantities of the sorbent and decreased reaction durations. FIGURE 16 shows that reaction rates of  $H_2S$  with the TU-24 sorbent increase with increased quantities of the sorbent as well as increased concentrations of  $H_2S$ . Dynamic absorption of  $H_2S$  into the TU-24 sorbent at 500°C increases with increased reaction durations and decreased quantities of the sorbent, as shown in FIGURE 17. FIGURE



18 shows that reaction rates of H<sub>2</sub>S with the TU-24 sorbent decrease drastically with reaction durations for the short reaction duration of 30 - 150 seconds.



The following reaction rate equation may be proposed, since reaction rates of H<sub>2</sub>S with TU-24 sorbent are dependent on concentrations of H<sub>2</sub>S and quantities of the sorbent, as shown in Figures 15 and 16.

$$-r_A = k_A C_A^\alpha M_S^\beta \quad (5)$$

- where
- r<sub>A</sub>: reaction rates of H<sub>2</sub>S, g-mole/cm<sup>3</sup>/s
  - C<sub>A</sub>: concentrations of H<sub>2</sub>S, g-mole/cm<sup>3</sup>
  - M<sub>S</sub>: quantities of sorbents, g/cm<sup>3</sup>
  - k<sub>A</sub>: reaction rate constant in terms of disappearance of H<sub>2</sub>S, cc<sup>(α+β-1)</sup>/g<sup>β</sup>/g-mole<sup>(α-1)</sup>/s
  - α: reaction order with respect to concentrations of H<sub>2</sub>S
  - β: reaction order with respect to quantities of sorbents
  - cc: cm<sup>3</sup>

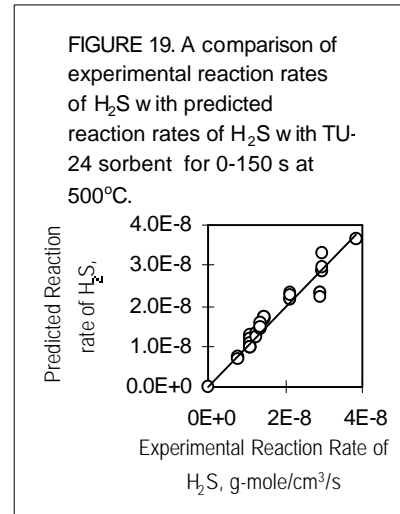
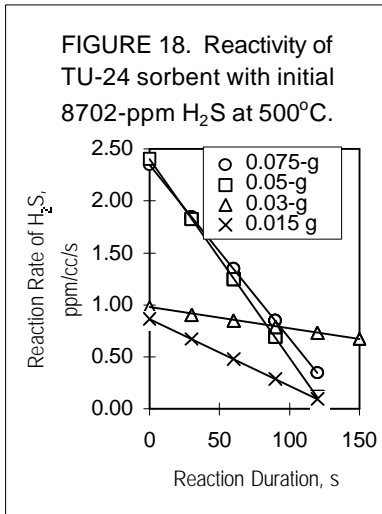
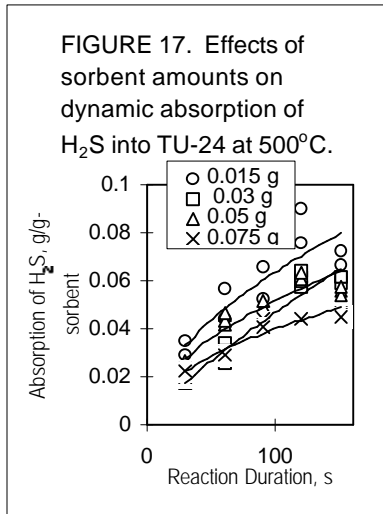
The equation (5) is linearized by applying a logarithm to the both sides of the proposed reaction rate equation<sup>4,5</sup>. The following linearized equation is obtained to evaluate k<sub>A</sub>, α and β.

$$\ln(-r_A) = \ln(k_A) + \alpha \ln(C_A) + \beta \ln(M_S) \quad (6)$$

The experimental data of H<sub>2</sub>S concentrations at various reaction durations (see FIGURE 14) are applied to equation (6), and then the reaction rate constant k<sub>A</sub> and the reaction orders such as α and β are obtained using the multiple linear regression method<sup>6</sup> as well as the Gauss-Seidel method<sup>7</sup>, as shown in equation 7.

$$-r_A = 9908 C_A^{1.5165} M_S^{1.1397} \quad (7)$$

The reaction rate constant  $k_A$  in terms of disappearance of  $H_2S$  was found to be  $9908 \text{ cm}^{4.9686}/\text{g}^{1.1397}/\text{g-mole}^{0.5165}/\text{s}$  at the reaction temperature  $500^\circ\text{C}$ . The reaction order  $\alpha$  with respect to concentrations of  $H_2S$  was found to be 1.5165, while the reaction order  $\beta$  with respect to quantities of the TU-24 sorbent was found to be 1.1397. Reaction rates of  $H_2S$  obtained from the experimental data points were compared with reaction rates of  $H_2S$  predicted from the developed reaction rate equation (see equation 7), as shown in FIGURE 19.



## ACCOMPLISHMENTS

The cylindrical rod model was developed to determine intraparticle diffusivity of hydrogen sulfide into metal oxide sorbents. The intraparticle diffusivity of  $H_2S$  into the TU-28 sorbent was found to be  $2.018 \times 10^{-3} \text{ cm}^2/\text{s}$  at  $500^\circ\text{C}$ . Dynamic absorption of  $H_2S$  into the 100-200 mesh TU-25 sorbent decreases with increased sorbent quantities and decreased reaction temperatures.

The reaction rate equation in terms of disappearance of  $H_2S$  with the TU-24 sorbent for short reaction durations of 30 -150 seconds at  $500^\circ\text{C}$  was developed with the experimental data in order to determine a reaction rate constant in terms of disappearance of  $H_2S$ , a reaction order with respect to concentrations of  $H_2S$ , and a reaction order with respect to quantities of the solid TU-24 sorbent. The reaction rate constant in terms of disappearance of  $H_2S$  was found to be  $9908 \text{ cm}^{4.9686}/\text{g}^{1.1397}/\text{g-mole}^{0.5165}/\text{s}$  at the reaction temperature  $500^\circ\text{C}$ . The reaction order with respect to concentrations of  $H_2S$  was found to be 1.5165, while the reaction order with respect to quantities of the TU-24 sorbent was found to be 1.1397.

Effects of hydrogen partial pressures on reactivity of the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at  $500^\circ\text{C}$ . Reactivity of the TU-25 sorbent with  $H_2S$  was found to be significantly affected by partial pressures of hydrogen. Equilibrium absorption as well as dynamic absorption of  $H_2S$  into metal oxide sorbents also was found to be significantly influenced by compositions of hydrogen

contained in simulated coal gas mixtures. Compositions of moisture contained in simulated coal gas mixtures were identified to affect equilibrium absorption of hydrogen sulfide into formulated metal oxide sorbents.

### *Application*

The developed reaction rate equation will be useful in designing a bench-scale or commercial reactor for removal of sulfur compounds from hot coal gas mixtures. Effects of hydrogen partial pressures and moisture on equilibrium absorption as well as dynamic absorption of H<sub>2</sub>S into formulated metal oxide sorbents should be incorporated into evaluating relative capacities and reactivities of metal oxide sorbents. Effects of moisture and hydrogen partial pressures on reaction kinetics should be considered in designing a fluidized-bed reactor or a transport reactor for removal of hydrogen sulfide from hot coal gas mixtures.

### *Future Activities*

A durable and reactive metal oxide sorbent with a high-sulfur-loading capacity will be formulated, and its reactivity, durability, and sulfur-loading capacity will be evaluated. A reaction rate equation in terms of disappearance of H<sub>2</sub>S at various reaction temperatures will be developed to evaluate effects of reaction temperatures on reaction rate constants in terms of disappearance of H<sub>2</sub>S. Effects of moisture as well as hydrogen partial pressures on reactivity of formulated sorbents will be delineated. Experiments on effects of hydrogen partial pressures and moisture on equilibrium absorption as well as dynamic absorption of H<sub>2</sub>S into formulated metal oxide sorbents will be conducted at various reaction conditions. Reaction kinetics on regeneration of sulfided metal oxide sorbents will be investigated at various regeneration conditions.

### *ACKNOWLEDGMENT*

Financial support for this work was provided by the U.S. Department of Energy's Morgantown Energy Technology Center, Grant DE-FG21-94MC31206. The authors appreciate guidance and comments on this paper given by Mrs. Susan K. Joines, METC Contracting Officer's Representative and Mr. Charles A. Komar. Valuable guidance, advice and comments on this research project were provided by Dr. Santosh K. Gangwal, Research Triangle Institute, the subcontractor of this research project.

### *References*

1. Kwon, N. Vahdat and W. Ayers, "Chemical Reaction Experiment for the Undergraduate Laboratory", *Chemical Engineering Education*, Vol. 21, No. 1, p. 30, 1987.
2. Kwon, E. R. Crowe, and S. K. Gangwal, "Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperature and Pressure, was accepted for publication in *Separation Science and Technology*.
3. Kwon, E. R. Crowe, and S. K. Gangwal, "Removal of Hydrogen Sulfide from Simulated Coal Gases, Using Metal Oxide Sorbents at High Temperature and High Pressure ", Pages 123 - 128, *The Proceedings for The Fourth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium*, Greensboro, North Carolina, April 2-4, 1996.
4. *Elements of Chemical Reaction Engineering*, H. Scott Fogler, 2nd Ed., Prentice-Hall, 1992
5. Octave Levenspiel, *Chemical Reaction Engineering*, 2nd Edition, John Wiley & Sons, 1972.
6. *Heat Transfer*, J. P. Holman, 7th Ed., McGraw-Hill, 1990.
7. *Schaum's Outline Series Statistics*, 2nd Edition, McGraw-Hill, New York.