

# ENERGY

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

# F O S S I L

Technical Progress Report for the Period  
October 1 to December 31, 1997

By  
K. C. Kwon

August 1998

Work Performed Under Contract no DE-FG21-94MC31206-12

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

By  
Tuskegee University  
Tuskegee, Alabama

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## CONTENTS

	Page
DISCLAIMER	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
MILESTONES	1
SUMMARY	1
INTRODUCTION	1
EXPERIMENTAL SETUP/PROCEDURE	2
RESULTS AND DISCUSSION	3
CONCLUSION	9
PRESENTATION	9

## LIST OF TABLES

Table		Page
1	Experimental conditions for the reaction of hydrogen sulfide with the TU-188 sorbent in the presence of moisture, nitrogen and hydrogen.	3
2	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at 0.12 s space time and 530°C.	4
3	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at 0.12 s space time and 530°C.	5
4	Weight loss of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at 0.12 s space time and 530°C.	5
5	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at 0.12 s space time and 530°C.	6

## LIST OF FIGURES

Figure		Page
1	A differential reactor assembly	2
2	Effects of hydrogen on equilibrium absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 0.12 s space time and 530°C.	7
3	Weight loss of 0.1-g TU-188 sorbent in reduction reaction with hydrogen in the absence of H <sub>2</sub> S at 0.12 s space time and 530°C.	7
4	Effects of hydrogen on transition of reaction control in the absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 0.12 s space time and 530°C.	8
5	Effects of hydrogen on initial absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 0.12 s space time and 530°C.	8

## 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													—————													

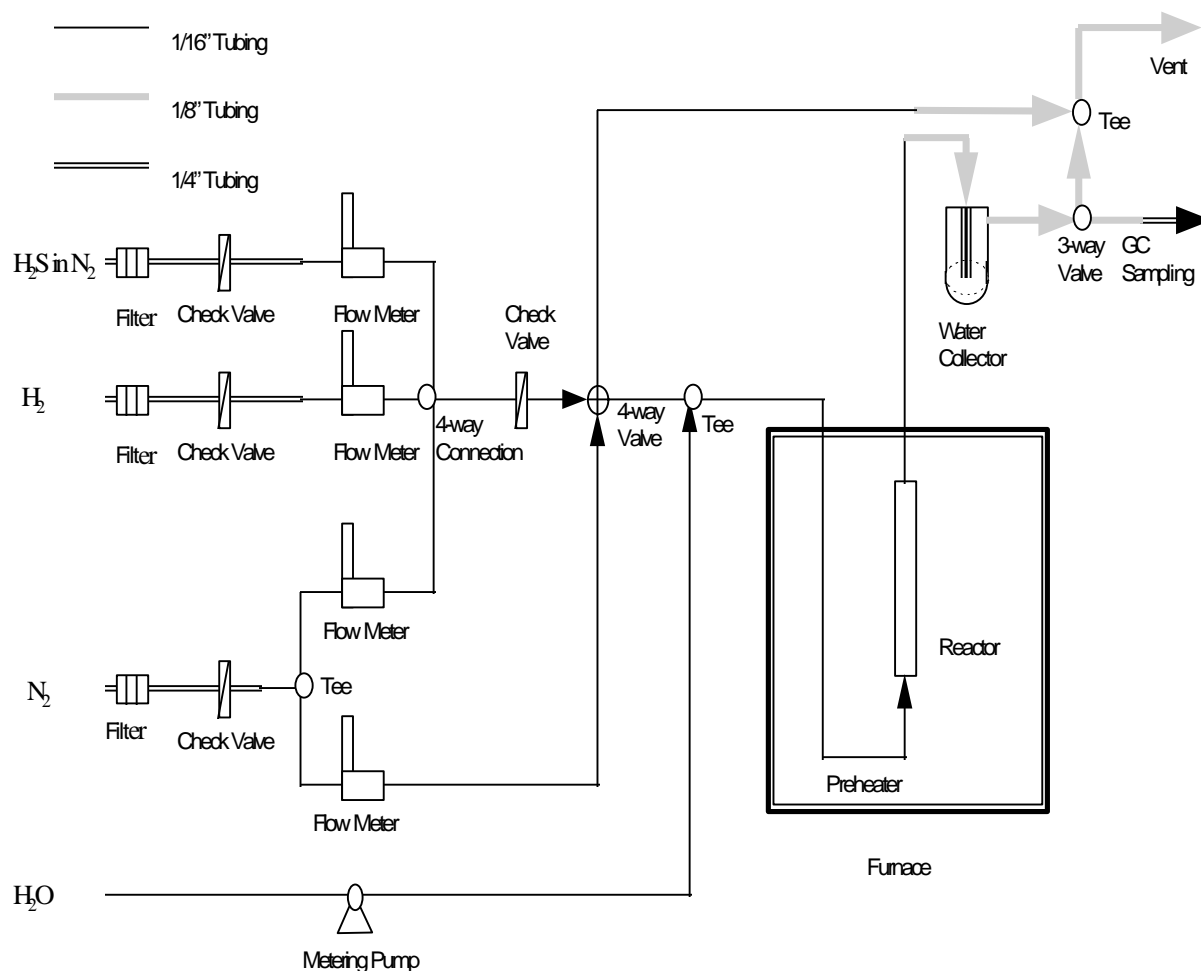
## SUMMARY

The main objective of this research project during this quarter is to investigate effects of hydrogen on initial absorption as well as equilibrium absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent in the presence of 10 vol % moisture at the 0.12-s space time and 530°C.

## INTRODUCTION

A differential micro reactor was fabricated with a titanium grade-2 tube. The volume of reactor is 1.64 cm<sup>3</sup>. 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. The crushed 100 - 200 mesh (74 –140 μm) particles were reacted with simulated coal gases containing hydrogen sulfide in the 1.64 cm<sup>3</sup> titanium Grade-2 differential micro reactor for 30- 120000 seconds at 105 psia and 530°C. Absorption amounts of hydrogen sulfide into the sorbent were analyzed with an electronic balance. The space (residence) time of the reaction gas mixture in the reactor was 0.12 s (300 cc/min) under the reaction conditions.

Figure 1. A Differential Reactor Assembly



### EXPERIMENTAL SETUP/PROCEDURE

A differential reactor assembly have 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). A differential reactor is fabricated with one 10-cm-long 1/4-inch titanium grade-2 tubing and two 1/4" external column end fittings. The preheater is made of 1/16" Hastelloy C tubing. The reactor was loaded with 0.1-g 74-140  $\mu\text{m}$  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 desired reaction duration, by switching nitrogen with a simulated coal gas mixture.



## RESULTS AND DISCUSSION

Research activities and efforts of this research project were concentrated on absorbing hydrogen sulfide into TU-188 sorbent at 105 psia and 530°C to understand effects of hydrogen on absorption of hydrogen sulfide into the sorbent, using the differential reactor.

Experiments on absorption of wet hydrogen sulfide into the sorbent were carried out for 5 – 120000 seconds at 530°C (see Table 1) to evaluate effects of hydrogen concentrations on dynamic absorption as well as equilibrium adsorption of hydrogen sulfide into the sorbent. A typical simulated coal gas mixture consists of 2500-ppm hydrogen sulfide, 10 vol % moisture, 10 - 40 vol % hydrogen, and nitrogen as remainder. The volumetric feed rate of the simulated coal gas mixture to the reactor is 300 cm<sup>3</sup> /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 105 psia. All the absorption experiments were conducted, using the sorbent reduced in the absence of H<sub>2</sub>S with hydrogen under the same experimental conditions as those of absorption experiments. Experimental data on absorption of H<sub>2</sub>S into the TU-188 sorbent at various absorption durations were shown in Tables 2 - 5.

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 <sup>3</sup> :	1.6
Temperature, °C:	530
Reaction Pressure, psia	105
Reaction Time, s:	5 -120000
Space Time under the absorption conditions, s:	0.12
Particle Size, μm	74 - 140
Amount of Sorbent, g	0.1
Gas Flow Rate, cc/min at room temperature	300
Hydrogen, vol %	10 - 40
Moisture, vol %:	10
Concentration of H <sub>2</sub> S, ppm	2500
Nitrogen, vol %	50 - 80

### *Effects of Hydrogen*

A series of experiments on equilibrium absorption of H<sub>2</sub>S into the sorbent were carried out for 5 – 120000 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on equilibrium absorption of H<sub>2</sub>S into the sorbent in the presence of 10-vol % moisture and 2500-ppm H<sub>2</sub>S. Absorption of H<sub>2</sub>S appears to either decrease or increase with increased concentrations of H<sub>2</sub>S for long absorption durations (see Figure 2). Absorption of H<sub>2</sub>S into the sorbent in the presence of 30-vol % hydrogen increases with increased absorption duration for the 28-hr absorption duration. These observations suggest that equilibrium absorption of H<sub>2</sub>S into the sorbent can not be reached for the 28-hr absorption duration. Absorption of H<sub>2</sub>S into

the sorbent in the presence of 10-vol % hydrogen decreases slightly with increased absorption duration for the 28-hr absorption duration. These observations may indicate that molecular hydrogen reduces the porous matrix of the metal oxide sorbent for the 28-hr absorption duration.

Table 2. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at 300 scc/min gas flow rate and 530°C.

Run 24		Absorption Duration, s	Weight Gain, g
		0	0.0000
H <sub>2</sub> S Concentration, ppmv:	2500	30	0.0010
H <sub>2</sub> O Concentration, vol %:	10	61	0.0013
H <sub>2</sub> Concentration, vol %:	40	121	0.0015
N <sub>2</sub> Concentration, vol %:	49.75	242	0.0016
		481	0.0019
		967	0.0031
		1987	0.0039
		3787	0.0043
		5587	0.0043
		9187	0.0056
		12787	0.0061
		16387	0.0059
		19507	0.0063
		23107	0.0066
		30307	0.0070
		44707	0.0075
		73507	0.0071
		87907	0.0070
		102307	0.0069
		116707	0.0063

### *Reduction Reaction with Hydrogen*

A series of reduction experiments on weight loss of the sorbent were carried out in the presence of 10 vol % H<sub>2</sub>, 10 vol % moisture, and 80 vol % N<sub>2</sub> for 30 – 24000 seconds at 105 psia and 530°C to understand reduction reaction of the sorbent with wet hydrogen. The weight of the sorbent decrease significantly in the absence of H<sub>2</sub>S for the reduction duration of 8 min (see Figure 3 and Table 4).

### *Surface Reaction Control and Intraparticle Pore Diffusion Control*

A series of experiments on absorption of H<sub>2</sub>S into the sorbent were carried out for 30 – 15000 seconds at 105 psia and 530°C to investigate reaction mechanisms on the gaseous H<sub>2</sub>S-solid metal oxide heterogeneous reaction system. The weight gain of the sorbent increases drastically during the initial absorption stage, and then increases slowly with increased absorption duration (see Figure 5). The transitional reaction control from the surface reaction control to the intraparticle pore diffusion control appears to be pronounced with increased concentrations of hydrogen in the simulated wet coal gas mixtures.

*Effects of Hydrogen on Surface Reaction*

A series of experiments on absorption of H<sub>2</sub>S into the sorbent were carried out for 6 – 140 seconds at 105 psia and 530°C to investigate effects of hydrogen on initial absorption of H<sub>2</sub>S into the solid sorbent (see Figure 4). Initial surface reaction of wet H<sub>2</sub>S with the solid sorbent increases with increased concentrations of hydrogen. These facts may indicate that hydrogen affects significantly the initial surface reaction at the outside surface of the solid metal oxide sorbent.

Table 3. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at 300 scc/min gas flow rate and 530°C.

Run 25		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	30	0.00070
H <sub>2</sub> O Concentration, vol %:	10	60	0.00070
H <sub>2</sub> Concentration, vol %:	10	121	0.00140
N <sub>2</sub> Concentration, vol %:	79.75	241	0.00169
		481	0.00249
		962	0.00217
		1863	0.00265
		3663	0.00420
		5463	0.00455
		9063	0.00545
		12663	0.00645
		16263	0.00665
		23463	0.00755
		37863	0.00765
		47163	0.00809
		68763	0.00789
		83163	0.00769
		99363	0.00754

Table 4. Weight loss of 0.1-g TU-188 sorbent in reaction with hydrogen at 300 scc/min gas flow rate and 530°C.

Run 26		Reaction Duration, s	Weight %
		0	100
H <sub>2</sub> S Concentration, ppmv:	0	30	99.8
H <sub>2</sub> O Concentration, vol %:	10	60	99
H <sub>2</sub> Concentration, vol %:	10	91	99
N <sub>2</sub> Concentration, vol %:	80	151	99.3
		241	99.3
		482	99.3
		7682	99
		23882	99

Table 5. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at 300 scc/min gas flow rate and 530°C.

Run 27		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	36	0.0002
H <sub>2</sub> O Concentration, vol %:	10	76	0.0006
H <sub>2</sub> Concentration, vol %:	10	136	0.0015
N <sub>2</sub> Concentration, vol %:	79.75	256	0.0014
		376	0.0018
		616	0.0018
		1096	0.0022
		1997	0.0028
		3797	0.0043
		7637	0.0051
		11237	0.0059

Run 29		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	6	0
H <sub>2</sub> O Concentration, vol %:	10	15	0.0002
H <sub>2</sub> Concentration, vol %:	30	36	0.0004
N <sub>2</sub> Concentration, vol %:	59.75	61	0.0014
		85	0.0014
		115	0.0013
		176	0.0018
		236	0.0019
		355	0.0029
		596	0.003
		1076	0.0035
		1856	0.0033
		3656	0.0041
		7256	0.0051
		10856	0.0056
		14456	0.0064
		18056	0.0072
		25256	0.0081
		32456	0.0085
		46856	0.009
		61256	0.0102
		75656	0.0106
		97436	0.0112

Figure 2. Effects of hydrogen on equilibrium absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530°C.

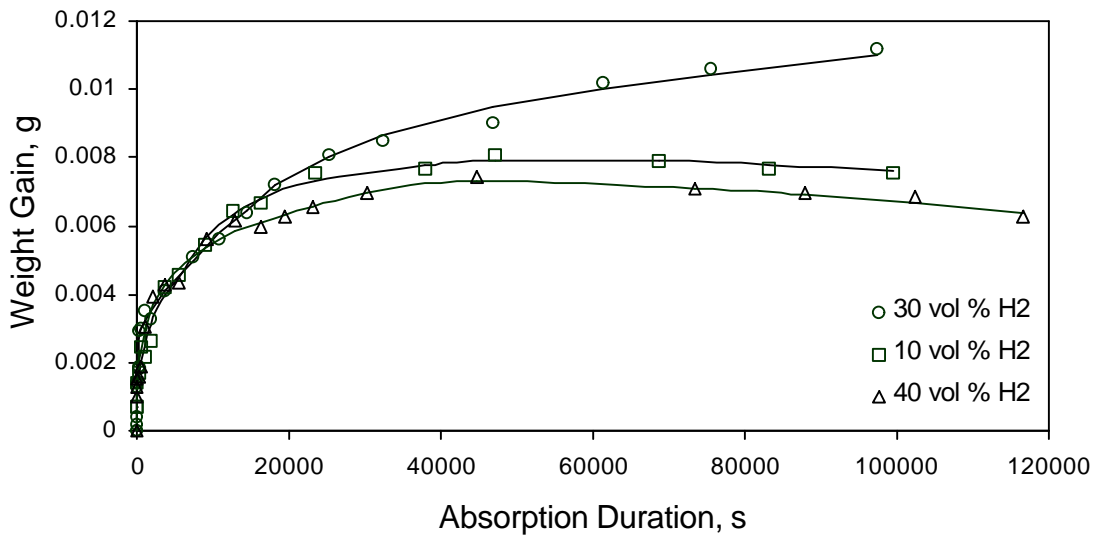


Figure 3. Weight loss of 0.1-g TU-188 sorbent in reduction reaction with hydrogen in the absence of H<sub>2</sub>S at 300 scc/min gas flow rate and 530°C.

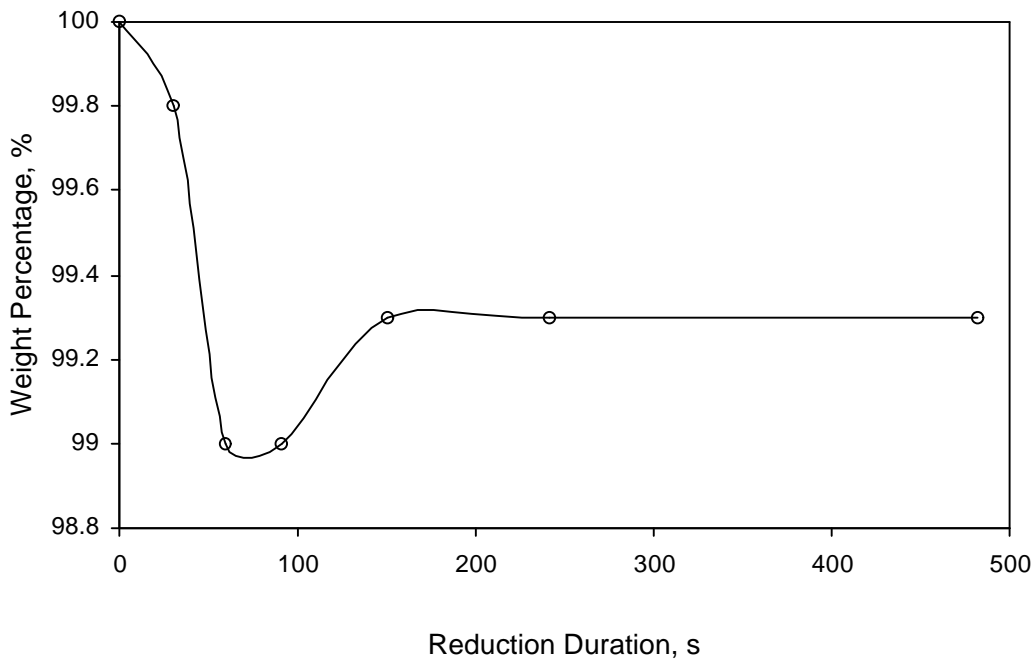


Figure 4. Effects of hydrogen on transition of reaction control in the absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530°C.

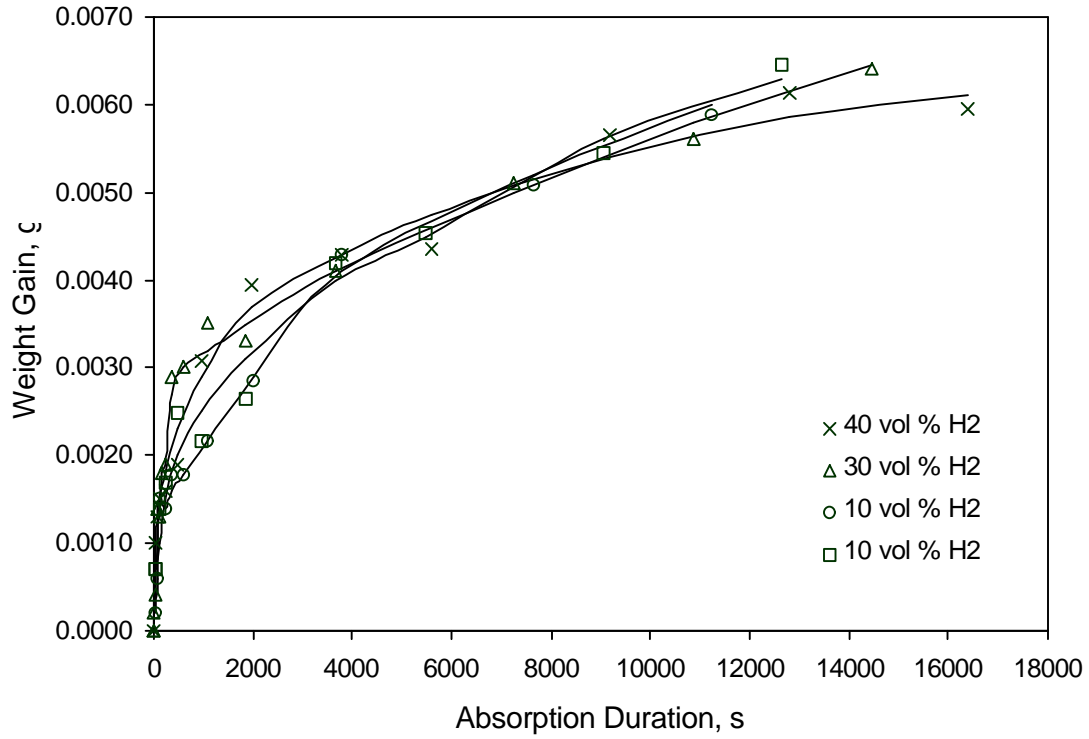
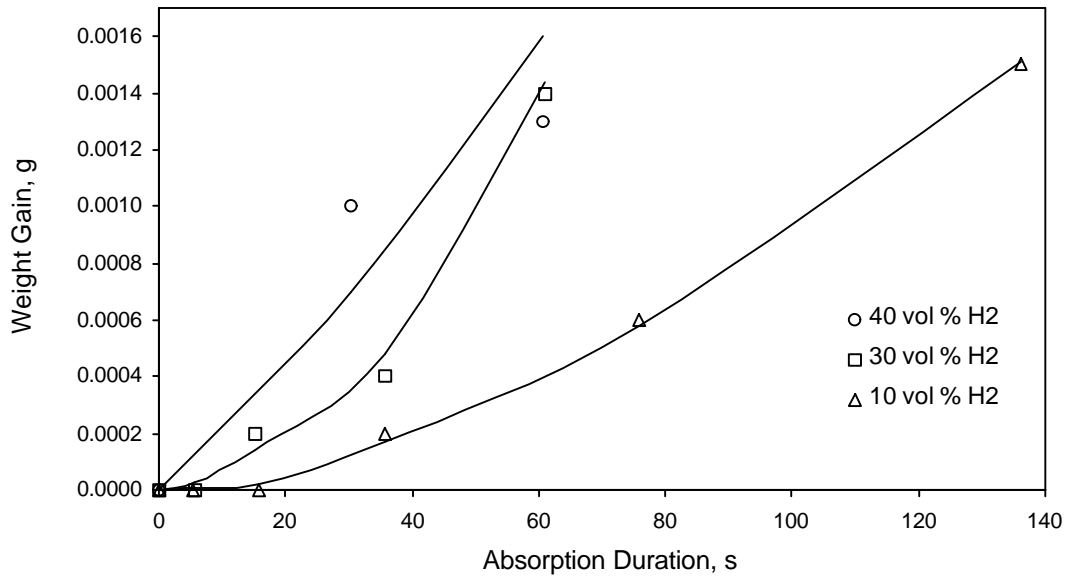


Figure 5. Effects of hydrogen on initial absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530 °C.



## CONCLUSIONS

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

- Equilibrium absorption of  $H_2S$  into the sorbent can not be reached in the presence of 30-vol % hydrogen for the 28-hr absorption duration. Equilibrium absorption of  $H_2S$  into the sorbent in the presence of 10-vol % hydrogen decreases slightly with increased absorption duration for the 28-hr absorption duration. These observations may indicate that molecular hydrogen reduces the porous matrix of the metal oxide sorbent for the 28-hr absorption duration.
- The weight of the sorbent decreases significantly in the reduction reaction of the sorbent in the absence of  $H_2S$  with hydrogen for the reduction duration of 8 min. This observation may suggest that hydrogen affects significantly initial surface reaction of the sorbent with  $H_2S$ .
- The transitional reaction control from the surface reaction control to the intraparticle pore diffusion control appears to be pronounced with increased concentrations of hydrogen in the simulated wet coal gas mixtures.
- Initial surface reaction of wet  $H_2S$  with the solid sorbent increases with increased concentrations of hydrogen. Hydrogen affects significantly the initial surface reaction of the solid metal oxide sorbent with wet hydrogen.

## PRESENTATION

“Effects of moisture and hydrogen on removal kinetics of hot hydrogen sulfide with metal oxide sorbents”, presented at the Tenth Symposium on Separation Science and Technology for Energy Applications, Park Vista Hotel & Convention Center, Gatlinburg, Tennessee, October 20-24, 1997.