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

Quarterly Report

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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 initial reaction rates of hydrogen sulfide with the formulated TU-24 and TU-25 sorbents for 30 -150 seconds at 400 - 550°C, to evaluate initial reaction rates of hydrogen sulfide with the formulated sorbents using reaction data of H₂S concentrations at various reaction durations, and to develop a reaction rate equation for the disappearance of hydrogen sulfide with the formulated sorbents, employing evaluated reaction rates of H₂S with the formulated sorbents, concentrations of H₂S, and sorbent quantities.

EXPERIMENTAL APPROACH

The metal oxide sorbents 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 1-mm cylindrical rods. The formulated metal oxide sorbents were calcined for 2 hours at 900°C. The ingredients of the TU-24 and the TU-25 sorbents were presented in Table 1. The fresh formulated metal oxide 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 the 35 cm³ 316 stainless steel batch reactor for 30-150 seconds at 400 - 550°C. Concentrations of hydrogen sulfide were analyzed with a gas

chromatograph at various reaction durations to evaluate reaction rates of H_2S as well as dynamic absorption of H_2S into the sorbents.

Table 1. Formulation of TU-24 and TU-25 sorbents.

	TU-24	TU-25
ZnO, g	1.8	0.5
TiO ₂ , g	1.2	2.5
Bentonite, g	0.15	0.15
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 conducting experiments on initial reaction rates of hydrogen sulfide with the formulated sorbents, and developing a reaction rate equation containing a reaction rate constant in terms of disappearance of H_2S , a reaction order with respect to hydrogen sulfide, and a reaction order with respect to the TU-24 metal oxide sorbent.

Experiments on reactivity of hydrogen sulfide contained in a simulated coal gas mixture with the TU-24 and TU-25 metal oxide sorbents were carried out for 30-150 seconds at 400 -550°C (see Table 2). 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 %).

Table 2. Experimental conditions for the reaction of hydrogen sulfide with TU-24 and TU-25 sorbents in the presence of water, nitrogen and hydrogen at 500°C.

Reactor Volume, cm ³ :	35
Temperature, °C:	400 - 550
Reaction Time, s:	30 - 150
Particle Size, mesh	100 - 200
Amount of Sorbent, g	0.015 - 0.24
Initial Partial Pressure of Hydrogen at 25°C, psia:	14.7 - 24.7
Initial Amount of Water, g:	0.085
Initial Concentration of H_2S , 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

Reactivity of H_2S with the reactor wall was investigated in the absence of sorbents for 1 min at 450 -550°C. The concentration of H_2S was decreased from the initial concentration 9107 ppm to 8700 ppm for the 1 min reaction duration, as shown in Table 3 and Figure 1. These experimental data were incorporated in calculating reaction rates of H_2S with the formulated sorbents as well as dynamic absorption of H_2S into the formulated sorbents.

Table 3. Reactivity of H_2S with the reactor wall in the presence of initial concentration 9107-ppm H_2S , 0.085-g moisture and initial 14.7-psia H_2 for 1 min at various temperatures.

Run #	Temperature, °C	Concentration of H_2S , ppm	Run #	Temperature, °C	Concentration of H_2S , ppm
374	500	8742	399	450	8543
378	550	8437	399	450	8795
378	550	8578	400	550	8676
382	550	8710	400	550	8977
386	550	8819	400	550	8950
390	450	9068	406	550	8858
393	450	8480	406	550	8844
393	450	8831	413	550	8688

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°C, as shown in Tables 4 and 5, and Figure 2. Reaction rates of H_2S with the TU-25 sorbent increase with amounts of the sorbent. 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. These data may

suggest that hydrogen itself affects initial reaction rates of H_2S with the formulated TU-25 sorbent.

Table 4. Reactivity of 100-200 mesh TU-25 sorbent with initial 8675-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at 500°C.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
364	0.0101	7915	0.40	0.04586	363	0.1004	5207	1.69	0.01931
364	0.0101	7544	0.58	0.06588	363	0.1004	5425	1.59	0.01813
362	0.031	6876	0.90	0.03321	367	0.1529	5170	1.71	0.01281
362	0.031	7331	0.68	0.02521	367	0.1529	4641	1.96	0.01470
362	0.031	7538	0.58	0.02157	368	0.2073	3807	2.36	0.01303
366	0.0489	6528	1.07	0.02493	368	0.2073	4980	1.80	0.00995
366	0.0489	7369	0.66	0.01556	368	0.2073	5013	1.79	0.00986
365	0.0696	6334	1.16	0.01903	368	0.2073	4999	1.79	0.00990
363	0.1004	4735	1.92	0.02187	368	0.2073	4856	1.86	0.01028

Table 5. Reactivity of 100-200 mesh TU-25 sorbent with initial 8014-ppm H_2S in the presence of 0.085-g moisture and initial 24.7-psia hydrogen for 60 seconds at 500°C.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
377	0.0106	6961	0.50	0.0541	369	0.0538	6688	0.63	0.0134
370	0.013	7333	0.32	0.0285	369	0.0538	7074	0.45	0.0095
376	0.0233	6907	0.53	0.0259	373	0.0752	6246	0.84	0.0128
372	0.0328	7056	0.46	0.0159	371	0.1014	6825	0.57	0.0064
372	0.0328	6468	0.74	0.0257	371	0.1014	6813	0.57	0.0065
372	0.0328	7097	0.44	0.0152	371	0.1014	6371	0.78	0.0088

Figure 2. Effects of hydrogen pressures on reactivity of 100-200 mesh TU-25 sorbent with H_2S in the presence of 0.085-g moisture for 1 min at 500°C.

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 $500^\circ C$, as shown in Tables 4 and 5, and Figure 3. 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. Dynamic absorption of H_2S into the sorbent decreases with increased quantities of the sorbent. This observation may indicate that dynamic absorption of H_2S into the sorbent is affected by partial pressures of hydrogen.

Various amounts of 100-200 mesh TU-25 sorbent were reacted with H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min at various temperatures to identify effects of reaction temperatures on reactivity of H_2S with the TU-25 sorbent, as shown in Tables 4, 6 and 7, and Figure 4. Reactivity of H_2S with the TU-25 sorbent increases with reaction temperatures, as expected. Reaction rates of H_2S with the TU-25 sorbent increase with increased quantities of the sorbent up to 0.1-g sorbent. However, reaction rates of H_2S with the TU-25

Table 6. Reactivity of 100-200 mesh TU-25 sorbent with initial 8694-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at $450^\circ C$.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
391	0.013	8549	0.07	0.0061	397	0.073	7221	0.70	0.0110
391	0.013	8674	0.01	0.0008	397	0.073	7199	0.71	0.0112
396	0.0299	7939	0.36	0.0138	396	0.0299	7913	0.37	0.0142
396	0.0299	8050	0.31	0.0117	397	0.073	7065	0.78	0.0122
392	0.0528	7457	0.59	0.0128	394	0.1004	7026	0.79	0.0091
392	0.0528	7563	0.54	0.0117	394	0.1004	7333	0.65	0.0074

sorbent for 1 min at 500°C appear to level off above 0.1-g sorbent, as observed from the previous experimental results.

Table 7. Reactivity of 100-200 mesh TU-25 sorbent with initial 8675-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at 550°C.

Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent
380	0.013	8022	0.31	0.0274	388	0.0405	7680	0.47	0.0134
380	0.013	8472	0.10	0.0085	381	0.0492	6902	0.84	0.0196
380	0.013	7631	0.50	0.0438	384	0.0715	5449	1.54	0.0246
387	0.0152	7579	0.52	0.0393	384	0.0715	5755	1.39	0.0223
387	0.0152	8120	0.26	0.0199	384	0.0715	5642	1.44	0.0231
379	0.0279	8051	0.30	0.0122	383	0.1043	3429	2.50	0.0274
379	0.0279	7225	0.69	0.0283	383	0.1043	2854	2.77	0.0304
388	0.0405	7008	0.79	0.0224

Effects of temperatures on dynamic absorption of H₂S into the TU-25 sorbent were investigated, as shown in Figure 5. Dynamic absorption of H₂S into the sorbent was calculated from changes in concentrations of H₂S in the reactor. Dynamic absorption of H₂S appears to be dependent on amounts of the sorbents as well as reaction temperatures. Dynamic absorption of H₂S increases generally with increased reaction temperatures. Dynamic absorption of H₂S into the TU-25 sorbent decreases with increased quantities of the sorbent for the 1-min reaction duration at the reaction temperature range of 500°C - 550°C up to 0.04-g sorbent. Dynamic absorption of H₂S into the sorbent for the 1-min reaction duration at 550°C appears to be almost same as that at 500°C up to 0.04-g sorbent.

Dynamic absorption of H_2S into the TU-25 sorbent increases with increased quantities of the sorbent for the 1-min reaction duration at $450^\circ C$ up to 0.04-g sorbent. Dynamic absorption of H_2S into the sorbent for the 1-min reaction duration at $450^\circ C$ appears to be almost same as that at $500^\circ C$ above 0.04-g sorbent. Dynamic absorption of H_2S into the TU-25 sorbent increases with increased quantities of the sorbent for the 1-min reaction duration at $550^\circ C$ above 0.04-g sorbent. These observation may suggest that absorption mechanisms on absorption of H_2S into the TU-25 sorbent are dependent on absorption temperatures.

Reproducibility of formulating the TU-25 sorbent was examined by comparing its reactivity with H_2S in the presence of 0.085-g moisture and 14.7-psia hydrogen for 1 min at $550^\circ C$, as shown in Tables 7 and 8, and Figure 6. The reactivity of the sorbent appeared to be independent of batch processing at below 0.04-g sorbent, while the reactivity of the sorbent from the batch 1 was higher than that from the batch 2 above 0.04-g sorbent. These data may indicate that reproducibility of formulation for the TU-25 sorbent is very poor.

Table 8. Reactivity of 100-200 mesh duplicated TU-25 sorbent with initial 8702-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at $550^\circ C$.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
411	0.014	7772	0.44	0.0362	408	0.0715	6824	0.89	0.0143
411	0.014	8117	0.28	0.0228	408	0.0715	6593	1.00	0.0161
409	0.0207	7827	0.42	0.0230	408	0.0715	6673	0.97	0.0155
409	0.0207	8045	0.31	0.0173	410	0.0812	6348	1.12	0.0158
407	0.0266	7697	0.48	0.0206	410	0.0812	6318	1.14	0.0160
407	0.0266	7487	0.58	0.0249	410	0.0812	6235	1.17	0.0166
407	0.0266	7507	0.57	0.0245	402	0.0994	6695	0.96	0.0110
403	0.0497	6967	0.83	0.0190	402	0.0994	6848	0.88	0.0102
403	0.0497	6952	0.83	0.0192	402	0.0994	6727	0.94	0.0108
403	0.0497	7137	0.75	0.0172	404	0.1001	6653	0.98	0.0112
412	0.0622	6549	1.03	0.0189	404	0.1001	6663	0.97	0.0111
412	0.0622	6667	0.97	0.0178

Reproducibility of formulation for the TU-25 sorbent was examined by comparing dynamic absorption of H_2S into the sorbent in the presence of 0.085-g moisture and 14.7-psia hydrogen for 1 min at 550°C, as shown in Tables 7 and 8, and Figure 7. Dynamic absorption of H_2S into the sorbent from the batch 1 processing appeared to be higher than that from the batch 2.

The 100-200 mesh TU-24 sorbent was reacted with H_2S for short reaction durations at various reaction temperatures, as shown in Tables 9 through 12, and Figure 8. 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 may indicate that reactivity of H_2S with the TU-24 sorbent is a function of reaction temperatures and amounts of the TU-24 sorbent.

Table 9. Reactivity of 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min at 400 °C.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
437	0.0131	7777	0.44	0.0385	439	0.0552	6302	1.14	0.0237
437	0.0131	7201	0.71	0.0625	439	0.0552	5825	1.37	0.0284
437	0.0131	7475	0.58	0.0510	439	0.0552	6052	1.26	0.0262
438	0.0304	7276	0.68	0.0256	440	0.0828	6011	1.28	0.0177
438	0.0304	6827	0.89	0.0336	440	0.0828	5657	1.45	0.0200
438	0.0304	6999	0.81	0.0305	440	0.0828	5736	1.41	0.0195

Table 10. Reactivity of 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min at 450 °C.

Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H_2S , ppm	Reaction Rate of H_2S , ppm/cc/s	Adsorption of H_2S , g/g-sorbent
433	0.0116	7333	0.65	0.0639	434	0.0297	6510	1.04	0.0401
433	0.0116	7509	0.56	0.0557	434	0.0297	6623	0.99	0.0380
433	0.0116	7492	0.57	0.0565	435	0.0491	5602	1.47	0.0343
433	0.0116	7519	0.56	0.0552	435	0.0491	5921	1.32	0.0308
434	0.0297	6505	1.04	0.0402	436	0.083	4503	2.00	0.0275
434	0.0297	6167	1.20	0.0464	436	0.083	3620	2.42	0.0333

Figure 8. Effects of temperatures on reactivity of 100-200 mesh TU-24 sorbent with H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min.

Table 11. Reactivity of 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at 500 °C.

Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent
424	0.0159	7218	0.71	0.0509	425	0.05	6425	1.08	0.0248
424	0.0159	7525	0.56	0.0403	425	0.05	6260	1.16	0.0266
424	0.0159	7251	0.69	0.0497	425	0.05	6168	1.21	0.0276
427	0.0309	5514	1.52	0.0562	426	0.0778	4587	1.96	0.0288
427	0.0309	5661	1.45	0.0536	426	0.0778	4366	2.06	0.0304
427	0.0309	5393	1.58	0.0584	426	0.0778	4501	2.00	0.0294

Table 12. Reactivity of 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 60 seconds at 550 °C.

Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent	Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm	Reaction Rate of H ₂ S, ppm/cc/s	Adsorption of H ₂ S, g/g-sorbent
428	0.0135	7063	0.78	0.0662	432	0.0704	3530	2.46	0.0400
429	0.033	5533	1.51	0.0523	428	0.0135	7115	0.76	0.0641
430	0.0468	4955	1.78	0.0436	429	0.033	5543	1.50	0.0522
431	0.0772	4154	2.17	0.0321	430	0.0468	4896	1.81	0.0443
431	0.0772	4238	2.13	0.0315					

Dynamic absorption of H₂S into the TU-24 sorbent increases with increased dynamic absorption temperatures, and decreases with increased amounts of the TU-24 sorbent for the 1-min absorption duration, as shown in Figure 9. These experimental data may suggest that dynamic absorption of H₂S into the sorbent is dependent on absorption temperatures as well as amounts of the TU-24 sorbent. These observations also were found from the previous experiments on equilibrium absorption of H₂S into formulated sorbents.

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 10. Concentrations of H_2S decrease with increased reaction durations as well as increased amounts of the sorbent. These facts may suggest that reaction rates of H_2S with the TU-24 sorbent may be dependent on reaction durations as well as quantities of the TU-24 sorbent.

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 11.

Reaction rates of H_2S with the TU-24 sorbent at 500°C were obtained from the experimental data of H_2S concentrations at various reaction durations, as shown in Tables 13 through 16, and

Figure 12. Reaction rates of H₂S with the TU-24 sorbent at 500°C increase with amounts of the sorbent, and decrease with reaction durations.

Table 13. Reactivity of 0.015-g 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500 °C.

Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent	Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent
450	30	7900	0.67	0.0291	452	90	6880	0.28	0.0661
450	30	7741	0.67	0.0348	453	120	6606	0.09	0.0761
451	60	7480	0.48	0.0443	453	120	6215	0.09	0.0903
451	60	7133	0.48	0.0569	454	150	6865	—	0.0667
452	90	7259	0.28	0.0524	454	150	6714	—	0.0721

Table 14. Reactivity of 0.03-g 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500 °C.

Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent	Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent
441	30	7749	0.91	0.0173	443	120	5189	0.73	0.0638
441	30	7664	0.91	0.0188	444	150	5434	0.67	0.0593
441	30	7741	0.91	0.0174	444	150	5318	0.67	0.0614
442	90	6400	0.79	0.0418	444	150	5288	0.67	0.0620
442	90	6491	0.79	0.0401	438	60	7276	0.85	0.0259
442	90	6293	0.79	0.0437	438	60	6827	0.85	0.0340
443	120	5531	0.73	0.0576	438	60	6999	0.85	0.0309
443	120	5319	0.73	0.0614					

Table 15. Reactivity of 0.05-g 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500 °C.

Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent	Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent
—	0	8702	2.40	—	447	90	4157	0.69	0.0495
445	30	6459	1.83	0.0244	447	90	3924	0.69	0.0521
445	30	6460	1.83	0.0244	448	120	3232	0.11	0.0596
445	30	6221	1.83	0.0270	448	120	3097	0.11	0.0611
446	60	4525	1.26	0.0455	448	120	2888	0.11	0.0634
446	60	4871	1.26	0.0418	449	150	3598	—	0.0556
446	60	4692	1.26	0.0437	449	150	3721	—	0.0543
446	60	4426	1.26	0.0466	449	150	3415	—	0.0576

Table 16. Reactivity of 0.075-g 100-200 mesh TU-24 sorbent with initial 8765-8702-ppm H₂S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500 °C.

Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent	Run #	Reaction Duration, s	Concentration of H ₂ S, ppm	Reaction Rate, ppm/cc/s	Absorption of H ₂ S, g/g-sorbent
455	30	5970	1.85	0.0198	457	90	2664	0.84	0.0439
455	30	5446	1.85	0.0236	457	90	2987	0.84	0.0415
455	30	5443	1.85	0.0237	457	90	3080	0.84	0.0408
455	30	5595	1.85	0.0226	458	120	2674	0.34	0.0438
456	60	4738	1.34	0.0288	458	120	2641	0.34	0.0440
456	60	4559	1.34	0.0301	458	120	2662	0.34	0.0439
456	60	4540	1.34	0.0302	459	150	2270	-0.17	0.0467
456	60	4702	1.34	0.0290	459	150	2422	-0.17	0.0456
457	90	3117	0.84	0.0406	459	150	2457	-0.17	0.0454
457	90	3257	0.84	0.0395					

Figure 13. Reaction rates of H₂S with 100-200 mesh TU-24 sorbent in the presence of initial 14.7-psia H₂ and 0.085-g moisture at 500°C and various quantities of the sorbent.

Figure 13 shows that reaction rates of H_2S with the 100 - 200 mesh TU-24 sorbent increase with increased quantities of the sorbent and decreased reaction durations. Figure 14 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 .

The following reaction rate equation may be proposed, since reaction rates of H_2S with TU-24 sorbent are dependent on concentrations of H_2S and quantities of the sorbent, as shown in Figures 13 and 14.

$$-r_A = k_A C_A^\alpha M_S^\beta \quad (1)$$

where $-r_A$: reaction rates of H_2S , g-mole/cm³/s

C_A : concentrations of H_2S , g-mole/cm³

M_S : quantities of sorbents, g/cm³

k_A : reaction rate constant in terms of disappearance of H_2S , cc^($\alpha+\beta-1$)/g ^{β} /g-mole^($\alpha-1$)/s

α : reaction order with respect to concentrations of H_2S

β : reaction order with respect to quantities of sorbents

cc: cm³

The equation (1) is linearized by applying a logarithm to the both sides of the proposed reaction rate equation. The following linearized equation is obtained to evaluate k_A , α and β .

$$\ln(-r_A) = \ln(k_A) + \alpha \ln(C_A) + \beta \ln(M_S) \quad (2)$$

The experimental data of H_2S concentrations at various reaction durations are applied to equation (2), and then the reaction rate equation constant k_A and the reaction orders such as α

and β are obtained using the multiple linear regression method as well as the Gauss-Seidel method, as shown in equation 4.

$$-r_A = 9908 C_A^{1.5165} M_S^{1.1397} \quad (3)$$

The reaction rate constant k_A in terms of disappearance of H_2S was found to be 9908 $cm^{4.9686}/g^{1.1397}/g\text{-mole}^{0.5165}/s$ at the reaction temperature 500°C. The reaction order α with respect to concentrations of H_2S was found to be 1.5165, while the reaction order β 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 3), as shown in Figure 15.

ACCOMPLISHMENTS

The reaction rate equation in terms of disappearance of H_2S for 30 -150 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 in terms of disappearance of H_2S was found to be 9908 $cm^{4.9686}/g^{1.1397}/g\text{-mole}^{0.5165}/s$ at the reaction temperature 500°C. The reaction order with respect to the concentration of H_2S was found to be 1.5165, while the reaction order with respect to the quantity 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°C. Reactivity of the TU-25

sorbent with H_2S was found to be significantly affected by partial pressures of hydrogen. Dynamic absorption of H_2S into the sorbent also is affected by partial pressures of hydrogen. Dynamic absorption of H_2S into the 100-200 mesh TU-25 sorbent decreases with increased sorbent quantities and decreased reaction temperatures.

PRESENTATION

The research paper, entitled "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. A research paper, entitled "Removal of Hydrogen Sulfide from Simulated Coal Gases, Using Metal Oxide Sorbents at High Temperature and High Pressure", was presented at The Fourth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Greensboro, North Carolina, April 2-4, 1996. A research paper, entitled "Reactivity of Metal Oxide Sorbents", was accepted for presentation at the Advanced Coal-Fired Power Systems '96 Review Meeting, Morgantown Energy Technology Center, West Virginia, July 16-18, 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 reaction kinetics of H_2S with fresh formulated sorbents will be investigated in the 35 cm³ 316 SS batch reactor at 450°C as well as 550°C.

APPENDIX A

A FORTRAN computer program for the development of a reaction rate equation of H_2S with the TU-24 sorbent at $500^\circ C$.

```

CC      MULTIPLE LINEAR LEAST SQUARES METHOD AND GAUSS-SEIDEL METHOD.
CC      *****
REAL K, K1A, K2A, K1E, K2E, KT, KB, ka
DIMENSION P(60), hs(60), CASR(60), A(60), ra(60), DELQ(60), DELQSQ(60)
DIMENSION X1(60), X2(60), X3(60), RQE(60), X1E(60), RT(60), sa(60)
dimension rap(60)
OPEN(6, FILE='Q-1-3-96.gen', STATUS='old')
WRITE(*,10)
10      FORMAT(' HOW MANY DATA POINTS ARE THERE? ')
      READ(*,102) N
102     FORMAT(I2)
105     FORMAT(e20.10)
      WRITE(*,30) N
30      FORMAT(' ENTER',I4,' reaction rate, g-mole-H2S/cc/s')
      READ(*,105) (ra(I), I=1,N)
      WRITE(*,40) N
40      FORMAT(' ENTER',I4,' concentration of H2S, g-mole/cc')
      READ(*,105) (hs(I), I=1,N)
      WRITE(*,410) N
410     FORMAT(' ENTER',I4,' amount of sorbent, g/cc')
      READ(*,105) (sa(I), I=1,N)
      WRITE(6,250)
      WRITE(*,250)
250     FORMAT('      RA g-mole/cc/s   H2S g-mole/cc      MS, g/cc ')
      SUMX1=0.0
      SUMX2=0.0
      SUMX3=0.0
      SUMX1S=0.0
      SUMX2S=0.0
      SUMX3S=0.0
      SMX1X2=0.0
      SMX1X3=0.0
      SMX2X3=0.0
      DO 200 I=1,N
        X1(I)=alog(ra(I))
        X2(I)=alog(hs(I))
        X3(I)=alog(sa(I))
        SUMX1=SUMX1+X1(I)
        SUMX2=SUMX2+X2(I)
        SUMX3=SUMX3+X3(I)
        SUMX1S=SUMX1S+X1(I)*X1(I)
        SUMX2S=SUMX2S+X2(I)*X2(I)
        SUMX3S=SUMX3S+X3(I)*X3(I)
        SMX1X2=SMX1X2+X1(I)*X2(I)
        SMX1X3=SMX1X3+X1(I)*X3(I)
        SMX2X3=SMX2X3+X2(I)*X3(I)
        WRITE(6,300) ra(I), hs(I), sa(I)
200     WRITE(*,300) ra(I), hs(I), sa(I)

```

```

WRITE(*,565)
565  FORMAT(' ')
WRITE(*,570)
570  FORMAT(' ')
WRITE(*,500)
500  FORMAT(' HOW MANY COEFFICIENTS ARE THERE')
READ (*,102) M
WRITE(*,510) M
510  FORMAT(' ENTER',I3, 'INITIAL ASSUMED COEFFICIENTS')
READ(*,105) (A(I), I=1,M)
WRITE(*,520)
WRITE(6,520)
520  FORMAT('      A1      A2      A3')
SUMK=0.0
600  AA=A(1)
K=N
A(1)=(SUMX1-A(2)*SUMX2-A(3)*SUMX3)/K
A(2)=(SMX1X2-A(1)*SUMX2-A(3)*SMX2X3)/SUMX2S
A(3)=(SMX1X3-A(1)*SUMX3-A(2)*SMX2X3)/SUMX3S
SUMK=SUMK+1.
300  FORMAT(5E13.6)
IF(ABS(AA-A(1)).GE.1.E-6) GOTO 600
WRITE(6,300) A(1), A(2), A(3)
WRITE(*,300) A(1), A(2), A(3)
WRITE(*,570)
WRITE(*,570)
WRITE(6,310)
WRITE(*,310)
310  FORMAT('      kA      alpha      betta')
WRITE(*,315)
WRITE(6,315)
315  FORMAT(' cc(a+b-1)/gb/g-mole(a-1)/s      ----      ----')
Ka=exp(A(1))
al=A(2)
be=A(3)
WRITE(6,300) Ka,al,be
WRITE(*,300) Ka,al,be
WRITE(*,550)
WRITE(6,550)
550  format('      RA actual      RA predicted, g-mole/cc/s')
do 700 i=1,n
rap(i)=ka*(HS(I)**al)*(sa(i)**be)
write(6,300)ra(i), rap(i)
700  write(*,300)ra(i), rap(i)
STOP
END

```