Investigation on Durability and Reactivity of Promising Metal Oxide Sorbents During Sulfidation and Regeneration

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SCHEDULE AND MILESTONES

	FY 1994-1995												FY 1995-1996											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Procurements of Materials and Equipment																								
Fabrication of a Micro Batch Reactor																								
Development of Analytical Procedures for Concentrations of Sulfur compounds																								
Development of Experimental Procedures for Sulfidation Reaction of Fresh Metal Oxide Sorbents																								
Formulation of Durable Metal Oxide Sorbents with High-Sulfur Removal Capacity																								
Reaction Kinetics on Sulfidation of Metal Oxide Sorbents																								
Reaction Kinetics on Regeneration of Sulfur-loaded Metal Oxide Sorbents																								
Development of an Intraparticle Diffusivity Model for Sulfidation of Metal Oxide Sorbents																								
Delineation of Effects of Hydrogen Partial Pressures and Moisture Amounts on Sulfidation of Metal Oxide Sorbents																								
Equilibrium Absorption of Hydrogen Sulfide into Metal Oxide Sorbents																								
Development of a Micro Differential Reactor																								

OBJECTIVES

The main objectives of this research project during this quarter are to conduct experiments on equilibrium absorption of hydrogen sulfide into formulated sorbents at 500°C, to identify effects of hydrogen partial pressures on equilibrium absorption of hydrogen sulfide into formulated sorbents, and develop a cylindrical rod model to evaluate intraparticulate diffusivity of H₂S into sorbents in the batch reactor

EXPERIMENTAL APPROACH

Fresh formulated metal oxide sorbent particles were reacted with simulated coal gases containing hydrogen sulfide in the 35 cm³ 316 stainless steel batch reactor. The metal oxide sorbents TU-19 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 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. The formulated metal oxide sorbents were calcined for 2 hours

at 800 - 900°C. Various sorbents were formulated during this quarter. The ingredients and the calcination procedures of the TU-19 and the TU-28 sorbents were presented in Table 1.

Table 1. Formulation of TU-19 and TU-28 sorbents.

	TU-19	TU-28
ZnO, g	1	1
TiO ₂ , g	2	2
Bentonite, g	0.15	0.1
Calcination Temperature, °C	800	830
Calcination Duration, min	100	100
Density of Sorbent, g/cm ³	1.73	
Specific Pore Volume, cm ³ /g	0.36	

STATUS

Research activities and efforts of this research project were concentrated on formulating metal oxide sorbents, conducting experiments on equilibrium absorption of hydrogen sulfide into formulated sorbents, and developing a cylindrical rod model to evaluate intraparticle diffusivity of H₂S into sorbents in the batch reactor.

Experiments on reactivity of a simulated coal gas mixture containing hydrogen sulfide on the 316 SS batch reactor wall were carried out in the absence of sorbents at 500°C (see Tables 2 and 3, and Figure 1). The simulated coal gas mixture consists of 9107-ppm hydrogen sulfide (0.005 g; 1 wt %), 0.085-g water (15.84 wt %), 0.0029-g hydrogen (0.58 wt %), and 0.4046-g nitrogen (81.34 wt %). Absorption of hydrogen sulfide into the reactor wall increases with absorption times.

Table 2. Experimental conditions for the reaction of hydrogen sulfide with TU-19 sorbent in the presence of water, nitrogen and hydrogen at 500°C.

Reactor Volume, cm ³ :	35
Temperature, °C:	500
Reaction Time, min:	1 - 60
Particle Size	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
Initial Concentration of H ₂ S, ppm	9107
Initial Partial Pressure of Nitrogen at 25°C, psia:	140 -150

Table 3. Reactivity of 316 stainless steel in the presence of 0.085-g moisture and the initial concentration 9107-ppm H_2S at 500°C.

Run #	Reaction Time, min	Concentration of H_2S , ppm	Run #	Reaction Time, min	Concentration of H_2S , ppm
297	5	9112	121	20	8209
297	5	8619	301	30	8133
113	10	8497	301	30	8536
113	10	8631	300	60	8158
302	15	8759	300	60	8272
302	15	8759	298	120	7639
121	20	8324	298	120	7670

A series of experiments on the effects of varying the amount of TU-19 sorbent on the removal of H_2S were carried out for 60 min at 500°C (see Table 4 and Figure 2). The removal of H_2S increases with the amounts of the sorbent, but appears to level off above 0.05-g sorbent.

Table 4. Effects of TU-19 sorbent amounts on removal of H_2S with the initial concentration 9107-ppm H_2S and 0.085-g moisture for 1 hour at 500°C.

RUN #	Amount of Sorbent, g	Concentration of H_2S , ppm	RUN #	Amount of Sorbent, g	Concentration of H_2S , ppm
303	0.1013	2074	308	0.0736	2051
303	0.1013	2110	308	0.0736	1976
304	0.2008	1452	309	0.0495	2223
304	0.2008	1477	309	0.0495	2278
304	0.2008	1569	310	0.3870	1390
304	0.2008	1536	310	0.3870	1884
305	0.0542	1706	310	0.3870	1629
305	0.0542	1749	310	0.3870	1680
306	0.0247	3718	310	0.3870	1696
306	0.0247	3205	312	0.0728	1937
306	0.0247	3162	312	0.0728	1812
307	0.0143	5051	312	0.0728	1987
307	0.0143	4974	313	0.0077	4181
			313	0.0077	4515

Reactivity of 0.1-g TU-19 sorbent was investigated in the presence of the initial concentration 9107-ppm H_2S and 0.085-g moisture at 500°C and various reaction times (see Table 5 and Figure 3). These experimental data showed that most absorption of H_2S into the sorbent occurs during the first 5-min reaction time.

Table 5. Reactivity of 0.1-g TU-19 sorbent with the initial concentration 9107-ppm H₂S in the presence of 14.7-psia H₂ (room temperature) and 0.085-g moisture at 500°C

Run #	Reaction Time, min	Concentration of H ₂ S, ppm	Run #	Reaction Time, min	Concentration of H ₂ S, ppm
277	0.5	6288	271	5	3154
277	0.5	6341	279	6	3355
274	1	6452	279	6	3417
274	1	5941	275	7	3343
273	2	5245	275	7	3347
273	2	5262	278	9	3279
280	3	4272	278	9	3248
280	3	4234	281	20	2632
276	4	3831	270	40	1873
276	4	3707	270	40	1921
271	5	3077			

Intraparticle diffusivity of H₂S through the TU-19 sorbent in the form of 1-mm cylindrical rod was evaluated at 500°C, using the following cylindrical rod model. The model was developed with the unreacted core assumption and the quasi steady state assumption. Left-side values of the equation 1 were plotted against the right-side values of the equation 1 (see Table 6 and Figure 4). Intraparticle diffusivity was determined from the slope of this plot. The intraparticle diffusivity of H₂S was found to be 2.018x10⁻³ cm²/s at 500°C.

$$\ln\left(\frac{r}{R}\right)r \frac{dr}{dt} = D_e \left(\frac{b}{b}\right)(1 + Ar^2) + \text{constant} \quad (1) \quad r = (R^2 - \left(\frac{C_{AO} - C_A}{b\pi L \rho_B}\right)V)^{0.5} \quad (2)$$

$$B = \frac{C_{AO}}{\rho_B} - \frac{bV_B}{V} \quad (3) \quad A = \frac{b\pi L}{BV} \quad (4)$$

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

Table 6. Left-side values vs. right-side values of the cylindrical rod model for the reaction of TU-19 sorbent with the initial-concentration 9107-ppm H₂S in the presence of 14.7-psia H₂ (room temperature) and 0.085-g moisture at 500°C.

Right-Side Values of the Cylindrical Rod Model x 1000	Left-Side Values of the Cylindrical Rod Model x 100000
0.70	13.80
0.72	13.33
0.85	10.59
0.88	9.97
0.97	8.65
0.98	8.52
1.19	5.90
1.20	5.86
1.36	4.45
1.44	3.82
1.45	3.73
1.48	3.54

Equilibrium absorption of H₂S into the TU-19 sorbent was investigated at various equilibrium concentrations of H₂S and 500°C. Equilibrium absorption of H₂S into the TU-19 sorbent are 0.02 - 0.16 g-H₂S/g-sorbent in the presence of 14.7-psia H₂ and 0.085-g moisture (see Table 7). Equilibrium absorption of H₂S into the TU-19 sorbent increases with concentrations of H₂S at 500°C and 450 psia (see Figure 5).

FIGURE 5. Equilibrium absorption of H₂S into TU-19 sorbent in the presence of 14.7-psia H₂ (room temperature) and 0.085-g moisture at 500°C.

Table 7. Equilibrium absorption of H₂S into TU-19 sorbent in the presence of 14.7-psia H₂ (room temperature) and 0.085-g moisture at 500°C.

RUN #	Amount of Sorbent, g	Equilibrium Concentration of H ₂ S, ppm	Equilibrium Absorption of H ₂ S, g/g-sorbent	RUN #	Amount of Sorbent, g	Equilibrium Concentration of H ₂ S, ppm	Equilibrium Absorption of H ₂ S, g/g-sorbent
307	0.0143	5051	0.1131	304	0.2008	1452	0.0181
307	0.0143	4974	0.1162	304	0.2008	1477	0.0181
306	0.0247	3205	0.1076	312	0.0728	1937	0.0463
306	0.0247	3162	0.1085	312	0.0728	1812	0.0473
309	0.0495	2223	0.0648	335	0.0087	5445	0.1605
309	0.0495	2278	0.0642	335	0.0087	5548	0.1538
308	0.0736	2051	0.0449	336	0.0199	4875	0.0863
308	0.0736	1976	0.0455	336	0.0199	4885	0.0860
303	0.1013	2074	0.0325				
303	0.1013	2110	0.0323				

Equilibrium absorption of H₂S into the TU-19 sorbent are 0.03 - 0.20 g-H₂S/g-sorbent in the presence of 24.7-psia H₂ and 0.085-g moisture (see Table 8). These data may indicate that absorption data at high pressures are higher than those at low pressures, which were investigated with the thermogravimetric analyzer (TGA) by many researchers. Equilibrium absorption of H₂S into the TU-19 sorbent increases with concentrations of H₂S (see Figure 6). Effects of equilibrium concentrations of H₂S on equilibrium absorption of H₂S into the sorbent matrix may show that a portion of H₂S is

adsorbed on active sites of the sorbent matrix, rather than absorbed into the sorbent matrix.

Table 8. Equilibrium absorption of H₂S into TU-19 sorbent in the presence of 24.7-psia H₂ (room temperature) and 0.085-g moisture at 500°C.

RUN #	Amount of Sorbent, g	Equilibrium Concentration of H ₂ S, ppm	Equilibrium Absorption of H ₂ S, g/g-sorbent	RUN #	Amount of Sorbent, g	Equilibrium Concentration of H ₂ S, ppm	Equilibrium Absorption of H ₂ S, g/g-sorbent
314	0.0531	2817	0.0485	318	0.0232	3236	0.1009
314	0.0531	2776	0.0490	319	0.0696	2288	0.0413
315	0.1003	2090	0.0298	320	0.2037	2030	0.0148
315	0.1003	2012	0.0302	321	0.051	2106	0.0584
316	0.0104	3577	0.2067	333	0.0162	2689	0.1635
316	0.0104	3619	0.2044	333	0.0162	2713	0.1627
317	0.0051	5606	0.1977	334	0.0086	4672	0.1783
317	0.0051	5882	0.1673	334	0.0086	4941	0.1607
317	0.0051	5835	0.1724	334	0.0086	4483	0.1907

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 7). This observation may indicate that partial

pressure of hydrogen appears to affect significantly equilibrium absorption of H_2S into the sorbent.

The equilibrium absorption curve of the TU-19 sorbent is quite different from that of the TU-28 sorbent in the presence of 24.7-psia H_2 and 0.085-g moisture at 500°C (see Table 9, and Figures 8 and 9). This fact may suggest that formulation procedures and methods affect equilibrium absorption capacity of sorbents (see Table 1).

Table 9. Equilibrium absorption of H_2S into TU-28 sorbent in the presence of 24.7-psia H_2 (room temperature) and 0.085-g moisture at 500°C.

RUN #	Amount of Sorbent, g	Equilibrium Concentration of H_2S , ppm	Equilibrium Absorption of H_2S , g/g-sorbent	RUN #	Amount of Sorbent, g	Equilibrium Concentration of H_2S , ppm	Equilibrium Absorption of H_2S , g/g-sorbent
324	0.0324	3420	0.0691	329	0.0081	5345	0.1426
324	0.0324	3466	0.0683	329	0.0081	5216	0.1516
323	0.0514	3268	0.0452	329	0.0081	5468	0.1341
323	0.0514	3303	0.0448	330	0.0096	5412	0.1164
328	0.0411	2812	0.0628	330	0.0096	5306	0.1226
328	0.0411	2807	0.0628	331	0.0198	4238	0.0898
325	0.0752	2366	0.0376	331	0.0198	4348	0.0867
325	0.0752	2392	0.0375	332	0.2019	2050	0.0149
325	0.0752	2202	0.0389	332	0.2019	2120	0.0147
329	0.0081	5845	0.1079				

FIGURE 8. Equilibrium absorption of H_2S into TU-28 sorbent in the presence of 24.7-psia H_2 (room temperature) and 0.085-g moisture at 500°C.

FIGURE 9. Effects of formulation procedures on equilibrium absorption of H_2S into sorbents with 24.7-psia H_2 and 0.085-g moisture at 500°C.

ACCOMPLISHMENTS

The 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-28 sorbent was found to be $2.018 \times 10^{-3} \text{ cm}^2/\text{s}$ at 500°C .

Equilibrium absorption of H_2S into the TU-19 sorbent increases with concentrations of H_2S . Partial pressures of hydrogen appear to affect significantly equilibrium absorption of H_2S into the sorbent.

PRESENTATION

The research paper, entitled "Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperature and Pressure", was submitted for publication in Separation Science and Technology. A research paper, entitled "Removal of Hydrogen Sulfide from Simulated Coal Gases, Using Metal Oxide Sorbents at High Temperature and High Pressure", was accepted for presentation at The Fourth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Greensboro, North Carolina, April 2-4, 1996.

PLANS ON FUTURE EXPERIMENTS

Various metal oxide sorbents will be formulated by a physical mixing method in order to search for a formulation of a durable sorbent with high-sulfur-absorbing capacity. Initial absorption kinetics of H_2S into fresh formulated sorbents will be investigated with the 35 cm^3 316 SS batch reactor at 500°C . A continuous differential reactor will be designed and fabricated, and tested. Durability of formulated sorbents will be examined.