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REACTIVITY OF FORMULATED METAL OXIDE SORBENTS WITH HOT HYDROGEN SULFIDE

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ABSTRACT

Three metal oxide sorbents, labeled TU-19, TU-24, and TU-25 were formulated with zinc oxide powder as an active sorbent ingredient, bentonite as a binding material, and titanium oxide as a supporting metal oxide. Equilibrium absorption of H₂S into sorbents increases with concentrations of H₂S. Reactivity of sorbents increases with increased reaction temperatures. Reaction rates of H₂S with the sorbent increase with increased amounts of sorbents.

A cylindrical rod model for a H₂S-metal-oxide-sorbent reaction system was developed with experimental reaction data obtained from a constant-volume batch reactor to compute intra-particle diffusivity of H₂S through sorbent matrix. An initial reaction rate equation was developed with initial experimental reaction data. Thermodynamic equilibrium constant for a heterogeneous H₂S-sorbent reaction keeps H₂S concentrations constant, in spite of increasing sorbent amounts in a constant-volume batch reactor.

Partial pressures of hydrogen appear to affect significantly equilibrium absorption of H₂S into the TU-19 sorbent at high equilibrium concentrations of H₂S, while partial pressures of hydrogen appear not to affect significantly equilibrium absorption of H₂S into the sorbent at low equilibrium concentrations of H₂S. However, reactivity of the TU-25 sorbent with H₂S in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen for the 1-min reaction duration.

INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. Coal minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur. Sulfur in coal is present as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occurring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products (1).

In gasification process, coal is reacted with steam and air or oxygen to produce a fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to reduce all forms of pollutants released from a coal conversion process through a lower fuel consumption (2).

Removal of hydrogen sulfide from hot coal gas produced in integrated gasification combined cycle power generation systems by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compound from coal gas products is investigated by using various metal oxide sorbents, and membrane separation methods. Current research results show that the removal of sulfur with metal oxide sorbents appears to be the most promising method compared to others. Main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles (3).



EXPERIMENTAL METHODS

Formulation of Metal Oxide Sorbents

Three metal oxide sorbents, labeled TU-19, TU-24, and TU-25 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 into 1-mm cylindrical rods. The ingredients and the calcination conditions of the sorbents are presented in TABLE 1. The viscosity of the pasty mixture appeared to be sensitive to amounts of water as well as amounts 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. Sorbents will be spallable because these pasty slurry mixtures, being not mixed homogeneously, result in non-uniform thermal stress to formulated sorbents at elevated temperatures. The formulated metal oxide sorbents were calcined for 100 min at 800 - 830°C (4).

ZT-4 sorbent with 200- μ m particles (5), formulated by the Research Triangle Institute, was utilized in comparing its reactivity with those of the sorbents formulated at Tuskegee University Laboratory.

The fresh formulated TU-19 metal oxide sorbent in the form of 1-mm cylindrical rod was used to conduct experiments on equilibrium absorption as well as dynamic absorption of hydrogen sulfide into the sorbents to study mainly effective diffusion of H₂S into the sorbents.

The fresh formulated TU-24 and TU-25 sorbents in the form of 1-mm cylindrical rod were crushed to obtain 100- 200 mesh particles, and were reacted with simulated coal gases containing hydrogen sulfide in a 316 stainless steel batch reactor for 30-150 seconds at 400 - 550°C to study initial surface reaction of H₂S with the 100 - 200 mesh sorbent particles.

Table 1. Formulation of the TU Sorbents

	TU-19	TU-24	TU-25
ZnO, g	1	1.8	0.5
TiO ₂ , g	2	1.2	2.5
Bentonite, g	0.15	0.15	0.15
Calcination Temperature, °C	800	800	830
Calcination Duration, min	100	100	100
Density of Sorbent, g/cm ³	1.73	1.73	1.72
Specific Pore Volume, cm ³ /g	0.36	0.36	0.35



Analysis of Hydrogen Sulfide

Concentrations of hydrogen sulfide were analyzed with a Buck Scientific gas chromatograph at various reaction durations to evaluate reaction rates of H₂S as well as absorption of H₂S into the sorbent. The gas chromatograph is equipped with a flame photometric detector

Batch Reactor Experiment

Fresh metal oxide sorbent particles and simulated coal gases containing hydrogen sulfide are introduced into a 35 cm³ batch reactor. The batch reactor, loaded with the fresh sorbent and the simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature (6).

Fine metal oxide sorbents will be used to reduce effects of intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles. The batch reactor, loaded with a mixture of fresh sorbent and simulated coal gas mixtures, is horizontally shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is terminated at the desired reaction time. Conversions of reactants were analyzed with a gas chromatograph. Typical experimental conditions were presented in TABLE 2.

Table 2. Operation Conditions for the Reaction of Hydrogen Sulfide with the Sorbents in the Presence of Water, Nitrogen and Hydrogen at Various Temperatures

Reactor Volume, cm ³ :	35
Temperature, °C:	350 - 550
Reaction Time, s:	30 - 9000
Particle Size:	200 µm or <200 mesh, 100-200 mesh, 1 mm cylindrical rod
Amount of Sorbent, g:	0.05 - 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 ₂ S, ppm:	8000 - 8700
Initial Partial Pressure of Nitrogen at 25°C, psia:	140 - 150
Initial Total Pressure of the Reaction Mixture at 25°C, psia:	164.7



DISCUSSION

Blank Experiments

A typical simulated coal gas mixture, containing hydrogen sulfide, consists of 9107-ppm hydrogen sulfide (0.005 g; 1 w%), 0.085-g water (15.84 w%), 0.0029-g hydrogen (0.58 w%), and 0.4046-g nitrogen (81.34 w%). Experiments on reactivity of hydrogen sulfide in the simulated coal gas mixture with the 316 SS batch reactor wall were carried out to differentiate absorption of H_2S into sorbents from that into the reactor wall (see FIGURE 1).

Absorption of hydrogen sulfide on the reactor wall increases with absorption temperatures. Absorption of H_2S into the 316 SS wall increases with absorption time above 400°C. Absorption of H_2S into the 316 SS wall does not take place, and previously-absorbed H_2S appears to be released from the 316 SS wall at 350°C. These experimental data on reactivity of hydrogen sulfide with the 316 SS batch reactor wall were used as blank experimental data in evaluating reactivity of the formulated metal oxide sorbents with hydrogen sulfide as well as absorption of hot hydrogen sulfide into the formulated sorbents.

ZT-4 Sorbent

Reactivity of ZT-4 sorbent with H_2S was examined at various reaction temperatures (see FIGURE 2). Reactivity of the sorbent with H_2S increases with re-

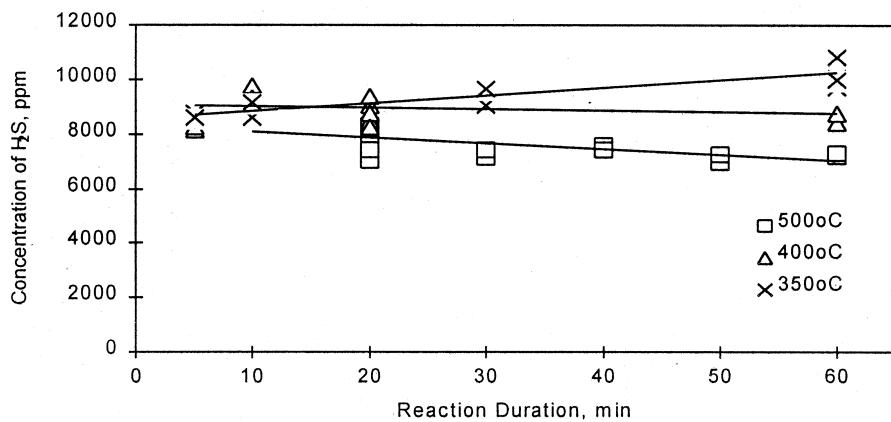


Figure 1. Reactivity of 316 stainless steel with the initial concentration 8700-ppm H_2S and 0.085-g moisture at various temperatures.



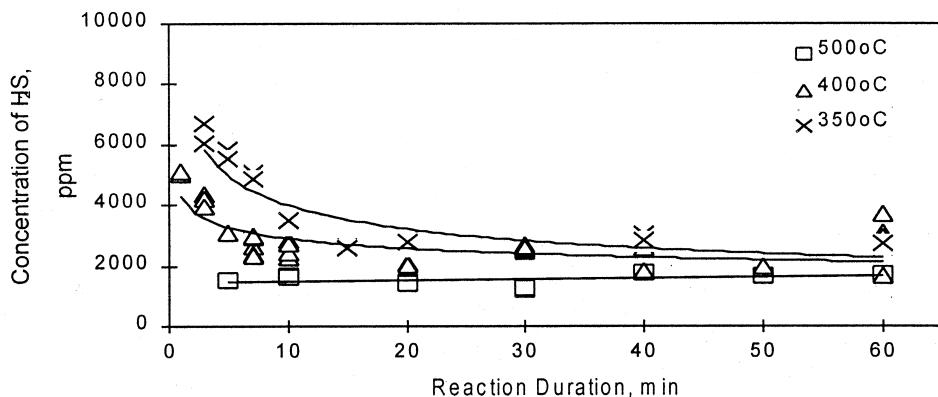


Figure 2. Reactivity of 0.1-g ZT-4 sorbent with 0.085-g moisture and the initial concentration 8700-ppm H_2S at various temperatures.

action temperatures. Equilibrium removal of H_2S increases with reaction temperatures, and requires longer reaction times with lower reaction temperatures.

Effects of particle sizes of ZT-4 sorbent on removal of H_2S were examined at 350°C, as shown in FIGURE 3. The minus-127 μm sorbent removes more H_2S than the 200- μm sorbent during the initial absorption duration (0 - 5 min). Effects of particle sizes on absorption of H_2S decrease as the absorption duration increases. This observation may suggest that absorption of H_2S into the sorbent is initially controlled by surface reaction at the outer surface of the sorbent particles,

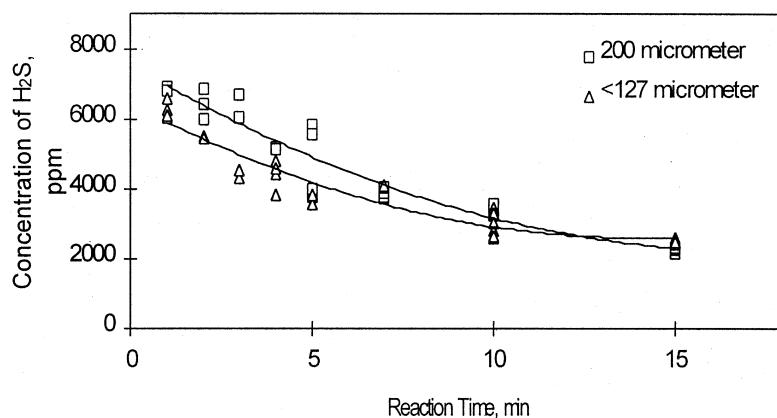


Figure 3. Effects of particle sizes on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 8700-ppm H_2 and 0.085-g moisture at 350°C.



whereas intraparticulate diffusion of H_2S into pores of the sorbent is a limited step in the absorption of H_2S into the sorbent for an extended absorption duration at 350°C. More likely it also suggest that there is a lot more reaction surface area with the finer particles, so the H_2S molecules contact the sorbent sooner.

Thermodynamic Equilibrium for a Heterogeneous Reaction System

A series of experiments on effects of varying the amount of 1-mm cylindrical rod TU-19 sorbent on the removal of H_2S were carried out for 60 min at 500°C (see FIGURE 4). Removal of H_2S increases with the amounts of the sorbent, but appears to level off above 0.05-g sorbent. The stoichiometric heterogeneous reaction formula for the absorption of H_2S into the sorbent is as follow:



The thermodynamic equilibrium constant K for the heterogeneous reaction system is described approximately in the following equation.

$$K \approx P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{S}} \quad (2)$$

where K : thermodynamic equilibrium constant for the heterogeneous reaction system

$P_{\text{H}_2\text{O}}$: partial pressure of moisture

$P_{\text{H}_2\text{S}}$: partial pressure of H_2S

Ratio of water partial pressure to H_2S partial pressure are evaluated with the raw data of Figure 4 and the stoichiometric heterogeneous reaction formula (see

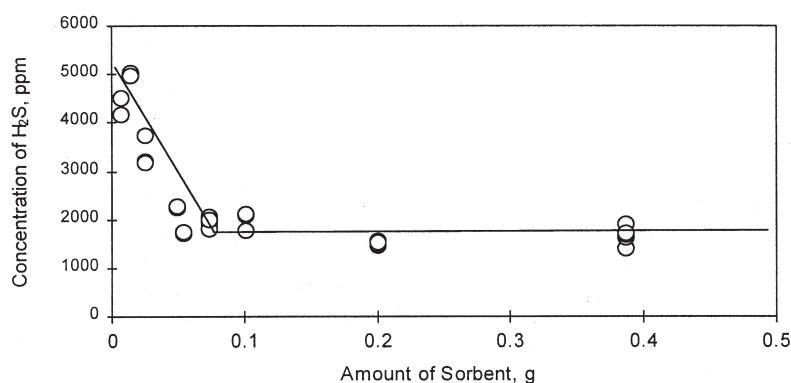


Figure 4. Effects of TU-19 sorbent amounts on removal of H_2S in the presence of the initial concentration 8700-ppm H_2S and 0.085-g moisture for 1 hour at 500°C.



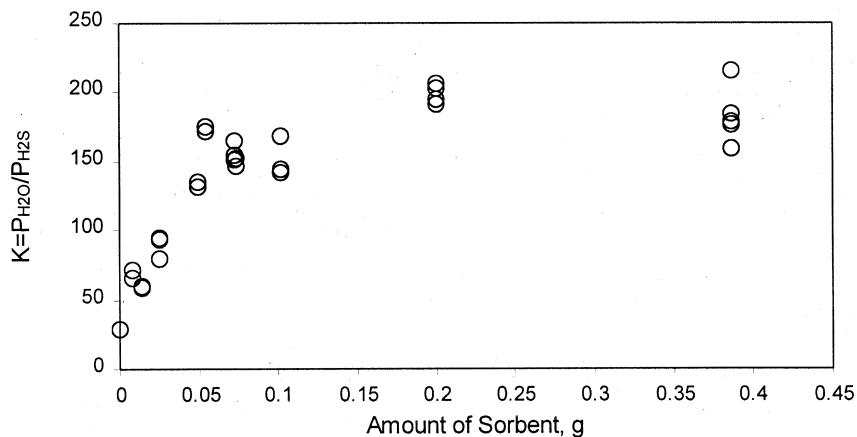


Figure 5. Effects of TU-19 sorbent amounts on equilibrium constant for removal of H_2S in the presence of the initial concentration 8700-ppm H_2S and 0.085-g moisture for 1 hour at 500°C.

Equation 1) to calculate equilibrium constants, as shown in the equilibrium constant equation (see Equation 2). Equilibrium constants of the heterogeneous reaction increase with sorbent amounts up to 0.05 g, and then level off above 0.05 g, as shown in Figure 5.

Equilibrium absorption of H_2S into the sorbent decreases drastically up to 0.05-g sorbent, and then tapers as sorbent amounts decrease further, as shown in Figure 6. These observations may suggest that equilibrium partial pressures of H_2S and moisture hinder absorption of H_2S into the sorbent, in despite of increasing sorbent amounts in the constant-volume batch reactor.

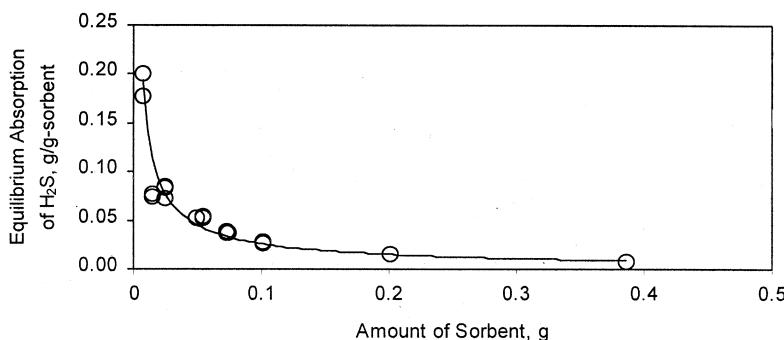


Figure 6. Equilibrium absorption of H_2S into TU-19 sorbent with initial concentration 8700-ppm H_2S and 0.085-g moisture for 1 hour at 500°C.



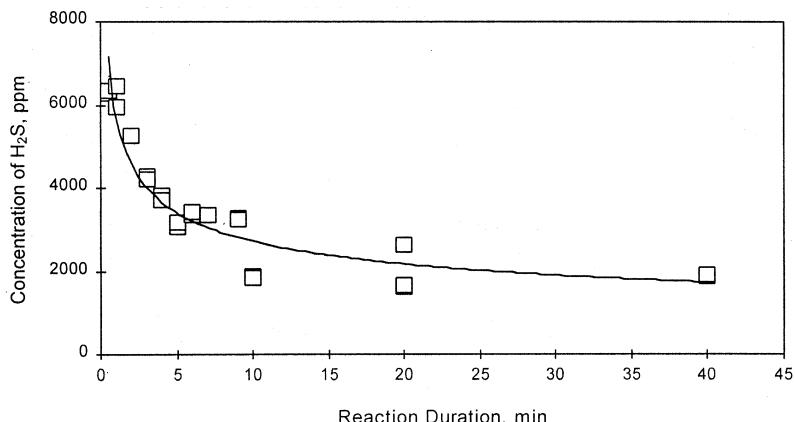


Figure 7. Reactivity of 0.1-g TU-19 sorbent with the initial concentration 8700-ppm H₂S in the presence 0.085-g moisture at 500°C and various reaction times.

Cylindrical Rod Model

Reactivity of 0.1-g TU-19 sorbent was investigated in the presence of the initial concentration 8700-ppm H₂S and 0.085-g moisture at 500°C and various reaction times (see FIGURE 7). These experimental data showed that most absorption of H₂S into the sorbent occurs during the first 5-min reaction time.

Intraparticle diffusivity of H₂S through the TU-19 sorbent in the form of 1-mm cylindrical rod was evaluated with the experimental data shown in Figure 7, using the following cylindrical rod model. The model was developed with the unreacted core assumption and the quasi steady state assumption (7, 8). Plotting the left-side values vs. the right-side values of the equation 3 (see FIGURE 8) de-

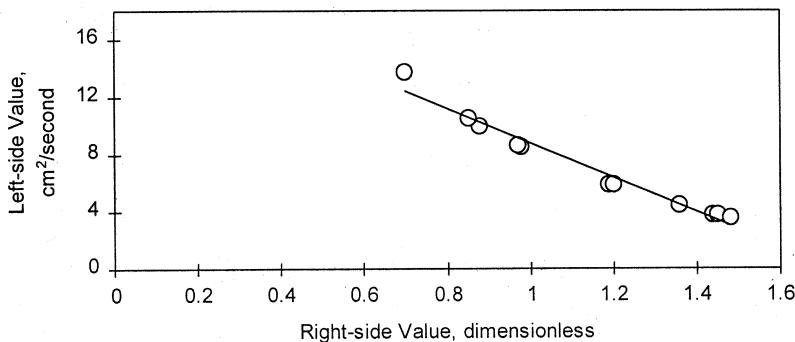


Figure 8. Left-side values vs. right-side values of the cylindrical rod model for the determination of intraparticle diffusivity through the TU-19 sorbent.



veloped a graph. Intraparticle diffusivity was determined from the slope of this plot. The intraparticle diffusivity of H₂S was found to be 2.02x10⁻³ cm²/s at 500°C.

$$\ln\left(\frac{r}{R}\right) r \frac{dr}{dt} = D_e \left(\frac{B}{b}\right) (1 + Ar^2) + \text{constant} \quad (3)$$

$$r = (R^2 - \left(\frac{C_{AO} - C_A}{b\pi l, \rho_B}\right) V)^{0.5} \quad (4)$$

$$B = \frac{C_{AO}}{\rho_B} - \frac{bV_B}{V} \quad (5)$$

$$A = \frac{b\pi l}{BV} \quad (6)$$

where

- r: radius of an unreacted core
- R: radius of cylindrical sorbent
- t: reaction time
- V_B: volume of cylindrical sorbent
- L: Length of a cylindrical-rod sorbent
- ρ_B: density of a cylindrical-rod sorbent
- D_e: intraparticle diffusivity
- V: reactor volume
- b: equilibrium absorption
- C_{AO}: initial concentration of H₂S
- C_A: concentration of H₂S

Effects of Hydrogen on Reactivity of Sorbents

Equilibrium absorption of the TU-19 sorbent in the presence of 24.7-psia H₂ (room temperature) is compared with that in the presence of 14.7-psia H₂. Equilibrium absorption of the TU-19 sorbent in the presence of 24.7-psia H₂ is higher than that in the presence of 14.7-psia H₂ (see FIGURE 9).

Partial pressures of hydrogen appear to affect significantly equilibrium absorption of H₂S into the sorbent at high equilibrium concentrations of H₂S. However, partial pressures of hydrogen appear not to affect significantly equilibrium absorption of H₂S into the sorbent at low equilibrium concentrations of H₂S.

Hydrogen appears to reduce the metal oxide sorbent and increase the absorbing capacity of the sorbent at high equilibrium concentrations of H₂S, although hydrogen does not affect equilibrium concentrations of H₂S and moisture (partial pressures) in the constant-volume batch reactor and the equilibrium constant. Hydrogen does not take part in the reaction of H₂S with active sites on the metal oxide sorbents (see the stoichiometric heterogeneous reaction formula).



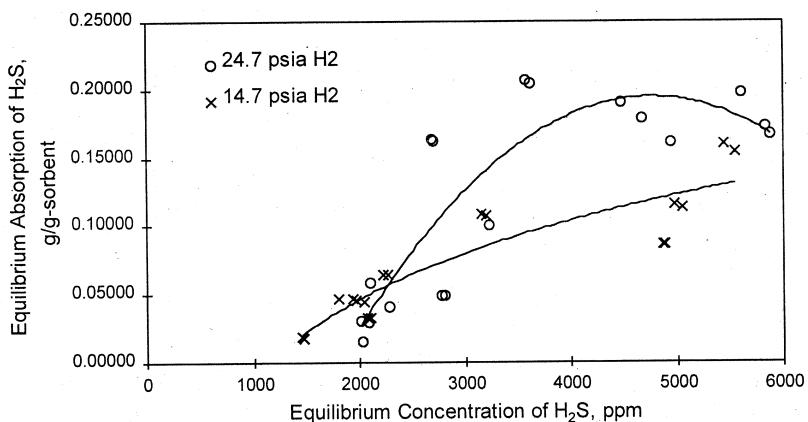


Figure 9. Effects of H₂S pressure on equilibrium absorption of H₂S into TU-19 sorbent in the presence of 0.085-g moisture at 500°C.

Effects of hydrogen partial pressures on dynamic absorption of H₂S into the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at 500°C (see FIGURE 10). The reactivity of the TU-25 sorbent with H₂S in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen for the 1-min reaction duration. These

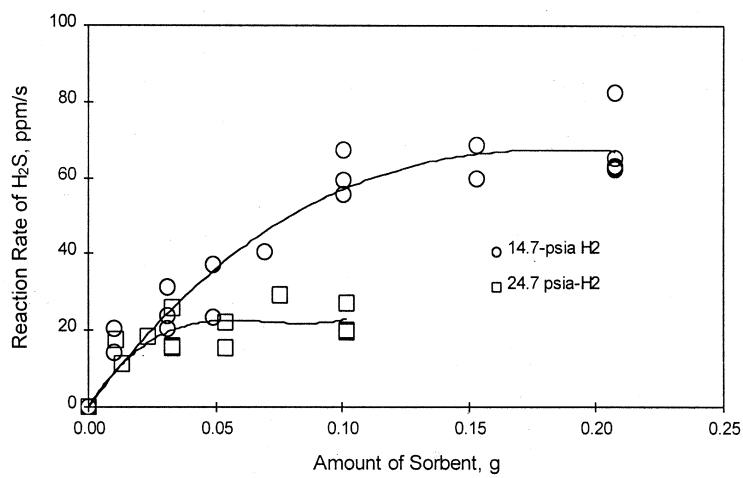


Figure 10. Effects of hydrogen pressures on reactivity of 100-200 mesh TU-25 sorbent with H₂S in the presence of 0.085-g moisture for 1 min at 500°C.



data suggest that hydrogen itself may affect reactivity of H_2S with the sorbent during short reaction durations.

Effects of hydrogen partial pressures on 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 (see FIGURE 11). 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. The differences in dynamic absorption of H_2S into the sorbent between the 14.7-psia hydrogen presence and the 24.7-psia hydrogen presence increases with the amounts of the TU-25 sorbent.

Effects of Temperatures and Sorbent Amounts on Reactivity of TU-24 Sorbent

The 100-200 mesh TU-24 sorbent was reacted with H_2S at various reaction temperatures for 1 min (see FIGURE 12). Reactivity of the sorbent increases with increased reaction temperatures. Reaction rates of H_2S with the sorbent increase with increased amounts of the sorbent. These observations also indicate that reactivity of H_2S with the TU-24 sorbent is a function of reaction temperatures and sorbent amounts.

Dynamic absorption of H_2S into the TU-24 sorbent increases with increased absorption temperatures, and decreases with increased amounts of the TU-24 sor-

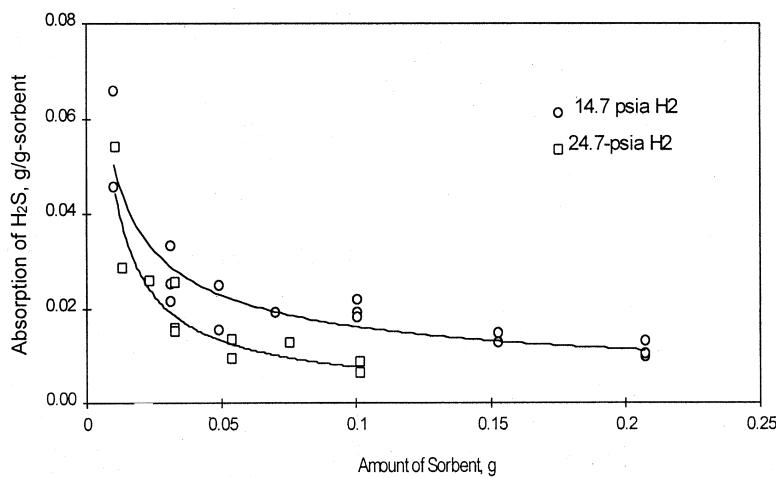


Figure 11. Effects of hydrogen partial pressure on absorption of H_2S into TU-25 sorbent in the presence of 0.085-g moisture for 1 min at 500°C.



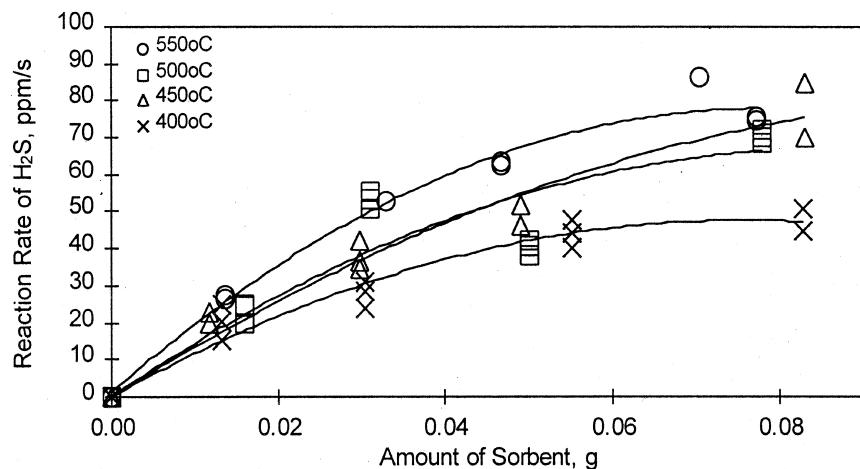


Figure 12. Effects of temperatures on reactivity of 100-200 mesh TU 24 sorbent with H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min.

bent for the 1-min absorption duration (see FIGURE 13). These experimental data may suggest that dynamic absorption of H₂S into the sorbent is dependent on concentrations of H₂S as well as amounts of the TU-24 sorbent in the constant-volume batch reactor.

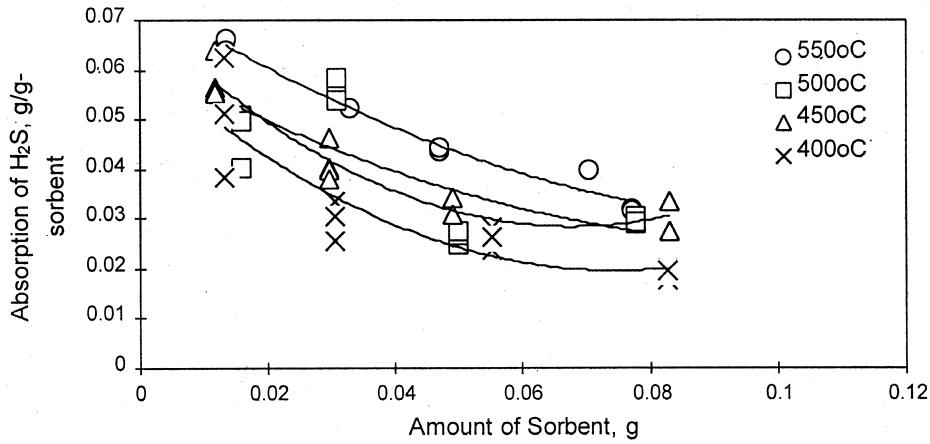


Figure 13. Effects of temperatures on dynamic absorption of H₂S into TU 24 sorbent in the presence of initial 14.7-psia H₂ and 0.085-g moisture for 1 min.



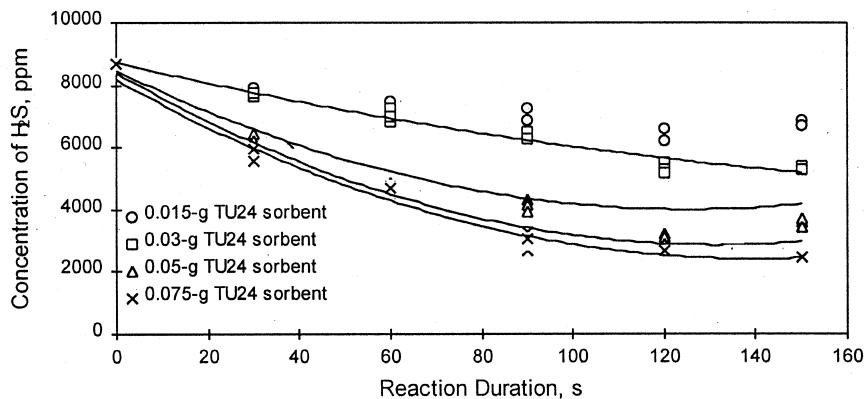


Figure 14. Concentrations of H₂S at various reaction durations in the presence of 14.7-psia hydrogen (room temperature) and 0.085-g moisture at 500°C.

Initial Surface Reaction Rates of TU-24 Sorbent

Reaction rates of H₂S with the TU-24 sorbent at 500°C were obtained from the experimental data of H₂S concentrations at various reaction durations (see FIGURE 14). Dynamic absorption of H₂S into the TU-24 sorbent at 500°C increases with increased reaction durations and decreased quantities of the sorbent (see FIGURE 15). The loading of H₂S on the sorbent (g H₂S/g-sorbent) will decrease, as the amount of the sorbent is increased, since the H₂S is depleted.

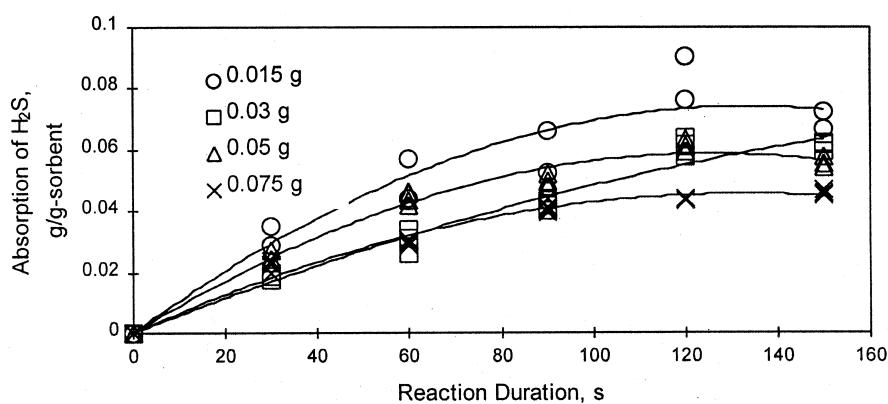


Figure 15. Effects of sorbent amounts on absorption of H₂S into TU-24 sorbent in the presence of initial 14.7-psia H₂ and 0.085-g moisture at 500°C.



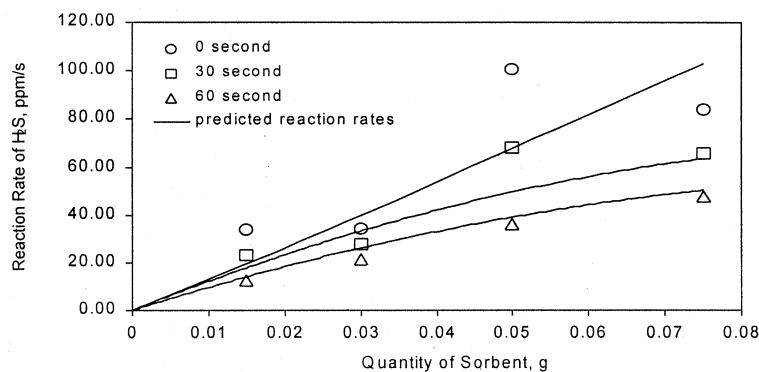


Figure 16. Reaction rates of H_2S with 100-200 mesh TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture at 500°C and various quantities of the sorbent.

Absorption of H_2S into the sorbent is initially controlled by the surface reaction of H_2S with active sites of the sorbent. However, absorption of H_2S into the sorbent is controlled by the intraparticle diffusivity of H_2S through pores of the metal oxide sorbent as reaction durations increase. The experimental data at the reaction durations of 30 s and 60 s, as shown in Figure 14, are used to obtain reaction rates. The experimental data at the reaction durations of 90 s, 120 s, and 150 s, as shown in Figure 14, are not used to obtain reaction rates, since intraparticle diffusivity of H_2S through pores of the metal oxide sorbents appears to be a rate-limited step for absorption of H_2S into the sorbent over those reaction durations.

Figures 16 through 18 are plotted with the first 60-s experimental data and reaction rates. Reaction rates of H_2S with the TU-24 sorbent at 500°C increase

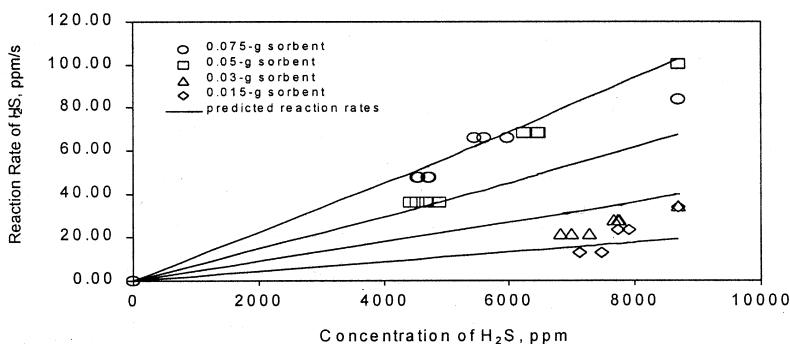


Figure 17. Reaction rates of H_2S with 100-200 mesh TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture at 500°C.



with amounts of the sorbent, and decrease with increased reaction durations (see FIGURE 16).

FIGURE 17 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 .

FIGURE 18 shows that reaction rates of H_2S with the TU-24 sorbent increase with increased quantities of the sorbent, and decrease with increased reaction durations.

The following reaction rate equation is proposed, since reaction rates of H_2S with TU-24 sorbent are dependent on concentrations of H_2S and quantities of the sorbent (see FIGURE 17).

$$r_A = k_A C_A^\alpha M_S^\beta \quad (7)$$

where

- r_A : reaction rates of H_2S , g-mole/cc/s
- C_A : concentrations of H_2S , g-mole/cc
- M_S : quantities of sorbents, g/cm^3
- k_A : reaction rate constant in terms of disappearance of H_2S , $\text{cc}^{(\alpha+\beta-1)}/\text{g}^\beta/\text{g-mole}^{(\alpha-1)}/\text{s}$
- α : reaction order with respect to concentrations of H_2S
- β : reaction order with respect to quantities of sorbents
- cc: cm^3

Applying a logarithm to the both sides of the proposed reaction rate equation linearizes equation (7). The following linearized equation is obtained to evaluate k_A , α , and β .

$$\ln(r_A) = \ln(k_A) + \alpha \ln(C_A) + \beta \ln(M_S) \quad (8)$$

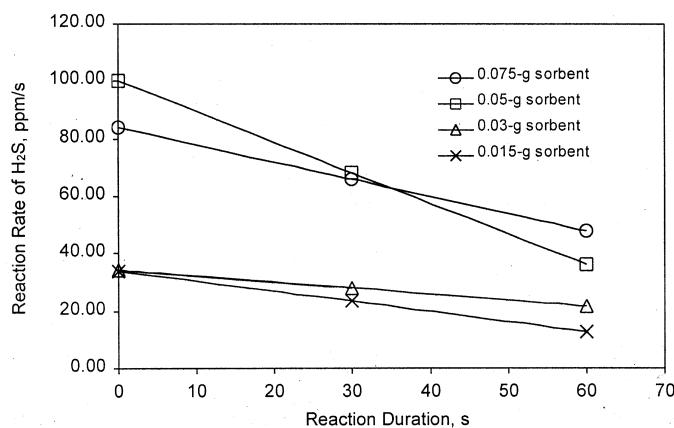


Figure 18. Reactivity of 100-200 mesh TU-24 sorbent with initial 8700-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500°C.



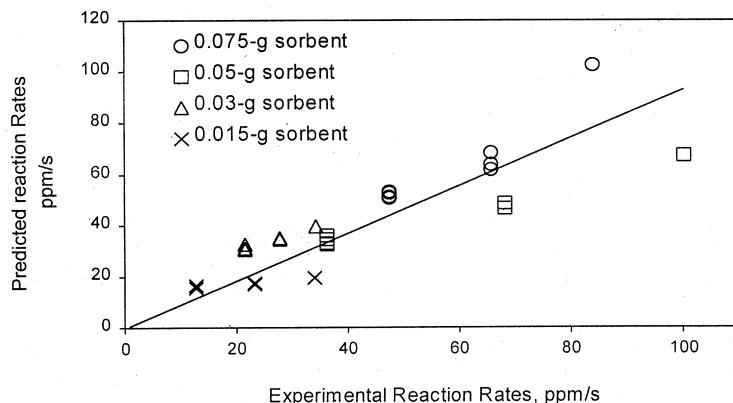


Figure 19. A comparison between experimental reaction rates and predicted reaction rates for 0 - 60 s at 500°C.

The experimental data of H₂S concentrations at various reaction durations are applied to Equation (8), and then the reaction rate constant k_A, and the reaction orders such as α , and β are obtained using the multiple linear regression method (9) as well as the Gauss-Seidel method (10). The values of k_A, α , and β are shown in Equation (9).

$$r_A = 19.29 C_A^{1.08} M_S^{1.04} \quad (9)$$

The reaction rate constant k_A in terms of disappearance of H₂S was found to be 19.29 cc^{1.12}/(g-mole-H₂S)^{0.08}/g^{1.04}/s at the reaction temperature 500°C. The reaction order α with respect to concentrations of H₂S was found to be 1.08, while the reaction order β with respect to quantities of the TU-24 sorbent was found to be 1.04. Reaction rates, calculated with the reaction rate equation obtained through the multiple linear least squares method, are shown as predicted reaction rates in Figures 16 through 19.

The curves in Figure 17 are approximately linear, and this agrees with the reactor order of 1.08 (approximately unity) with respect to the hydrogen sulfide concentration derived from the regressions and shown in equation (9). Experimental reaction rates are compared with those predicted from the reaction rate equation obtained through the multiple linear least squares method, as shown in Figure 19.

CONCLUSIONS

The following conclusions are drawn, based on experimental data generated from a batch reactor, and their interpretations.



- Three metal oxide sorbents, labeled TU-19, TU-24, and TU-25 were formulated with zinc oxide powder as an active sorbent ingredient, bentonite as a binding material, and titanium oxide as a supporting metal oxide. Equilibrium absorption of H_2S into the TU-19 sorbent increases with concentrations of H_2S . Reactivity of the 100-200 mesh TU-24 sorbent increases with increased reaction temperatures. Reaction rates of H_2S with the sorbent increase with increased amounts of the sorbent.
- Equilibrium partial pressures of H_2S and moisture hinder absorption of H_2S into the TU-19 sorbent, in despite of increasing sorbent amounts in the constant-volume batch reactor.
- Partial pressures of hydrogen appear to affect significantly equilibrium absorption of H_2S into the TU-19 sorbent at high equilibrium concentrations of H_2S , while partial pressures of hydrogen appear not to affect significantly equilibrium absorption of H_2S into the sorbent at low equilibrium concentrations of H_2S . However, reactivity of the TU-25 sorbent with H_2S in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen for the 1-min reaction duration.
- A cylindrical rod model was developed with the unreacted core assumption and the quasi steady state assumption to determine intraparticle diffusivity of hydrogen sulfide into metal oxide sorbents. The intraparticle diffusivity of H_2S into the TU-19 sorbent was found to be $2.02 \times 10^{-3} \text{ cm}^2/\text{s}$ at 500°C .
- A reaction rate equation in terms of disappearance of H_2S for 30 - 60 seconds at 500°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 k_A in terms of disappearance of H_2S was found to be $19.29 \text{ cc}^{1.12}/(\text{g-mole-}H_2S)^{0.08}/\text{g}^{1.04}/\text{s}$ at the reaction temperature 500°C . The reaction order α with respect to concentrations of H_2S was found to be 1.08, while the reaction order β with respect to quantities of the TU-24 sorbent was found to be 1.04.

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REFERENCES

1. Hessley, J.W. Reasoner, and J.T. Riley, *Coal Science (An Introduction to Chemistry, Technology, and Utilization)*, A Wiley Interscience Publication, John Wiley& Sons (1986).
2. Thambimuthu, Kelly V., Strategy for Coal-Liquid Mixture Commercialization in *the Proceedings of the International Energy Agency/Coal Liquid Mixture Workshop at The 18th International Conference on Coal Utilization and Fuel Systems*, Clearwater, Florida (1993).
3. Andrus, H. E., Thibeault, P. R. and Gibson, C. R., Combustion Engineering IGCC Repowering Project in *the Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Volume I, pg 9, edited by Richard A. Johnson and Suresh C. Jain, September 1992.
4. 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, Proceedings for The Fourth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Greensboro, North Carolina, April 2-4, 1996.
5. Gangwal, Santosh K. and R. P. Gupta, Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed in Proceedings of the Coal-Fired Power Systems 93 - Advances in IGCC and PFBC Review Meeting, edited by D. L. Bonk, U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center, Morgantown, West Virginia (1993).
6. Kwon, K. C., N. Vahdat and W. Ayers, "Chemical Reaction Experiment for the Undergraduate Laboratory", Chemical Engineering Education, Vol. 21, No. 1, p. 30, 1987.
7. Fogler, H. S., *Elements of Chemical Reaction Engineering*, 2nd Ed., Prentice-Hall, New York (1992).
8. Octave Levenspiel, *Chemical Reaction Engineering*, 2nd Edition, John Wiley & Sons, New York (1972).
9. Schaum's Outline Series Statistics, 2nd Edition, McGraw-Hill, New York.
10. Holman, J. P. *Heat Transfer*, 7th Ed., McGraw-Hill, New York (1990).



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