

# 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  
January 1 to March 31, 1998

By  
K. C. Kwon

August 1998

Work Performed Under Contract no DE-FG21-94MC31206-13

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

By  
Tuskegee University  
Tuskegee, Alabama

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

Technical Progress Report for the Period  
January 1 to March 31, 1998

K. C. Kwon

August 1998

Work Performed Under Contract No.: DE-FG21-94MC31206

For  
U.S. Department of Energy  
Office of Fossil Energy  
Federal Energy Technology Center  
P.O. Box 880  
Morgantown, West Virginia 26507-0880

By  
Tuskegee University  
Tuskegee, Alabama 36088

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof

## 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
PUBLICATION	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 the 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 the 0.072 s space time and 470°C.	4
4	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at the 0.072 s space time and 500°C.	5
5	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at the 0.072 s space time and 530°C.	5
6	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at the 0.072 s space time and 500°C.	6
7	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at the 0.072 s space time and 500°C.	6
8	Weight gain of 0.1-g TU-188 sorbent in reaction with H <sub>2</sub> S at the 0.072 s space time and 530°C.	7

## LIST OF FIGURES

Figure		Page
1	A differential reactor assembly	2
2	Effects of temperature on absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent in the 10-volume % moisture and 10-volume % hydrogen at the 0.072-s space time.	7
3	Effects of moisture on initial absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent with 10-volume % hydrogen at the 0.072-s space time and 530°C.	8
4	Effects of space time on initial absorption of 2500-ppm H <sub>2</sub> S into 0.1-g TU-188 sorbent with 10-volume % hydrogen and 10 vol % moisture at 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																								

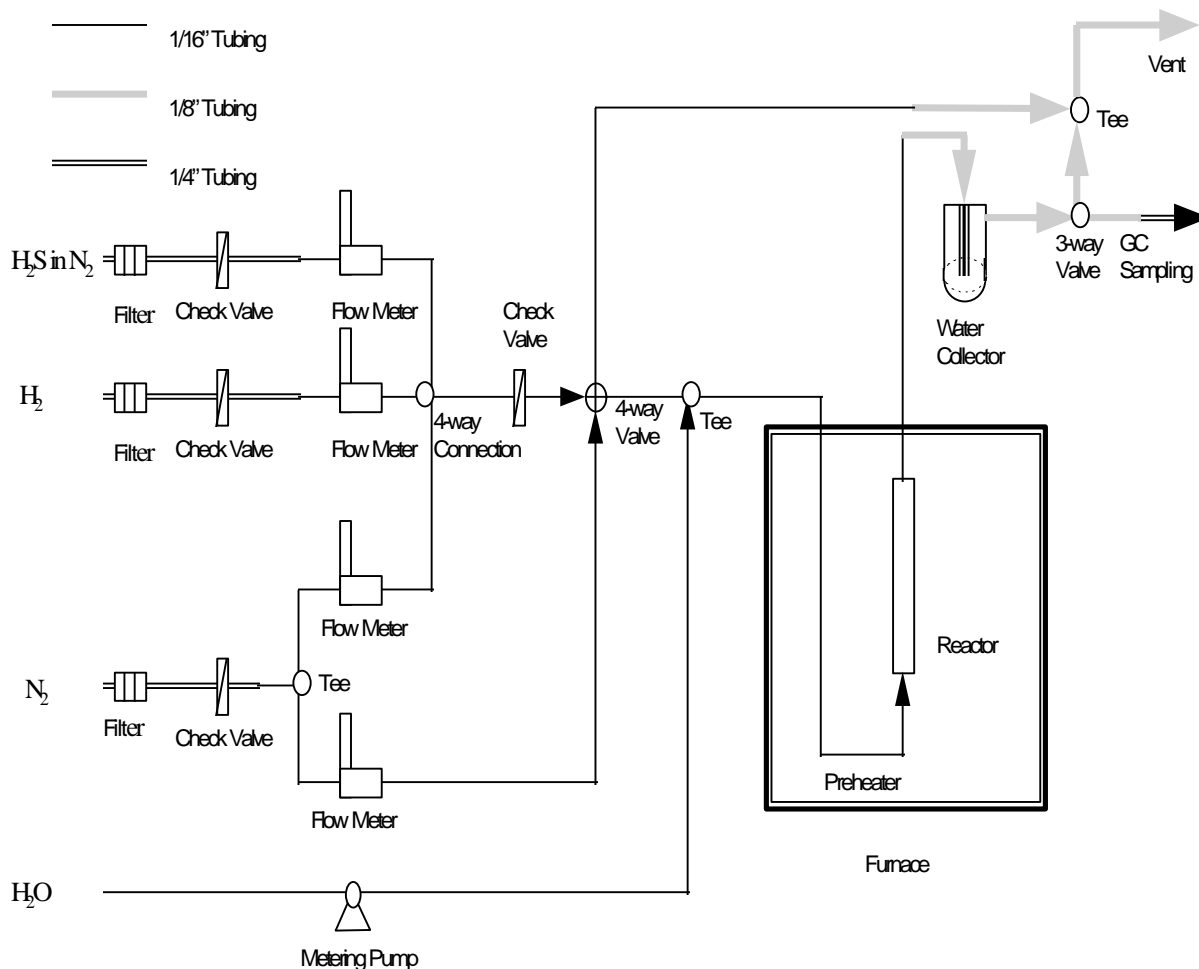
### SUMMARY

The main objective of this research project during this quarter is to investigate effects of temperature, moisture, and space time of reaction gas mixtures on initial absorption of H<sub>2</sub>S into the TU-188 sorbent at 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. These 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 6 - 1100 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 0.072 - 0.12 s (500 - 300 cc/min) under the reaction conditions.

Figure 1. A Differential Reactor Assembly



### EXPERIMENTAL SETUP/PROCEDURE

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 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 the 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 various operation conditions to understand effects of moisture, temperature, and space time of simulated coal gas mixtures 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 6 – 1100 seconds at 530°C (see Table 1) to evaluate effects of moisture concentrations, temperature, and space time on initial dynamic absorption of hydrogen sulfide into the sorbent. A typical simulated coal gas mixture consists of 2500 ppm hydrogen sulfide, 5 – 10 vol % moisture, 10- 30 vol % hydrogen, and nitrogen as remainder. The volumetric feed rate of the simulated coal gas mixture to the reactor is 300 –500 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 with hydrogen in the absence of H<sub>2</sub>S under the same experimental conditions as those of absorption experiments. Experimental data of absorption of H<sub>2</sub>S into the TU-188 sorbent at various absorption durations were shown in Tables 2 - 8.

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:	6 -1100
Space Time under the absorption conditions, s:	0.072 - 0.12
Particle Size, μm	74 - 140
Amount of Sorbent, g	0.1
Gas Flow Rate, cc/min at room temperature	500 - 300
Hydrogen, vol %	10 - 40
Moisture, vol %:	5 - 10
Concentration of H <sub>2</sub> S, ppm	2500
Nitrogen, vol %	60 - 85

### *Effects of Temperature on Initial Dynamic Absorption of H<sub>2</sub>S*

A series of experiments on initial absorption of H<sub>2</sub>S into the sorbent were carried out for 6 – 950 seconds at 105 psia and 530°C to find effects of temperature on initial dynamic absorption of H<sub>2</sub>S with the sorbent. The concentrations of both moisture and hydrogen are maintained at 10-vol %. The concentration of hydrogen sulfide in the simulated coal gas mixture is 2500 ppm. Initial absorption of H<sub>2</sub>S decreases generally with increased absorption temperature for short absorption durations of 5 – 950 seconds (see Figure 2). These observations may indicate

Table 2. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.12 s space time 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

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

Table 3. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 470°C.

Run 30-3		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	6	0.0002
H <sub>2</sub> O Concentration, vol %:	10	16	0.0004
H <sub>2</sub> Concentration, vol %:	10	37	0.0008
N <sub>2</sub> Concentration, vol %:	79.75	77	0.0008
		118	0.0014
		158	0.0024
		198	0.0022
		288	0.0026
		468	0.0037
		828	0.0041

Run 34		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	5	0.0003
H <sub>2</sub> O Concentration, vol %:	10	16	0.0004
H <sub>2</sub> Concentration, vol %:	10	36	0.0005
N <sub>2</sub> Concentration, vol %:	79.75	76	0.0012
		116	0.0013
		157	0.0015
		197	0.0017
		236	0.0017
		326	0.002
		516	0.0027
		876	0.0033

Table 4. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 500°C.

Run 31		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	6	0.0001
H <sub>2</sub> O Concentration, vol %:	10	16	0
H <sub>2</sub> Concentration, vol %:	30	36	0.0003
N <sub>2</sub> Concentration, vol %:	59.75	76	0.001
		116	0.0014
		156	0.0016
		196	0.0027
		237	0.0036
		277	0.0042
		318	0.0042
		407	0.0037
		587	0.0041
		947	0.005

Table 5. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 530°C.

Run 31-b		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	5	0
H <sub>2</sub> O Concentration, vol %:	10	36	0.0003
H <sub>2</sub> Concentration, vol %:	10	77	0.0002
N <sub>2</sub> Concentration, vol %:	79.75	117	0.0006
		157	0.0011
		197	0.0014
		237	0.0014
		328	0.0019
		507	0.0021
		868	0.0028

Run 32		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	5	0.0004
H <sub>2</sub> O Concentration, vol %:	10	16	0.0001
H <sub>2</sub> Concentration, vol %:	10	36	0.0003
N <sub>2</sub> Concentration, vol %:	79.75	76	0.0011
		117	0.0013
		157	0.0016
		197	0.0017
		287	0.0021
		489	0.003
		849	0.0036

that initial reduction reaction of the metal oxide sorbent with hydrogen may be dominant over initial absorption reaction of the metal oxide sorbent with hydrogen sulfide at higher absorption temperature.

Table 6. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 500°C.

Run 33		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	6	0.0003
H <sub>2</sub> O Concentration, vol %:	10	17	0.0005
H <sub>2</sub> Concentration, vol %:	30	37	0.001
N <sub>2</sub> Concentration, vol %:	59.75	77	0.0012
		118	0.0014
		158	0.0013
		198	0.0025
		239	0.0022
		279	0.0028
		319	0.0028
		409	0.0025
		589	0.0029
		949	0.0038

Table 7. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 500°C.

Run 35		Absorption Duration, s	Weight Gain, g
		0	0
H <sub>2</sub> S Concentration, ppmv:	2500	6	0.0004
H <sub>2</sub> O Concentration, vol %:	10	16	0.0008
H <sub>2</sub> Concentration, vol %:	10	37	0.0007
N <sub>2</sub> Concentration, vol %:	79.75	77	0.001
		117	0.001
		157	0.0017
		197	0.002
		237	0.0025
		277	0.0025
		368	0.0027
		547	0.0031
		908	0.0036

### *Effects of Moisture on Initial Dynamic Absorption of H<sub>2</sub>S*

A series of experiments on initial absorption of H<sub>2</sub>S into the sorbent were carried out for 6 – 970 seconds at 105 psia and 530°C to find effects of moisture concentrations on initial dynamic absorption of H<sub>2</sub>S with the sorbent. The concentrations of H<sub>2</sub>S and hydrogen are

Table 8. Weight gain of 0.1-g TU-188 sorbent in reaction with H<sub>2</sub>S at the 0.072 s space time and 530°C.

Run 36		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 %:	5	16	0.0002
H <sub>2</sub> Concentration, vol %:	10	36	0.0007
N <sub>2</sub> Concentration, vol %:	84.75	77	0.0017
		117	0.002
		157	0.0023
		197	0.0026
		237	0.0032
		277	0.0035
		317	0.0039
		357	0.0038
		447	0.0042
		627	0.0049
		987	0.006

Figure 2. Effects of temperature on absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent in the 10-volume % moisture and 10-volume % hydrogen at the 0.072-s space time.

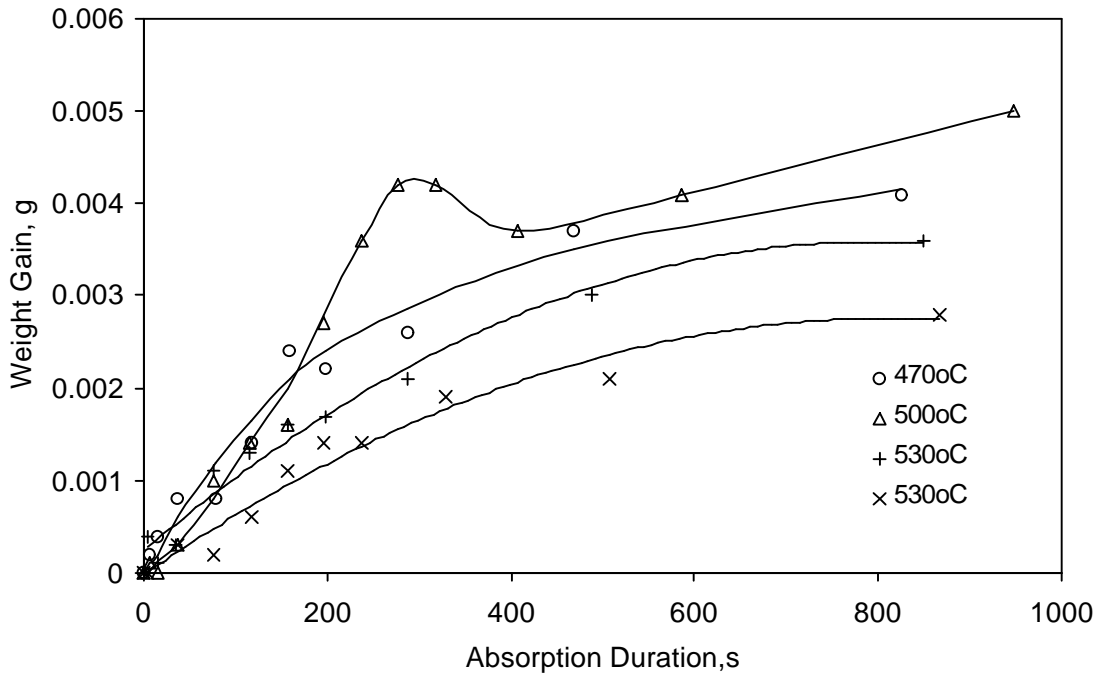


Figure 3. Effects of moisture on initial absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent with 10-volume % hydrogen at the 0.072-s space time and 530°C.

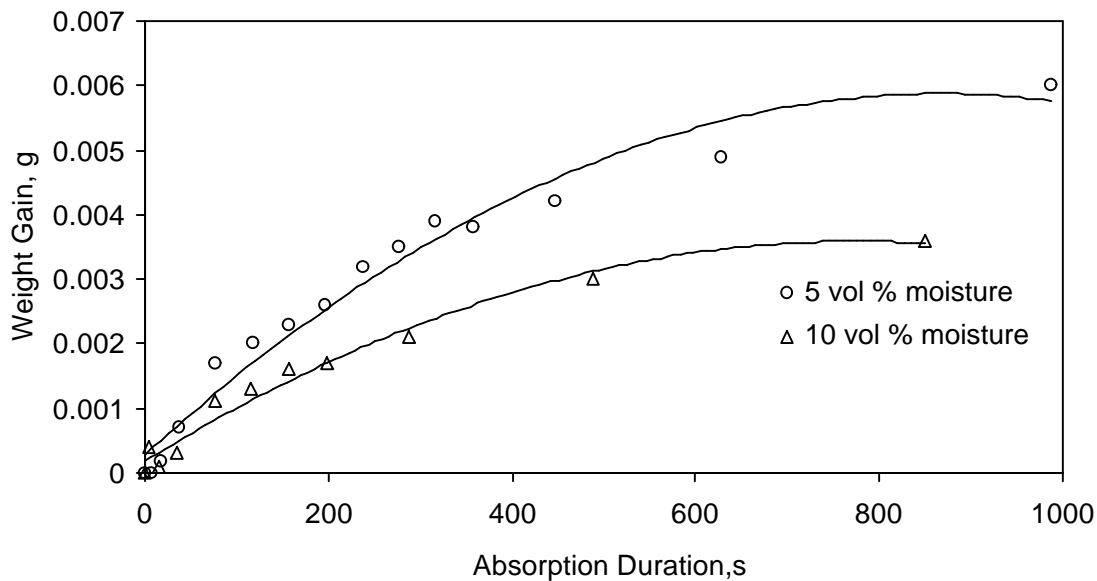
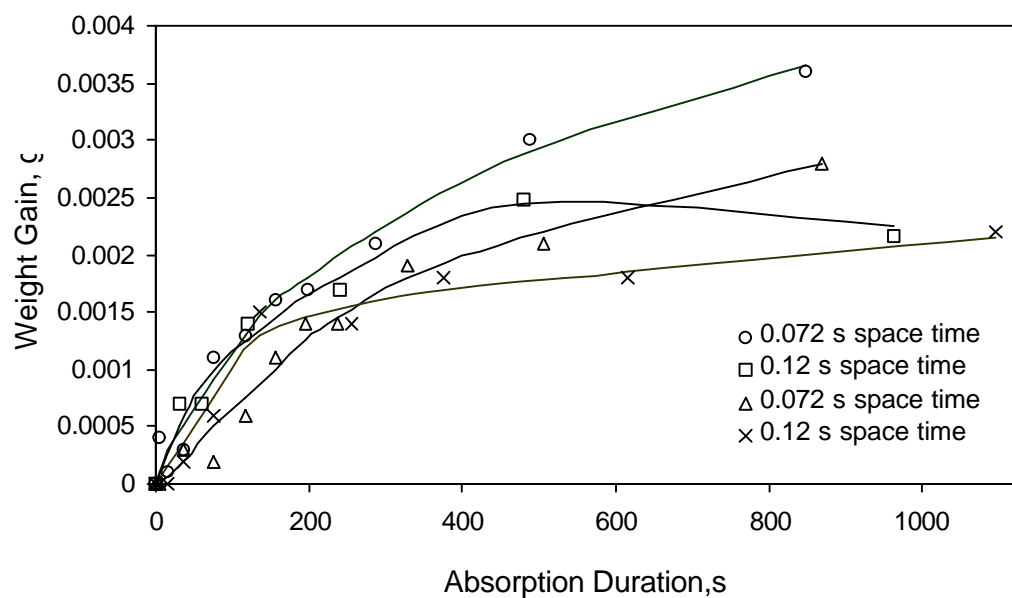


Figure 4. Effects of space time on initial absorption of 2500-ppm H<sub>2</sub>S into 0.1-g TU-188 sorbent with 10-volume % hydrogen and 10 vol % moisture at 530°C.



maintained at 2500 ppm and 10 vol %, respectively. The concentrations of moisture in the simulated coal gas mixture are 5 – 10 vol %. Initial absorption of H<sub>2</sub>S into the sorbent increases with decreased concentrations of moisture for short absorption duration of 5 – 970 seconds (see Figure 4). These facts may indicate that moisture, lighter than H<sub>2</sub>S, retard initial surface reaction of the metal oxide sorbent by oxygen dissolved into distilled water. Distilled water, containing dissolved air, is evaporated in the preheater. Gaseous oxygen is released into the simulated coal gas mixture upon evaporation of distilled water in the preheater

#### *Effects of Space Time on Initial Dynamic Absorption of H<sub>2</sub>S*

A series of experiments on effects of space (residence) time on initial dynamic absorption of H<sub>2</sub>S into the sorbent were conducted for the reaction duration of 6 – 1100 seconds at the 300 scc/min (0.12 s space time) and the 500 scc/min (0.072 s space time). Space time does not affect significantly initial dynamic absorption of H<sub>2</sub>S into the sorbent under these absorption conditions. These observations may suggest that transfer rate of H<sub>2</sub>S from the simulated coal gas mixture toward the outer surface in the macro porous matrix of the solid sorbent particles does not affect significantly initial dynamic absorption of H<sub>2</sub>S into the sorbent under these absorption conditions.

## CONCLUSIONS

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

- Initial absorption of H<sub>2</sub>S decreases generally with increased absorption temperature for short absorption duration of 5 – 950 seconds. Reduction reaction of the metal oxide sorbent with hydrogen may be dominant over initial absorption reaction of the metal oxide sorbent with hydrogen sulfide at higher absorption temperature.
- Initial absorption of H<sub>2</sub>S into the sorbent increases with decreased concentrations of moisture for short absorption duration of 5 – 970 seconds. Moisture, lighter than H<sub>2</sub>S, may retard initial surface reaction of the metal oxide sorbent by oxygen dissolved into distilled water. Distilled water containing dissolved air is fed into the preheater to produce steam, where gaseous oxygen is released.
- Space time does not affect significantly initial dynamic absorption of H<sub>2</sub>S into the sorbent under these absorption conditions. Transfer rates of H<sub>2</sub>S from the reactive gas mixture toward the outer surface in the macro porous matrix of the solid sorbent particles may not affect significantly initial dynamic absorption of H<sub>2</sub>S into the sorbent at the space time of 0.072 - 0.12 seconds and 530°C.

## PUBLICATION/PRESENTATION

“Reactivity of metal oxide sorbents with hot hydrogen sulfide in wet coal gases”, presented at

the 1998 Spring National Meeting, Sheraton New Orleans Hotel, New Orleans, LA, March 8-12, 1998.

“Reactivity of formulated metal oxide sorbents with hot hydrogen sulfide”, submitted for publication in Separation Science and Technology.