

Reactivity of Sorbents with Hot Hydrogen Sulfide

Kyung C. Kwon (kwonk@acd.tusk.edu; 334-727-8976)
Chemical Engineering Department, College of Engineering,, Architecture and Physical Sciences
Tuskegee University, Tuskegee, Alabama 36088

Santosh K. Gangwal (skg@rti.org; 919-541-8033)
Fuel Technology, Research Triangle Institute, P. O. Box 12194, Research Triangle Park, NC 27709

Susan K. Joines (sjoine@fetc.doe.gov; 304-285-4063), FETC Contracting Officer's Representative
DOE FETC, 3610 Collins Ferry Road, P.O. Box 880, Morgantown, WV 26507-0880

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telephone: (334) 727-8976/(334) 724-4528; fax: (334) 724-4188/(334) 727-8090

Introduction

Removal of hydrogen sulfide in hot coal gases 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, a durable metal oxide sorbent was formulated. Reactivity of the formulated metal oxide sorbent with hydrogen sulfide in simulated coal gas mixtures was examined in the presence of hydrogen and moisture at their various concentrations.

Objectives

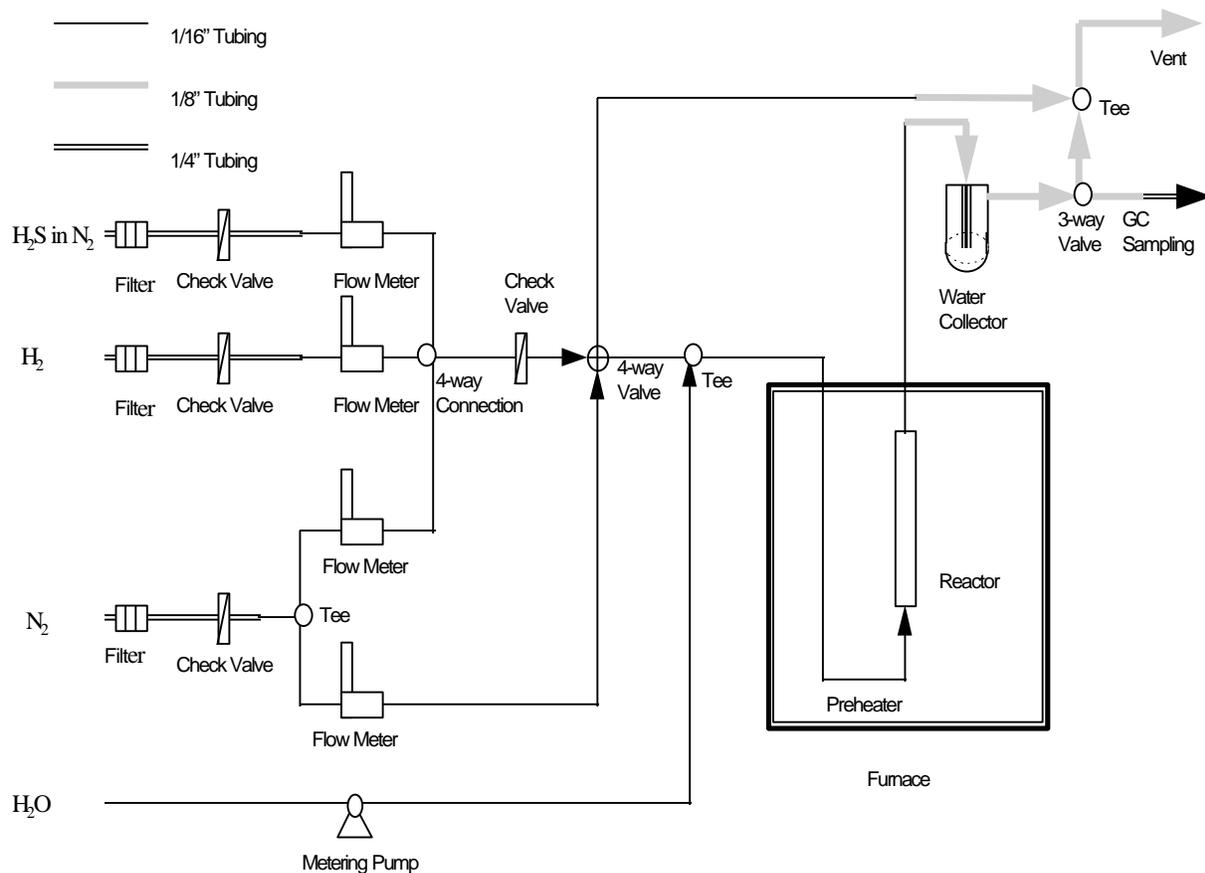
The main objectives of this research are to study initial reaction kinetics for a H₂S-sorbent reaction system, to formulate a durable metal oxide sorbent with a high capacity of absorbing hydrogen sulfide, to investigate effects of hydrogen, moisture, concentrations of H₂S, and residence time of reaction gas mixtures on equilibrium absorption as well as dynamic absorption of H₂S into the TU-188 sorbent at 530°C, and to evaluate effective diffusivity of H₂S through the sorbent particles, using the newly-fabricated differential reactor.

Experimental Approach

A differential reactor mainly consists of one 10-cm-long ¼-inch titanium grade-2 tubing and two 1/4" external column end fittings. A differential reactor assembly mainly consists of four mass flow meters for gases, one differential reactor, one preheater, one high pressure liquid pump for water, one four-way switch valve, one muffle furnace, three filters for gases, four check valves, and one water collection bottle (see Figure 1). The reactor was

loaded with 0.1-g 74-140 μm TU-188 sorbent particles. The reactor, loaded with the sorbent particles, was placed inside the muffle furnace to be heated at a desired temperature. Nitrogen was introduced into the sorbent-loaded reactor during preheating the reactor. When the temperature of the reactor was raised at the desired temperature, a reaction mixture was introduced into the reactor for a desired reaction duration, by switching nitrogen with a simulated coal gas mixture. A typical simulated coal gas mixture consists of 2500 – 7500 ppm hydrogen sulfide, 0 – 10 vol % moisture, 0- 33 vol % hydrogen, and nitrogen as remainder. The volumetric feed rate of the simulated coal gas mixture to the reactor is 100 – 300 cm^3/min at room temperature and 105 psia. The temperature of the reactor is controlled in the furnace oven at 530°C. The pressure of the reactor is maintained at 105 psia.

Figure 1. A Differential Reactor Assembly



Project Description

A differential micro reactor was fabricated with a titanium grade-2 tube. The volume of reactor is 1.64 cm^3 . The fresh formulated metal oxide sorbent TU-188 in the form of 1-mm

cylindrical rod were crushed to obtain 100 - 200 mesh (74 –140 μm) particles, and were reacted with simulated coal gases containing hydrogen sulfide in the 1.64 cm^3 titanium Grade-2 differential micro reactor for 5- 25000 seconds at 530°C. Absorption amounts of hydrogen sulfide into the sorbent were analyzed with an electronic balance. The range for the space (residence) time of the reaction gas mixture in the reactor was 0.12 - 0.36 s (300 - 100 cc/min) under the reaction conditions.

Table1. Experimental conditions for the reaction of hydrogen sulfide with the TU-188 sorbent in the presence of moisture, nitrogen and hydrogen.

| | |
|--|-------------|
| Reactor Volume, cm^3 : | 1.6 |
| Temperature, °C: | 530 |
| Reaction Time, s: | 5 -25000 |
| Space Time, s: under the absorption conditions | 0.12 - 0.36 |
| Particle Size, μm | 74 - 140 |
| Amount of Sorbent, g | 0.1 |
| Gas Flow Rate at room temperature and 105 psia, cc/min | 100 - 300 |
| Hydrogen, vol % | 0 - 33 |
| Moisture, vol %: | 0 - 10 |
| Concentration of H_2S , ppm | 2500 - 7500 |
| Nitrogen, vol % | 10 - 40 |

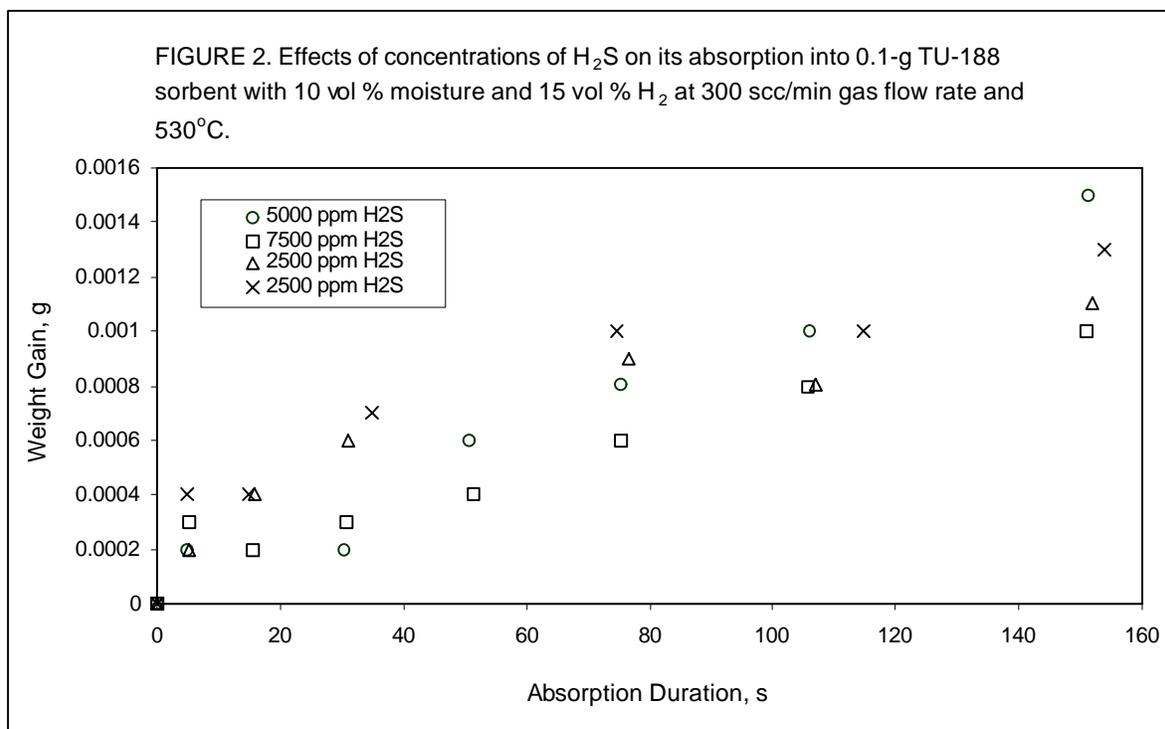
Table 2. Properties of the TU-188 metal oxide sorbent

| | |
|------------------------|------------------------------------|
| Main Ingredients | TiO_2 , ZnO, Clay, Starch |
| Surface Area: | 6.4 m^2/g |
| Average Pore Diameter: | 1300 Å |
| Bulk Density: | 2.09 g/cm^3 |
| Apparent Density: | 4.27 g/cm^3 |
| Porosity | 0.42 |

Results

Research activities and efforts of this research project were concentrated on absorbing hydrogen sulfide into TU-188 sorbent at various operation conditions to understand effects of moisture, hydrogen, concentration of H_2S , and space velocity of a simulated coal gas mixture on absorption of hydrogen sulfide into the sorbent, using a newly designed differential reactor. Experimental data of absorption of H_2S into the TU-188 sorbent at various absorption duration's were shown in Figures 2 - 10.

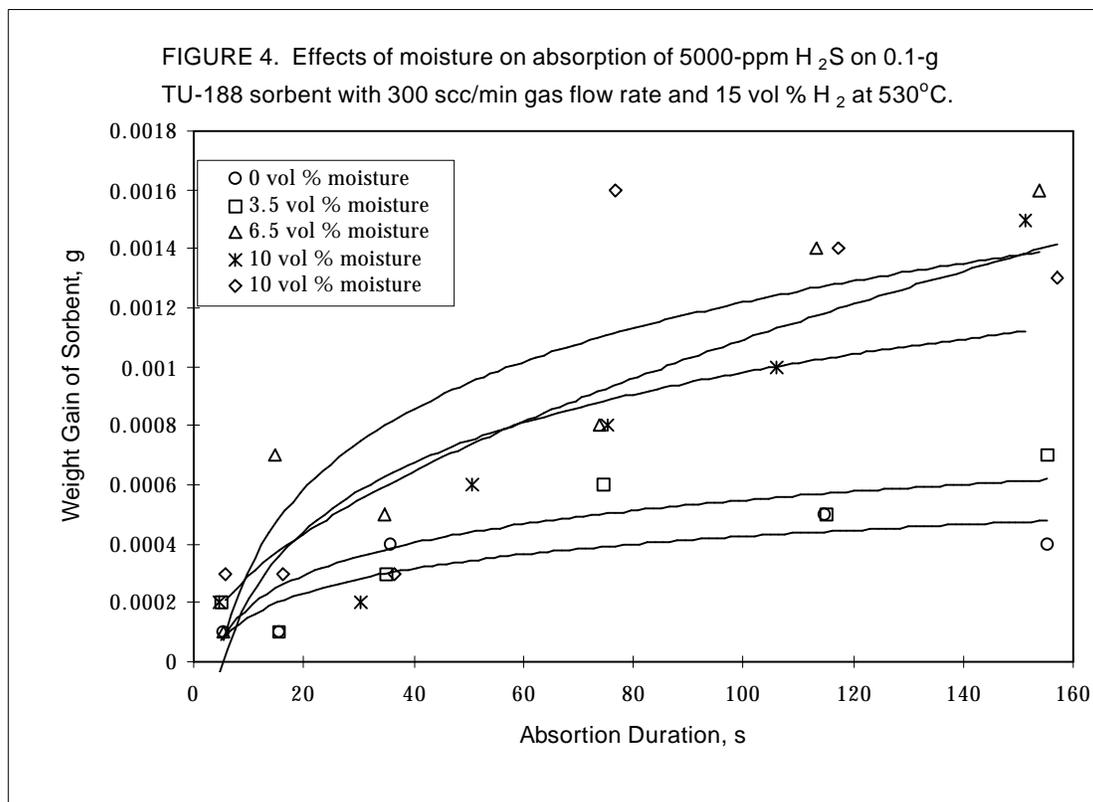
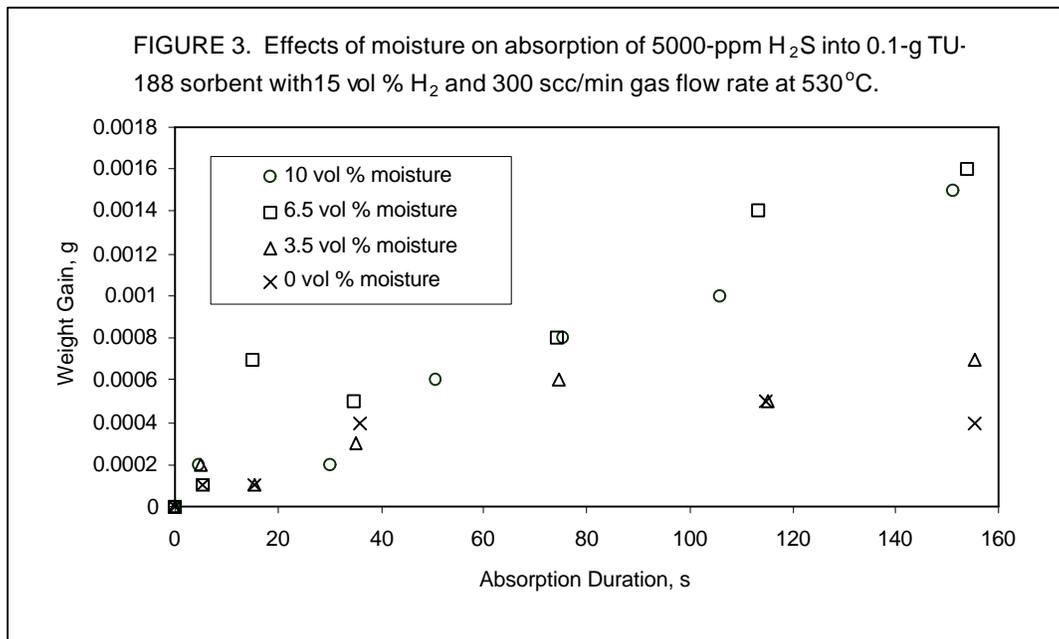
A series of experiments on absorption of H₂S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of H₂S concentrations on initial reaction of H₂S with the sorbent. The concentrations of moisture and hydrogen are maintained at 10-vol % and 15 vol %, respectively. The concentrations of hydrogen sulfide in the simulated coal gas mixture are 2500 –7500 ppm. Absorption of H₂S decreases with increased concentrations of H₂S for short absorption durations of 5 – 150 seconds (see Figure 2). These observations may indicate that hydrogen sulfide absorbed into the porous matrix of the sorbent retards transfer of H₂S into micro pores of the sorbent with increased concentrations of H₂S.

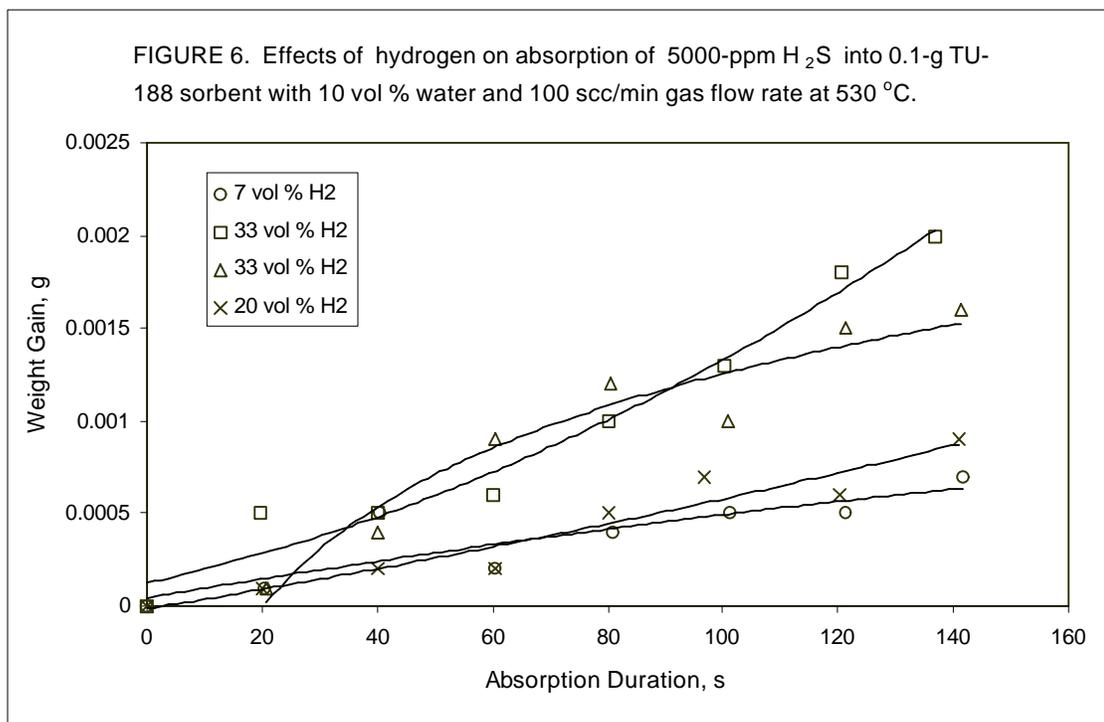
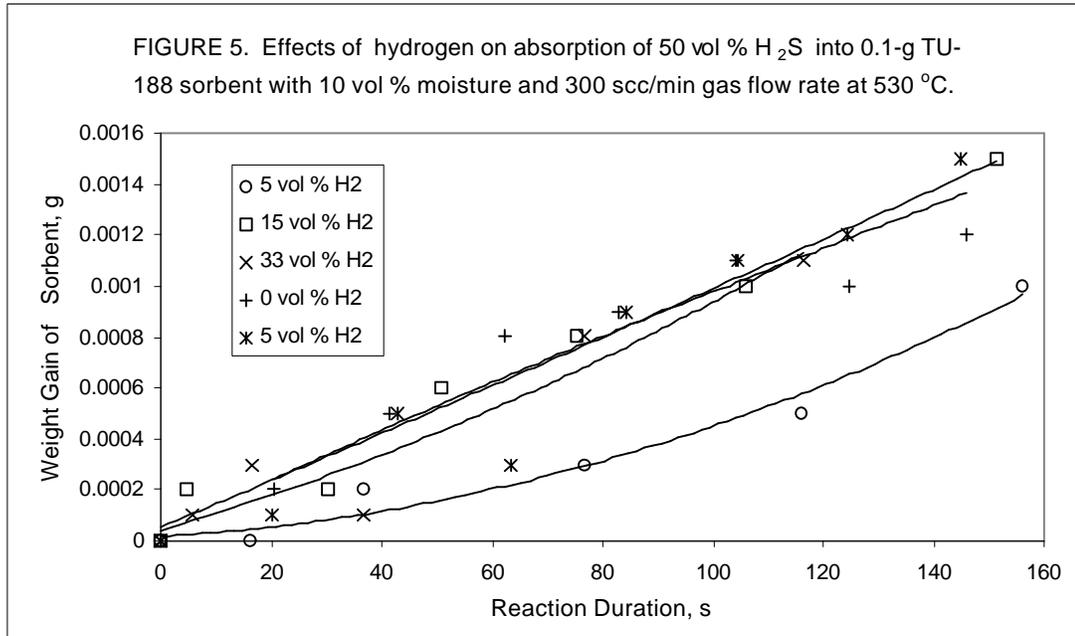


A series of experiments on absorption of H₂S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of moisture concentrations on initial reaction of H₂S with the sorbent. The concentrations of H₂S and hydrogen are maintained at 5000 ppm and 15 vol %, respectively. The concentrations of moisture in the simulated coal gas mixture are 0 – 10 vol %. Initial absorption of H₂S into the sorbent increases with increased concentrations of moisture for short absorption durations of 5 – 150 seconds (see Figures 3 and 4). These facts may indicate that moisture, lighter than H₂S, enhances mobility of H₂S through the porous matrix of the sorbent.

A series of experiments on absorption of H₂S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on initial reaction of H₂S with the sorbent. The concentrations of H₂S and moisture are maintained at 5000 ppm and 10 vol %, respectively. The concentrations of hydrogen in the simulated coal gas mixture are 0 - 33 vol %. Initial absorption of H₂S into the sorbent increases with increased concentrations of hydrogen for short absorption durations of 5 – 150 seconds at 300 scc/min total gas flow rate as well as 100 scc/min total gas flow rate (see Figures 5 and 6).

These results may suggest that a reducing gas such as hydrogen increases active surface area accessible to H₂S by the reaction of hydrogen with the porous metal oxide matrix of the sorbent and enlarging pore diameters of the sorbent.





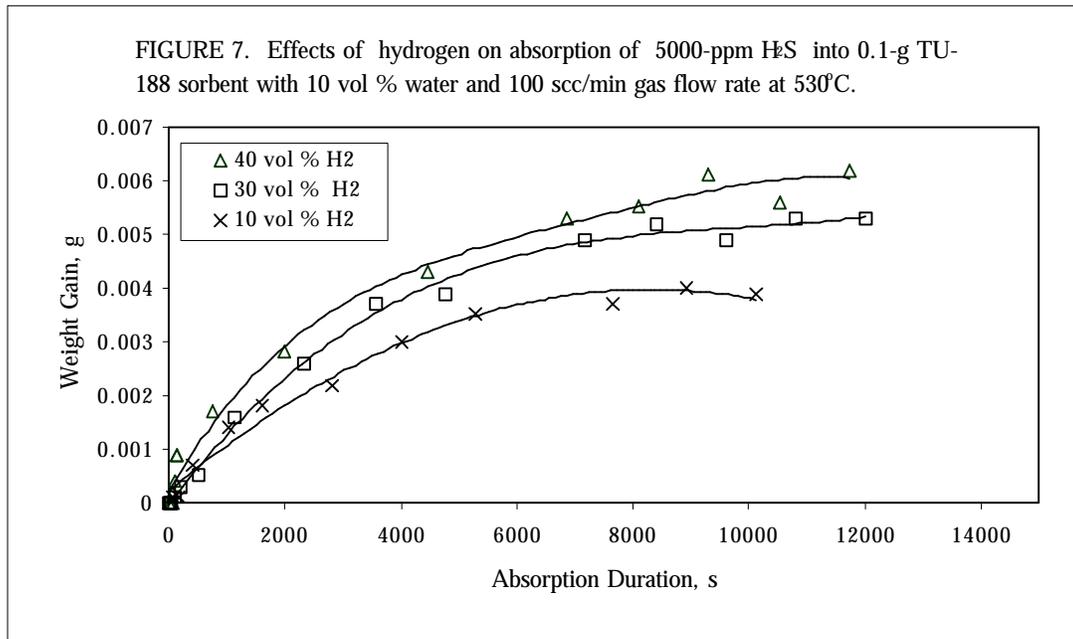
A series of experiments on absorption of H₂S into the sorbent were carried out for 30 – 12000 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on effective diffusivity of H₂S with the sorbent. The concentrations of H₂S and moisture are maintained at 5000 ppm and 10 vol %, respectively. The concentrations of hydrogen in the simulated coal gas mixture are 10 – 40 vol %. The total gas flow rate of gas is maintained at 100 cm³/min.

The experimental data, shown in Figure 7, were applied to the unreacted core model (see Equation 1) to find the effective diffusivity of hydrogen sulfide into the sorbent.

$$\left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \right] = \frac{6bdC_{Ag}}{r_B R^2} t \quad (1)$$

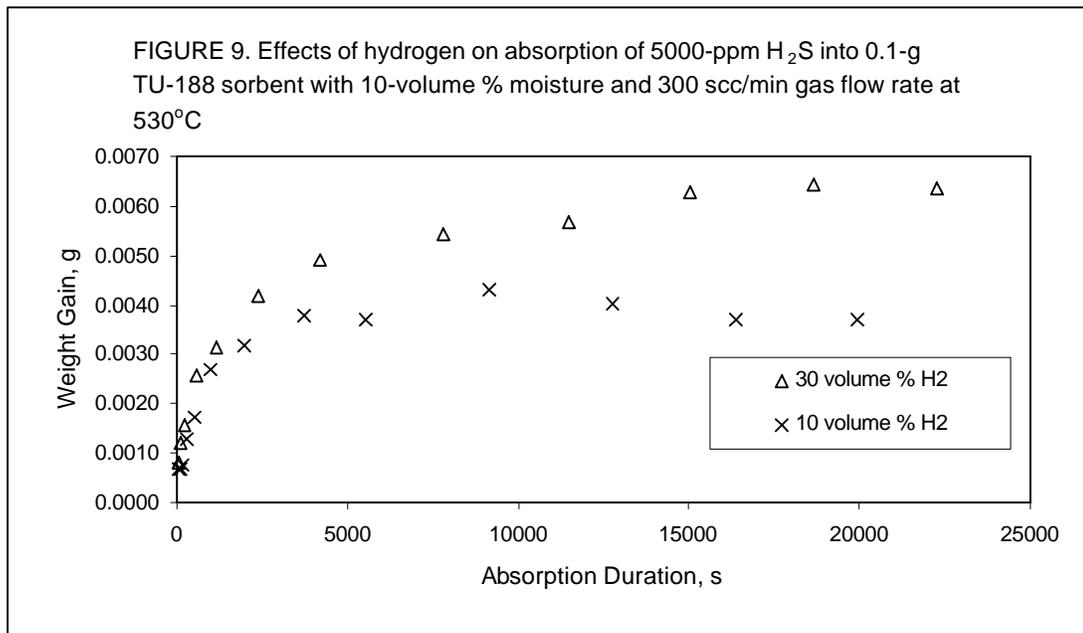
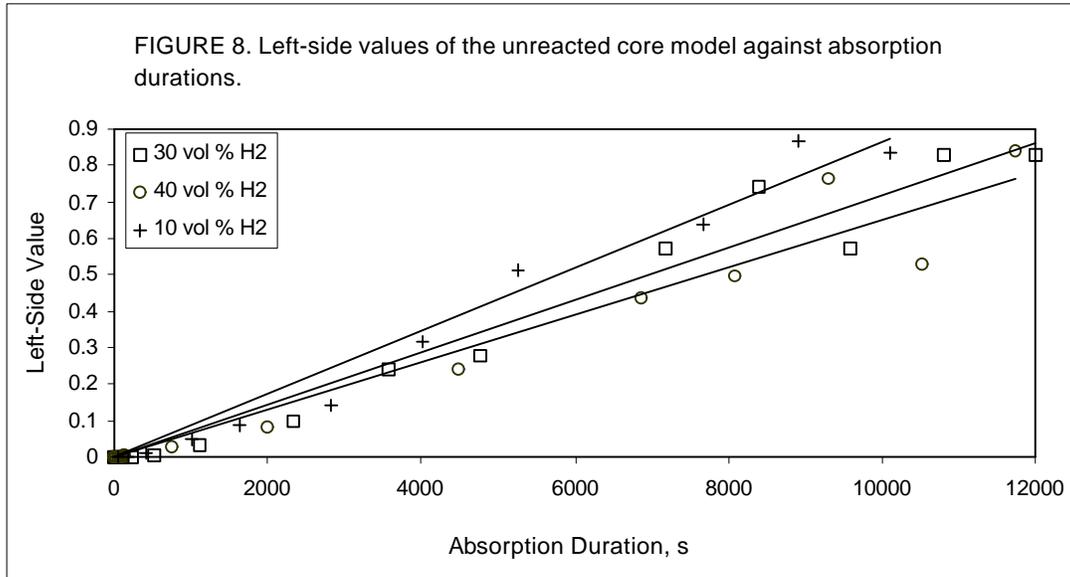
- where r_c : radius of the unreacted core.
 R : geometric average radius of a particle.
 b : stoichiometry.
 δ : effective diffusivity
 C_{Ag} : concentration of an active gas
 ρ_B : bulk density of particles
 t : reaction duration

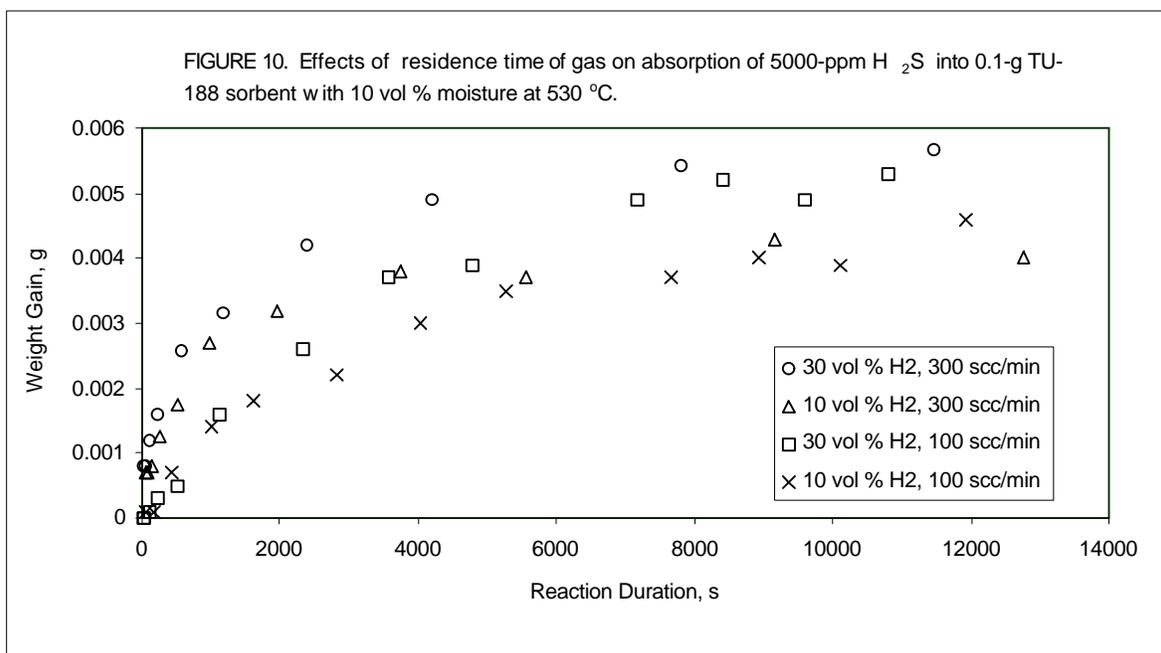
The effective diffusivity of H_2S into the sorbent is $2.274 \times 10^{-3} \text{ cm}^2/\text{s}$ in the presence of 10-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is $1.381 \times 10^{-3} \text{ cm}^2/\text{s}$ in the presence of 30-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is $1.08 \times 10^{-3} \text{ cm}^2/\text{s}$ in the presence of 40-vol % hydrogen. The magnitude of these diffusivity values of H_2S are agreeable with the value obtained from the unreacted-core cylindrical rod model, where the experimental data were obtained from the 35-cc batch reactor at 500°C . These experimental data indicate that hydrogen concentrations affect significantly intraparticle diffusivity of H_2S into the sorbent (see Figure 8).



A series of experiments on absorption of H_2S into the sorbent were carried out for 30 – 25000 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on

equilibrium absorption of H₂S into the sorbent. The concentrations of H₂S and moisture are maintained at 5000 ppm and 10-vol %, respectively. The equilibrium absorption of hydrogen sulfide in the sorbent increases with increased hydrogen concentrations (see Figures 7 and 9). These experimental results may explain that a reducing gas such as hydrogen increases absorption capacity of the sorbent by the reaction of hydrogen with the porous metal oxide matrix of the sorbent. The reaction of hydrogen with the sorbent may result in increasing pore sizes as well as active surface areas of the sorbent in favor of absorption of H₂S. These observations appear to be agreeable with those shown in Figures 5 and 6.





A series of experiments on effects of space (residence) times on dynamic absorption of H₂S into the sorbent were conducted at the 100 cm³/min (0.36 s residence time) and the 300 cm³/min (0.12 s residence time). Decreased residence time results in increased dynamic absorption of H₂S into the sorbent. These observations may suggest that transfer rate of H₂S from the reactive gas mixture toward the surface of the porous solid sorbent particles affect significantly dynamic absorption of H₂S into the sorbent. These data may indicate that space times do not affect equilibrium absorption capacity of the sorbent in the presence of H₂S as an absorbed reactive gas.

Conclusions

The following conclusions were drawn based on the experimental data, generated from the differential reactor system, and their interpretations.

- Hydrogen sulfide absorbed into the porous matrix of the sorbent retards transfer of H₂S into micro pores of the sorbent with increased concentrations of H₂S.
- Moisture, lighter than H₂S, enhances mobility of H₂S through the porous matrix of the sorbent..
- A reducing gas such as hydrogen increases active surface area accessible to H₂S by the reaction of hydrogen with the porous metal oxide matrix of the sorbent and enlarging pore diameters of the sorbent.

- Hydrogen concentrations affect significantly intraparticle diffusivity of H₂S into the sorbent .
- A reducing gas such as hydrogen increases absorption capacity of the sorbent by the reaction of hydrogen with the porous metal oxide matrix of the sorbent. The reaction of hydrogen with the sorbent may result in increasing pore sizes as well as active surface areas of the sorbent in favor of absorption of H₂S
- Space times do not affect equilibrium absorption capacity of the sorbent in the presence of H₂S as an absorbed reactive gas.

Application

Effects of moisture and hydrogen partial pressures on reaction kinetics for a H₂S-sorbent system 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

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 H₂S 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.

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