ENERGY

INVESTIGATION ON DURABILITY AND REACTIVITY OF PROMISING METAL OXIDE SORBENTS DURING SULFIDATION AND REGENERATION

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Technical Progress Report for the Period
July 1 to September 30, 1997

By
K. C. Kwon

December 1997

Work Performed Under Contract no DE-FG21-94MC31206–14

For
U.S. Department of Energy
Federal EnergyTechnology Center
Morgantown, West Virginia

By
Tuskegee University
Tuskegee, Alabama

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Morgantown, West Virginia 26507-0880

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Tuskegee, Alabama 36088

DISCLAIMER

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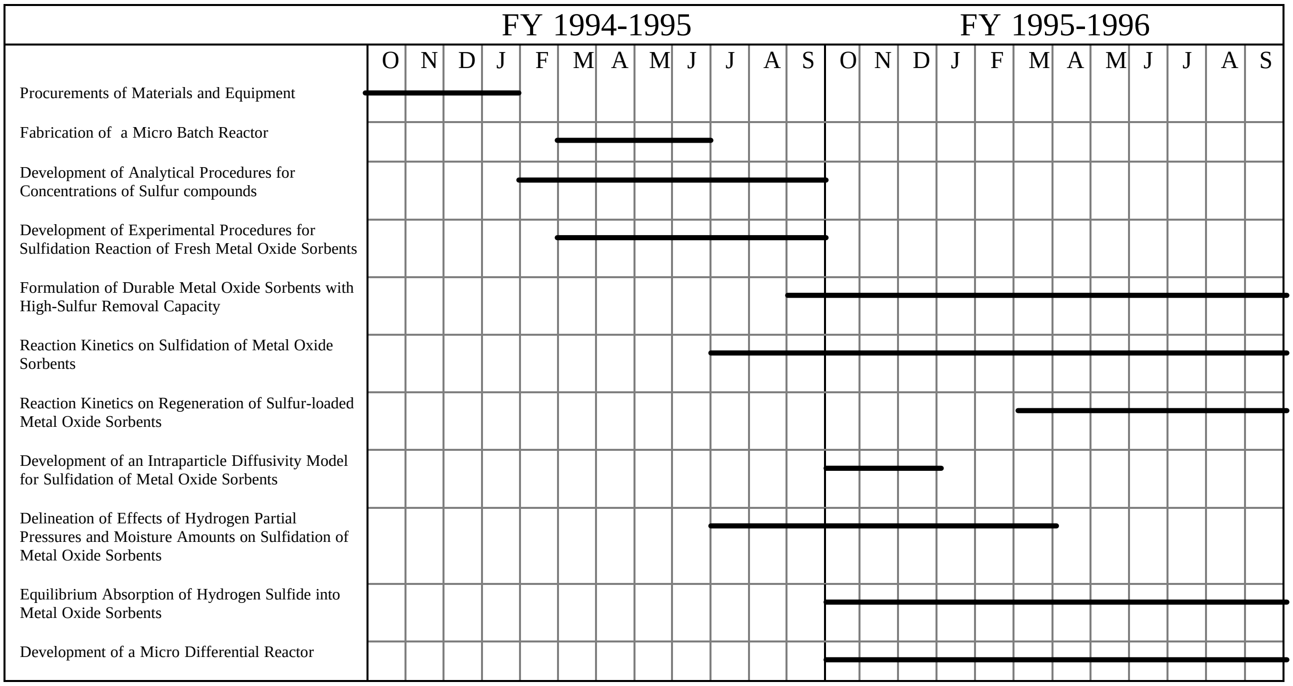


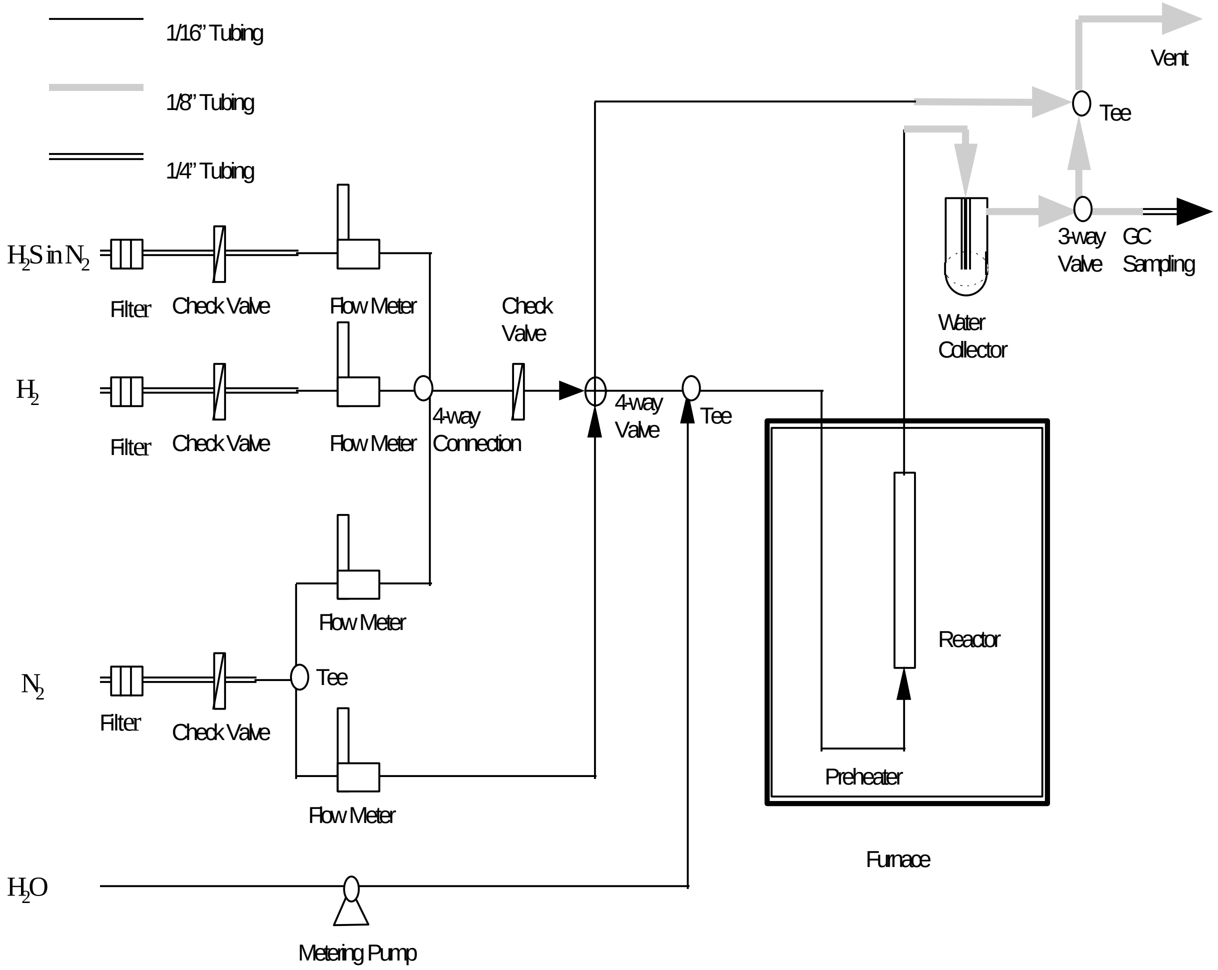
EXECUTIVE SUMMARY

The main objectives of this research project during this quarter are to investigate effects of hydrogen, moisture, concentrations of H_2S, and residence time of reaction gas mixtures on equilibrium absorption as well as dynamic absorption of H_2S into the TU-188 sorbent at 530°C, and to evaluate effective diffusivity of H_2S through the sorbent particles, using the newly-fabricated differential reactor.

INTRODUCTION

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.

Figure 1. A Differential Reactor Assembly



EXPERIMENTAL SETUP/PROCEDURE

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 the reaction mixture.

RESULTS AND DISCUSSION

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 gas on absorption of hydrogen sulfide into the sorbent, using a newly designed differential reactor.

Experiments on absorption of wet hydrogen sulfide into the sorbent were carried out for 5 – 25000 seconds at 530°C (see Table 1) to evaluate effects of moisture concentrations, hydrogen concentrations, space time, H_2S concentrations on dynamic absorption of hydrogen sulfide into the sorbent. 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 1 atm. The temperature of the reactor is controlled in the furnace oven at 530°C. The pressure of the reactor is maintained at 104 psia. Experimental data of absorption of H_2S into the TU-188 sorbent at various absorption duration's were shown in Tables 2 - 4.

TABLE 1. 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:	8
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, cc/min at room temperature	100 - 300
Hydrogen, vol %	0 - 33
Moisture, vol %:	0 - 10
Concentration of H_2S, ppm	2500 - 7500
Nitrogen, vol %	10 - 40

A series of experiments on absorption of H_2S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of H_2S concentrations on initial reaction of H_2S 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 H_2S decreases with increased concentrations of H_2S 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 H_2S into micro pores of the sorbent with increased concentrations of H_2S.

Table 2. Weight gain of 0.1-g TU-188 sorbent in reaction with H_2S at 300 scc/min gas flow rate and 530^oC.

Run # 1	Absorption Duration, s	Weight Gain, g	Run # 2	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	4.7	0.0002	H_2S Concentration, ppmv : 7500	5.17	0.0003
H_2O Concentration, vol % 10	30.28	0.0002	H_2O Concentration, vol % 10	15.57	0.0002
H_2 Concentration, vol %: 15	50.74	0.0006	H_2 Concentration, vol %: 15	30.81	0.0003
N_2 Concentration, vol %: 74.5	75.46	0.0008	N_2 Concentration, vol %: 74.25	51.29	0.0004
	106.06	0.001		75.43	0.0006
	151.3	0.0015		105.75	0.0008
				150.8	0.001

Run # 3	Absorption Duration, s	Weight Gain, g	Run # 4	Adsorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 2500	5.14	0.0002	H_2S Concentration, ppmv : 2500	4.88	0.0004
H_2O Concentration, vol % : 10	15.68	0.0004	H_2O Concentration, vol % : 10	14.83	0.0004
H_2 Concentration, vol %: 15	31.12	0.0006	H_2 Concentration, vol %: 15	35.07	0.0007
N_2 Concentration, vol %: 74.75	76.7	0.0009	N_2 Concentration, vol %: 74.75	74.66	0.001
	107.03	0.0008		114.59	0.001
	152.06	0.0011		153.76	0.0013

Run # 5	Absorption Duration, s	Weight Gain, g	Run # 6	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	5.54	1E-04	H_2S Concentration, ppmv : 5000	5.11	0.0002
H_2O Concentration, vol % : 6.5	14.9	0.0007	H_2O Concentration, vol % : 3.5	15.46	1E-04
H_2 Concentration, vol %: 15	34.83	0.0005	H_2 Concentration, vol %: 15	35.01	0.0003
N_2 Concentration, vol %: 78	74.01	0.0008	N_2 Concentration, vol %: 81	74.65	0.0006
	113.4	0.0014		115.11	0.0005
	153.9	0.0016		155.22	0.0007

Run 22	Absorption Duration, s	Weight Gain, g	Run 23	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	61.73	0.000693	H_2S Concentration, ppmv : 5000	30.43	0.0008
H_2O Concentration, vol % : 10	92.02	0.000690	H_2O Concentration, vol % : 10	55.31	0.0008
H_2 Concentration, vol %: 10	152.12	0.000783	H_2 Concentration, vol %: 30	115.74	0.0012
N_2 Concentration, vol %: 79.5	272.54	0.001270	N_2 Concentration, vol %: 59.5	236.17	0.0016
	512.39	0.001744		586.27	0.0026
	992.83	0.002691		1187.16	0.0031
	1952.26	0.003187		2397.26	0.0042
	3752.26	0.003790		4197.26	0.0049
	5552.26	0.003693		7797.26	0.0054
	9152.26	0.004300		11457.27	0.0057
	12752.26	0.004007		15057.27	0.0063
	16352.26	0.003713		18657.27	0.0064
	19952.26	0.003719		22257.27	0.0063

Table 3. Weight gain of 0.1-g TU-188 sorbent in reaction with H_2S at 300 scc/min gas flow rate and 530°C.

Run 7	Absorption Duration, s	Weight Gain, g	Run # 8	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	5.49	1E-04	H_2S Concentration, ppmv : 5000	5.48	0.0004
H_2O Concentration, vol % : 0	15.49	1E-04	H_2O Concentration, vol % : 10	15.95	0.0007
H_2 Concentration, vol %: 15	35.96	0.0004	H_2 Concentration, vol %: 25	35.99	0.0007
N_2 Concentration, vol %: 84.5	114.78	0.0005	N_2 Concentration, vol %: 63.5	76.26	0.0014
	155.27	0.0004		114.04	0.0011
				153.24	0.0013

Run # 9	Absorption Duration, s	Weight Gain, g	Run 10	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	5.11	0.0002	H_2S Concentration, ppmv : 5000	5.82	0.0001
H_2O Concentration, vol % : 10	15.46	1E-04	H_2O Concentration, vol % : 10	16.58	0.0003
H_2 Concentration, vol %: 5	35.01	0.0003	H_2 Concentration, vol %: 33	36.61	1E-04
N_2 Concentration, vol %: 84.5	74.65	0.0006	N_2 Concentration, vol %: 56.5	76.93	0.0008
	115.11	0.0005		116.34	0.0011
	155.22	0.0007			

Run 11	Absorption Duration, s	Weight Gain, g	Run 12	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	5.71	0.0003	H_2S Concentration, ppmv : 5000	20.57	0.0002
H_2O Concentration, vol % : 10	16.28	0.0003	H_2O Concentration, vol % : 10	41.4	0.0005
H_2 Concentration, vol %: 15	36.62	0.0003	H_2 Concentration, vol %: 0	62.23	0.0008
N_2 Concentration, vol %: 74.5	76.67	0.0016	N_2 Concentration, vol %: 89.5	83.04	0.0009
	117.14	0.0014		104.16	0.0011
	157.01	0.0013		124.73	0.001
				145.86	0.0012

Run 13	Absorption Duration, s	Weight Gain, g	Run 14	Absorption Duration, s	Weight Gain, g
	0	0		0	0
H_2S Concentration, ppmv : 5000	20.35	1E-04	H_2S Concentration, ppmv : 5000	20.35	1E-04
H_2O Concentration, vol % : 10	42.86	0.0005	H_2O Concentration, vol % : 10	42.86	0.0005
H_2 Concentration, vol %: 5	63.53	0.0003	H_2 Concentration, vol %: 33	63.53	0.0003
N_2 Concentration, vol %: 84.5	84.34	0.0009	N_2 Concentration, vol %: 56.5	84.34	0.0009
	104.46	0.0011		104.46	0.0011
	124.43	0.0012		124.43	0.0012
	144.97	0.0015		144.97	0.0015

Table 4. Weight gain of 0.1-g TU-188 sorbent in reaction with H_2S at 100 scc/min gas flow rate and 530°C.

Run 15		Absorption Duration, s	Weight Gain, g	Run 16		Absorption Duration, s	Weight Gain, g
		0	0			0	0
H_2S Concentration, ppmv :	5000	19.74	0.0005	H_2S Concentration, ppmv :	5000	20.22	1E-04
H_2O Concentration, vol % :	10.5	39.99	0.0005	H_2O Concentration, vol % :	10.5	40.43	0.0005
H_2 Concentration, vol %:	33	60.13	0.0006	H_2 Concentration, vol %:	7	60.41	0.0002
N_2 Concentration, vol %:	56	80.33	0.001	N_2 Concentration, vol %:	82	80.91	0.0004
		100.33	0.0013			101.08	0.0005
		120.77	0.0018			121.46	0.0005
		136.68	0.002			141.2	0.0007

Run 17		Absorption Duration, s	Weight Gain, g	Run 18		Absorption Duration, s	Weight Gain, g
		0	0			0	0
H_2S Concentration, ppmv :	5000	20.76	1E-04	H_2S Concentration, ppmv :	5000	20.11	1E-04
H_2O Concentration, vol % :	10.5	40.18	0.0004	H_2O Concentration, vol % :	10.5	40.15	0.0002
H_2 Concentration, vol %:	33	60.37	0.0009	H_2 Concentration, vol %:	20	60.32	0.0002
N_2 Concentration, vol %:	56	80.63	0.0012	N_2 Concentration, vol %:	69	80.11	0.0005
		100.77	0.001			96.62	0.0007
		121.31	0.0015			120.32	0.0006
		141.31	0.0016			140.92	0.0009

Run 19		Absorption Duration, s	Weight Gain, g	Run 20		Absorption Duration, s	Weight Gain, g
		0	0			0	0
H_2S Concentration, ppmv :	5000	20.47	0	H_2S Concentration, ppmv :	5000	20.6	0
H_2O Concentration, vol % :	10.5	60.96	0	H_2O Concentration, vol % :	10.5	41.4	0
H_2 Concentration, vol %:	40	80.91	0.0002	H_2 Concentration, vol %:	30	101.82	1E-04
N_2 Concentration, vol %:	49	101.69	0.0004	N_2 Concentration, vol %:	59	222.24	0.0003
		122.2	0.0009			522.65	0.0005
		142.3	0.0009			1122.63	0.0016
		751.77	0.0017			2342.68	0.0026
		1996.77	0.0028			3581.25	0.0037
		4477.77	0.0043			4780.69	0.0039
		6877.77	0.0053			7180.79	0.0049
		8091.07	0.0055			8398.86	0.0052
		9292.3	0.0061			9599.2	0.0049
		10521.31	0.0056			10810.5	0.0053
		11739.98	0.0062			12010.5	0.0053

Run 21		Absorption Duration, s	Weight Gain, g	Absorption Duration, s	Weight Gain, g
		0	0	2820.58	0.0022
H_2S Concentration, ppmv :	5000	59.94	1E-04	4028.58	0.003
H_2O Concentration, vol % :	10.5	180.33	1E-04	5270.27	0.0035
H_2 Concentration, vol %:	10	420.41	0.0007	7669.27	0.0037
N_2 Concentration, vol %:	79	1021.1	0.0014	8915.67	0.004
		1621.14	0.0018	10115.96	0.0039

A series of experiments on absorption of H_2S 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 H_2S with the sorbent. The concentrations of H_2S 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 H_2S 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, ligher than H_2S, inhances mobility of H_2S through the porous matrix of the sorbent.

A series of experiments on absorption of H_2S into the sorbent were carried out for 5 – 150 seconds at 105 psia at 530°C to find effects of hydrogen concentrations on initial reaction of H_2S with the sorbent. The concentrations of H_2S 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 H_2S 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 H_2S by the reaction of hydrogen with the porous metal oxide matrix of the sorbent and enlarging pore diameters of the sorbent.

FIGURE 2. Effects of concentrations of H_2S on its absorption into 0.1-g TU-188 sorbent with 10 vol % moisture and 15 vol % H_2 at 300 scc/min gas flow rate and 530°C.

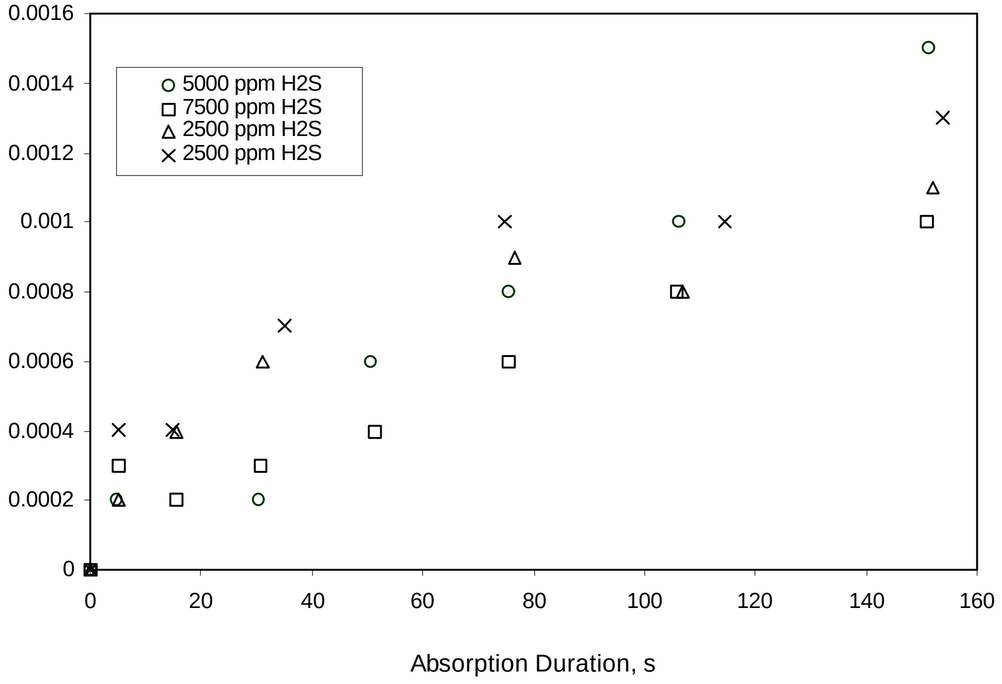


FIGURE 3. Effects of moisture on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with15 vol % H_2 and 300 scc/min gas flow rate at 530°C.

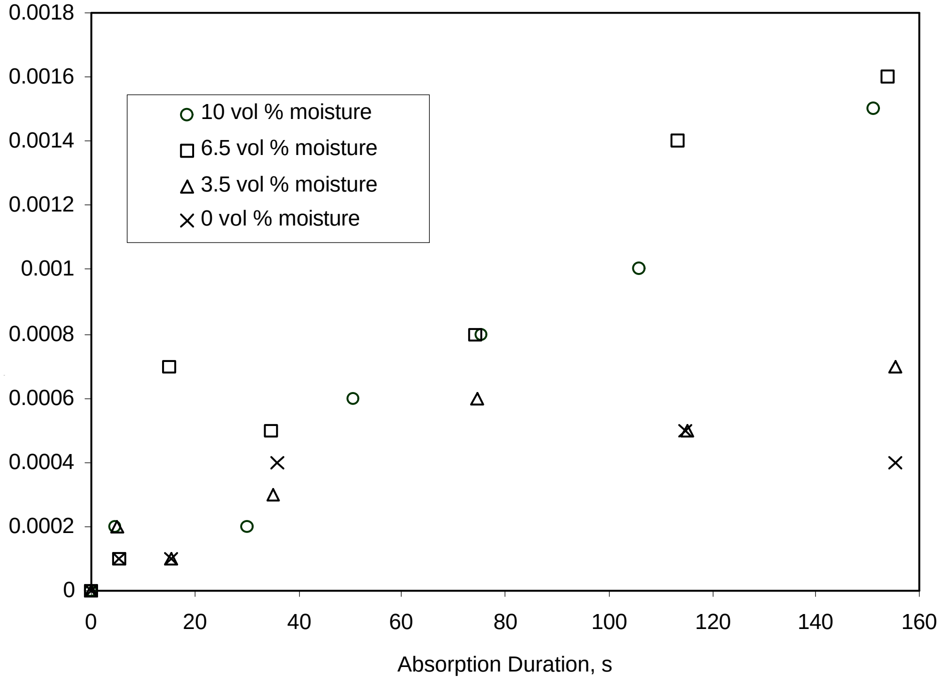


FIGURE 4. Effects of moisture on absorption of 5000-ppm H_2S on 0.1-g TU-188 sorbent with 300 scc/min gas flow rate and 15 vol % H_2 at 530°C.

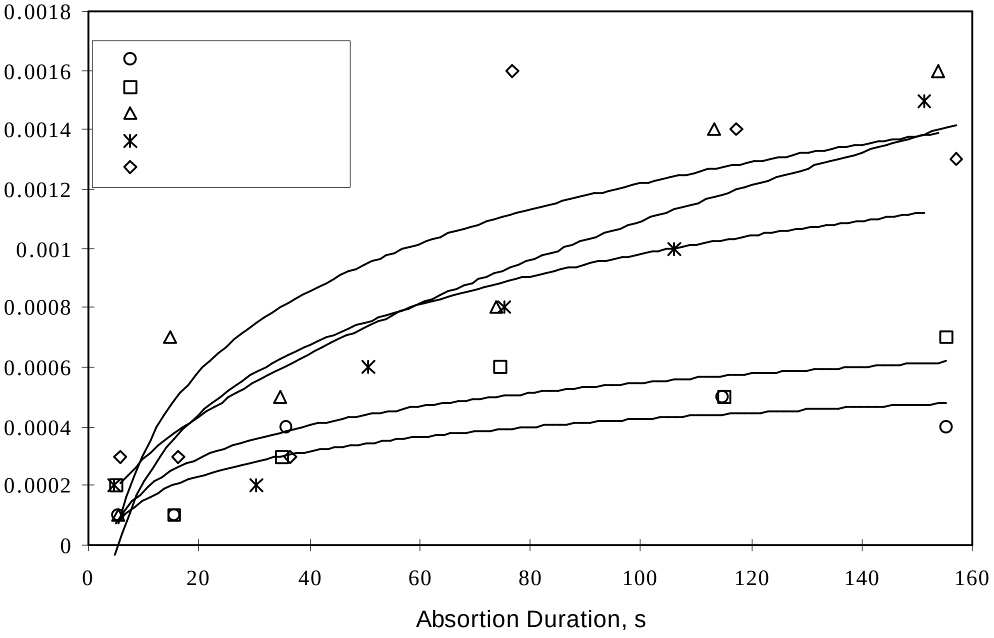


FIGURE 5. Effects of hydrogen on absorption of 50 vol % H_2S into 0.1-g TU-188 sorbent with 10 vol % moisture and 300 scc/min gas flow rate at 530°C.

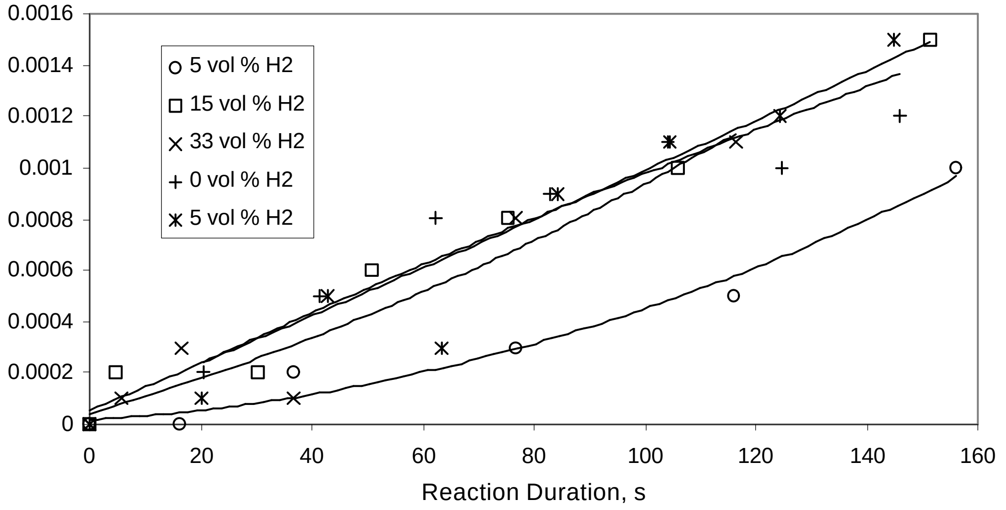
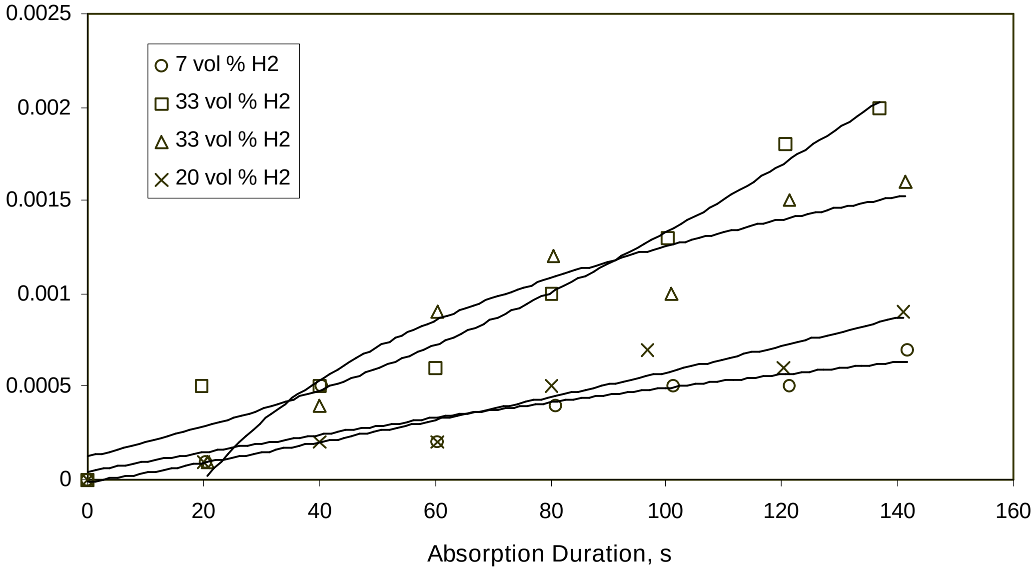


FIGURE 6. Effects of hydrogen on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % water and 100 scc/min gas flow rate at 530°C.



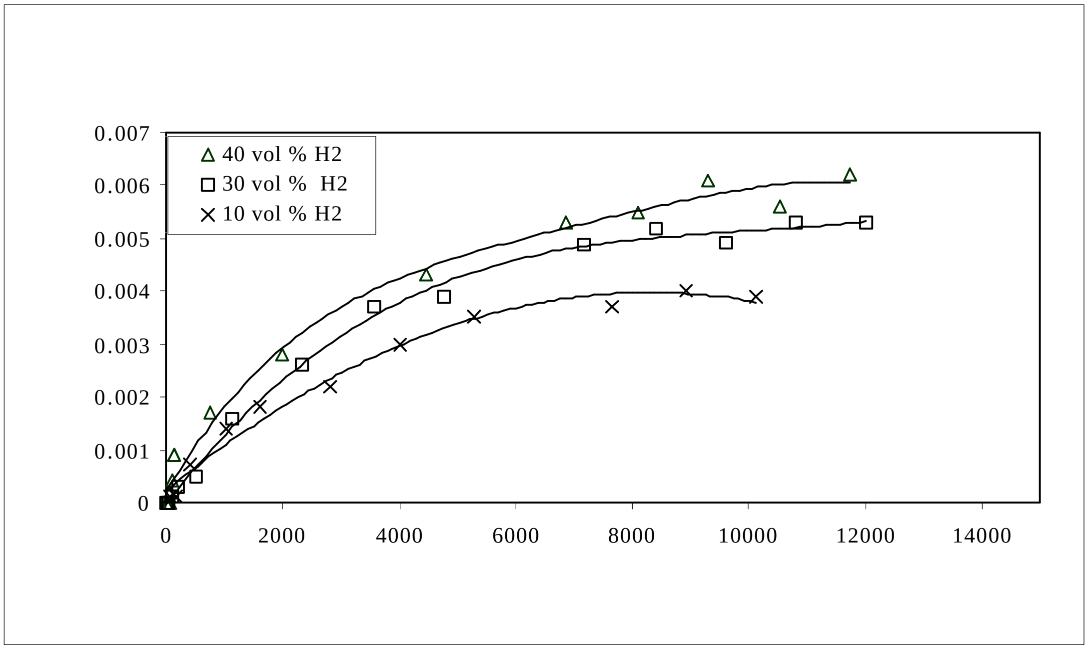
A series of experiments on absorption of H_2S into the sorbent were carried out for 30 – 12000 seconds at 105 psia at 530°C to find effects of hydrogen concentrations on effective diffusivity of H_2S with the sorbent. The concentrations of H_2S and moisture are maintained at 5000 ppm and 10 vol %, respectively. 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 scc/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.

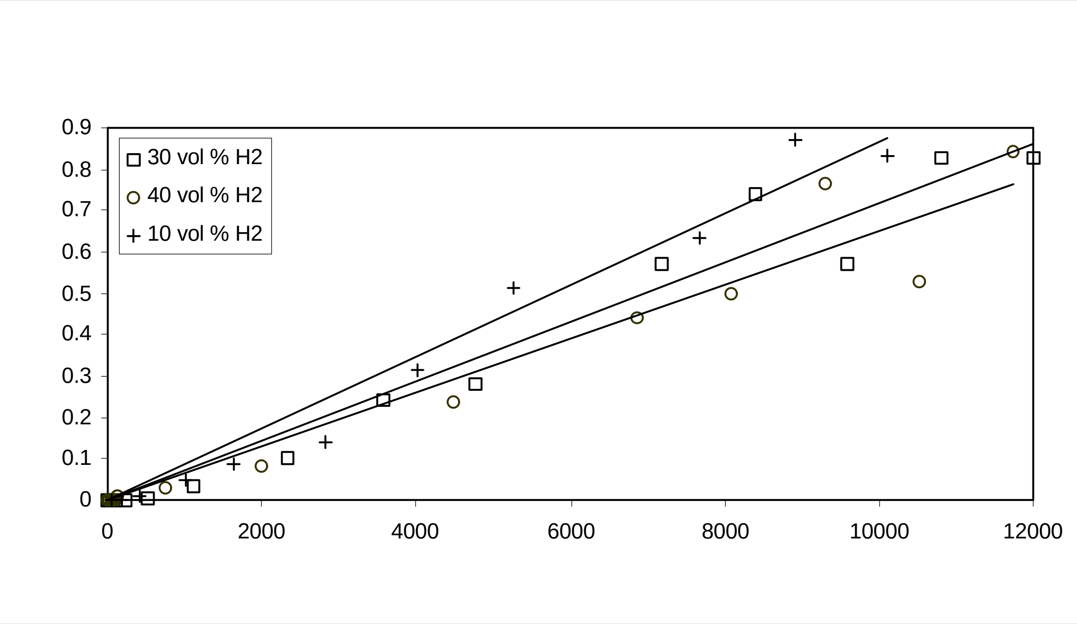
$$\left[\, 1-3\left(\frac{r_C}{R}\right)^2+2\left(\frac{r_C}{R}\right)^3 \,\right]=\frac{6b\delta C_{Ag}}{\rho_B R^2}\,t \qquad (1)$$

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 $1.07\text{x}10^{-3}$ cm^2/s in the presence of 10-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is $0.65\text{x}10^{-3}$ cm^2/s in the presence of 30-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is $0.51\text{x}10^{-3}$ cm^2/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 H_2S with the sorbent. The concentrations of H_2S 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 H_2S. These observations appear to be agreeable with those shown in Figures 5 and 6.



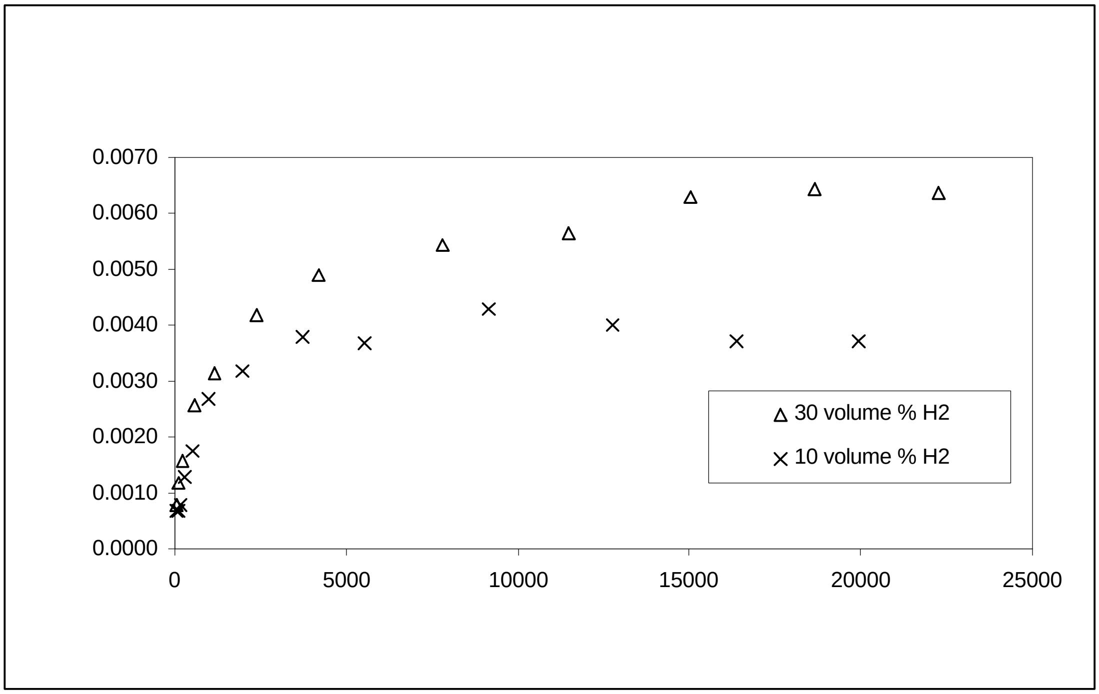
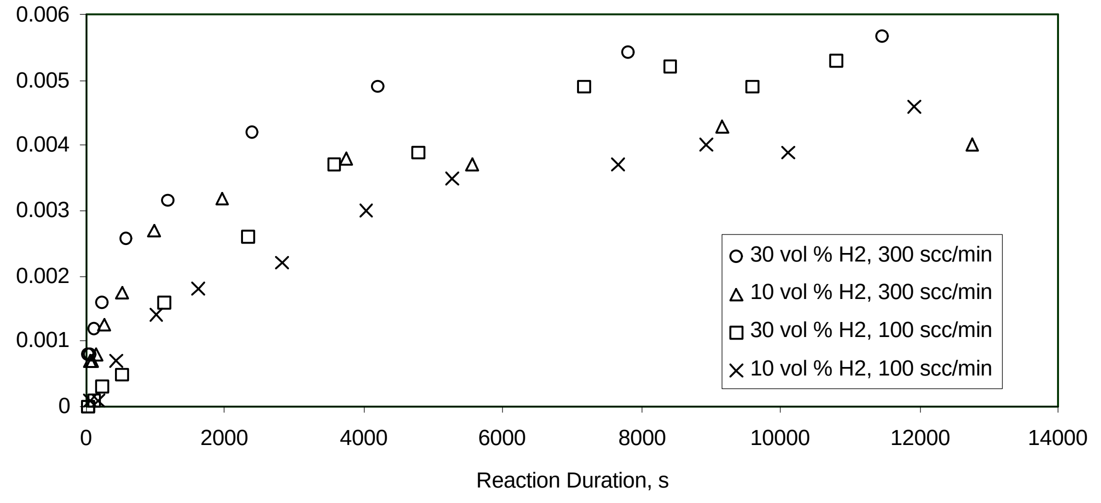


FIGURE 10. Effects of residence time of gas on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % moisture at 530 °C.



A series of experiments on effects of space (residence) times on dynamic absorption of H_2S into the sorbent were conducted at the 100 scc/min (0.36 s residence time) and the 300 scc/min (0.12 s residence time). Decreased residence time results in increased dynamic absorption of H_2S into the sorbent. These observations may suggest that transfer rate of H_2S from the reactive gas mixture toward the surface of the porous solid sorbent particles affect significantly dynamic absorption of H_2S into the sorbent. These data may indicate that space times do not affect equilibrium absorption capacity of the sorbent in the presence of H_2S as an absorbed reactive gas.

CONCLUSIONS

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

- Hydrogen sulfide absorbed into the porous matrix of the sorbent retards transfer of H_2S into micro pores of the sorbent with increased concentrations of H_2S.

- Moisture, ligher than H_2S, inhances mobility of H_2S through the porous matrix of the sorbent..

- A reducing gas such as hydrogen increases active surface area accessible to H_2S 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 H_2S 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 area of the sorbent in favor of absorption of H_2S

- Space times do not affect equilibrium absorption capacity of the sorbent in the presence of H_2S as an absorbed reactive gas.

PUBLICATION

Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperature and Pressure", Separation Science and Technology, V. 32, No. 1-4, Pg. 775-792, 1997.

PLANS ON FUTURE EXPERIMENTS

Effects of moisure concentrations, H_2S concentrations, absorption temperatures, particle sizes on equilibrium absorption as well as dynamic absorption of H_2S into metal oxide sorbents, using the differential reactor.