ENERGY

**Kinetics of Hot-Gas Desulfurization
Sorbents for Transport Reactors**

Annual Technical Progress Report for the Period
October 1, 1998 to September 30, 1999

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January 2000

Work Performed Under Contract No
DE-FG26-98FT40145--01

For
U.S. Department of Energy
National Energy Technology Laboratory
Pittsburgh, PA 15236-0940

By
Tuskegee University
Tuskegee, Alabama 36088

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SUMMARY

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide with various metal oxide sorbents at elevated temperatures. Various metal oxide sorbents are formulated with metal oxides such as Fe, Co, Zn, and Ti. Initial reaction kinetics of formulated sorbents with hydrogen sulfide is studied in the presence of various amounts of moisture and hydrogen at various reaction temperatures. The objectives of this research are to study initial reaction kinetics for a sorbent-hydrogen sulfide heterogeneous reaction system, to investigate effects of concentrations of hydrogen sulfide, hydrogen, and moisture on dynamic absorption of H_2S into sorbents, to understand effects of space time of reaction gas mixtures on initial reaction kinetics of the sorbent- hydrogen sulfide system, and to evaluate effects of temperature and sorbent amounts on dynamic absorption of H_2S into sorbents. Experimental data on initial reaction kinetics of hydrogen sulfide with metal oxide sorbents were obtained with a 0.83-cm^3 differential reactor. The reactivity of MCRH-67 sorbent and AHI-1 was examined. These sorbents were obtained from the Research Triangle Institute (RTI). The sorbents in the form of $70\text{ }\mu\text{m}$ particles are reacted with 1000 - 4000 ppm hydrogen sulfide at $450\text{ -}600^\circ\text{C}$. The range of space time of reaction gas mixtures is $0.03\text{ -}0.09\text{ s}$. The range of reaction duration is $4\text{ -}14400\text{ s}$.

INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become attractive for chemical feedstocks as well as for a source of liquid and gaseous fuels as petroleum resources become continually depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. The minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur. Sulfur in coal is present in organic, pyritic and sulfate forms. Although the sulfur occurring in the form of relatively coarse pyrite particles is removed largely by density separation, very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products from combustion not only pollute the environment, but are also detrimental to combustion systems because of the corrosive action of their combustion products. In the gasification process, coal is reacted with steam and oxygen to produce a medium to high calorific value fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to remove all forms of pollutants released from a coal conversion process through lower fuel consumption.

The removal of hydrogen sulfide from hot coal gas produced in the IGCC- based system by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. The removal of sulfur compounds from coal gas products is

investigated by using various metal oxide sorbents and membrane separation methods. Current investigations show that the removal of sulfur with metal oxide sorbents appears to deliver the most promising results. The main requirements of these metal oxide sorbents are durability and a high sulfur-loading capacity during absorption-regeneration cycles.

EXPERIMENTAL SETUPS

A differential micro reactor was fabricated with a titanium grade-2 tube. The volume of reactor is 0.83 cm^3 . The RTI MCRH-64 sorbent and the RTI AHI-1 sorbent in the form of $70\text{-}\mu\text{m}$ spherical particles were examined. These sorbent particles were reacted with simulated coal gases containing hydrogen sulfide in the 0.83 cm^3 titanium Grade-2 differential micro reactor for 4 - 14400 seconds at $450 - 600^\circ\text{C}$. Absorption amounts of hydrogen sulfide into the sorbent were analyzed with the LECO Sulfur Analyzer. The range of space (residence) time of the reaction gas mixture in the reactor was 0.03 - 0.09 s under the reaction conditions.

Figure 1. A Differential Reactor Assembly

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 5-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 70 μm 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 simulated coal gas mixture, containing H_2S , was introduced into the reactor for desired reaction duration, by switching nitrogen with the simulated coal gas mixture. The typical reaction conditions are shown in Table 1. The properties of the sorbents are shown in Table 2.

Table 1. Experimental conditions for the reaction of hydrogen sulfide with the sorbents.

Reactor Volume, cm^3 :	0.83
Temperature, $^{\circ}\text{C}$:	450 – 600
Reaction Pressure, psia	18
Reaction Time, s:	4 – 14400
Space Time under the absorption conditions, s:	0.03 – 0.09
Mean Particle Size, μm	70
Amount of Sorbent, g	0.005 – 0.05
Gas Flow Rate, cc/min at room temperature	250 – 750
Hydrogen, vol %	0 – 20
Moisture, vol %:	0 – 20
Concentration of H_2S , ppm	1000 – 4000
Nitrogen, vol %	Remainder

Table 2. Properties of the sorbents from the Research Triangle Institute (RTI).

Sorbent	MCRH-67	AHI-1
BET Area, m^2/g	81.8	NA
Avg. Pore Diameter, $\text{\AA}$	207	NA
Density, g/cm^3	2.7671	1.7103
Pore Volume, cm^3/g	0.2167	NA
Mean Particle Size, μm	130	130
Composition	15% ZnO 5% CO 5% Ni	20% Fe_2O_3 10% ZnO

Table 3. Absorption of hydrogen sulfide into MCRH-67 sorbent in the presence of hydrogen and moisture at various absorption conditions.

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
323	0.0503	10	10	4000	0.045	550	15.01	0.8829	1.52	
256	0.0498						29.99	1.824		
257	0.0494						60.33	3.239		
258	0.0493						179.97	5.566		
259	0.0498						360.34	6.643		
324	0.0249	10	10	4000	0.045	550	15.19	1.268	1.74	
294	0.025						30.03	2.631		
291	0.0252						60.3	3.604		
292	0.0251						180.36	5.825		
293	0.025						360.1	6.82		
290	0.0249						31.86	2.259		
535	0.01	10	10	4000	0.045	550	7.04	1.037	2.57	
318	0.0101						15.17	1.578		
295	0.0103						30.17	3.142		
361	0.103						60.13	4.738		
299	0.0103						179.94	6.1465		
298	0.0101						360.23	6.778		
533	0.0108						720.12	7.434		
534	0.0105						1440.53	7.666		
569	0.0105						3600	8.326		
582	0.0107						7200	8.69		
296	0.0106						60.17	4.05		
297	0.0102						180.18	5.32		
579	0.0049	10	10	4000	0.045	550	4.07	1.637	3.89	
580	0.0054						7.1	1.242		
581	0.0054						14.34	2.068		
583	0.0054						30.15	3.97		
587	0.0053						60.34	4.705		
588	0.0054						180.07	6.921		
590	0.0053						360.3	6.88		
589	0.0053						360.21	6.448		
568	0.0104	10	10	4000	0.036	550	7.34	0.8113	2.48	
317	0.0105						9.51	1.179		
300	0.0103						30.3	3.124		
402	0.0101						60.13	4.587		
302	0.0105						180.17	6.039		
303	0.0105						360.11	7.173		
376	0.0104						60.27	0.451		
301	0.0104						60	4.195		

Table 3. Continued-1

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
564	0.0102	10	10	4000	0.09	550	7.23	0.8466	1.57	
319	0.0103						15.4	1.179		
321	0.0107						30.3	1.897		
322	0.0105						60.18	3.228		
306	0.0101						179.88	5.492		
307	0.0102						359.94	6.245		
305	0.0102						60.17	3.105		
304	0.0105						30.4	2.489		
316	0.0106	10	10	4000	0.06	550	7.28	1.219	1.96	
314	0.0104						15.3	1.431		
308	0.0102						30.25	2.338		
312	0.0107						60.33	3.861		
315	0.0105						180.27	5.918		
313	0.0106						359.76	6.735		
309	0.0101						60	3.691		
311	0.0103						360.03	6.653		
310	0.01						180.1	5.175		
547	0.0105	10	10	2500	0.045	550	7.54	0.7313	2.59	0.0074
326	0.0102						15.17	1.438		
327	0.01						30.28	1.951		
328	0.0107						60.28	3.278		
329	0.0103						180.2	5.611		
330	0.0106						360.2	6.239		
546	0.0103	10	10	1000	0.045	550	7.04	0.7359	2.84	0.0079
331	0.0103						15.21	1.253		
332	0.0105						30.1	0.8114		
333	0.01						60.26	1.44		
334	0.0103						179.63	3.863		
335	0.0096						360.27	5.384		
542	0.0105	10	10	4000	0.045	600	7.3	0.8374	2.76	
336	0.0102						15.32	1.278		
337	0.0104						30.24	3.246		
338	0.0105						60.06	4.821		
339	0.0104						180.19	6.451		
340	0.0104						360.17	7.129		
541	0.0107	10	10	4000	0.045	500	7.38	1.195	2.58	
341	0.0101						15.5	1.749		
342	0.0101						30.27	3.434		
343	0.0104						60.12	4.923		
344	0.0101						180.12	6.182		
345	0.0101						360.08	7.319		

Table 3. Continued-2

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
553	0.0102	20	10	4000	0.045	550	7.93	0.8658	2.56	
369	0.0103						15.5	1.526		
367	0.0104						30.34	2.97		
348	0.0103						60.18	4.834		
349	0.0105						180.07	5.969		
350	0.0104						360.29	6.978		
346	0.0103						15.04	2.047		
347	0.0107						30.17	2.703		
552	0.0107	5	10	4000		550	7.36	0.8439	2.44	
351	0.0106						15.33	1.912		
352	0.01						30.36	3.385		
353	0.0101						60.14	4.765		
354	0.0106						180.43	5.949		
355	0.0103						360.04	6.617		
559	0.0103	10	15	4000	0.045	550	7.27	0.7263	2.51	
369	0.0103						15.5	1.526		
357	0.0107						30.01	2.953		
358	0.0107						60.07	4.725		
368	0.0105						180.22	6.363		
360	0.0102						360.14	7.136		
359	0.0102						180.18	5.478		
356	0.01						15.27	2.228		
558	0.0103	10	5	4000	0.045	550	7.39	0.9176	2.41	
362	0.0105						15.23	1.97		
363	0.0107						30	3.423		
370	0.01						60.04	4.492		
365	0.0101						180.1	6.059		
366	0.0102						360.54	6.988		
364	0.0106						60.04	5.891		
371	0.0105	10	10	4000	0.03	550	15.32	2.264	2.48	
400	0.0103						30.11	3.122		
401	0.0101						60.12	4.469		
374	0.0106						180.14	6.098		
375	0.0106						360.5	6.854		
372	0.0101						30.07	0.4074		
373	0.0102						60.08	0.4939		
639	0.0103	10	10	4000	0.045	450	4.23	1.273	1.75	
640	0.0105						7.24	0.8421		
641	0.0101						15.3	1.33		
642	0.0105						30.08	2.322		
643	0.0103						60.34	3.988		
644	0.0103						180.2	5.209		
645	0.0104						360.28	6.249		

Table 4. Absorption of hydrogen sulfide into AHI-1 sorbent in the presence of hydrogen and moisture at various absorption conditions.

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
536	0.0103	10	10	4000	0.045	550	7.14	0.6968	0.53	0.00058
377	0.0103						15.44	0.9313		
398	0.0101						30.1	1.304		
379	0.0107						60.18	1.921		
380	0.0105						180.08	3.32		
381	0.0103						360.49	4.39		
531	0.0101						720.12	4.837		
532	0.0103						1440	5.545		
570	0.0105						3600	6.408		
586	0.0103						7200	6.907		
585	0.0104						14400	7.048		
508	0.0104						60.23	1.719		
378	0.0102						29.96	0.1763		
544	0.0104	10	10	1000	0.045	550	7.28	0.6422	0.24	0.00014
382	0.0102						15.25	0.9142		
383	0.0102						30.53	0.5879		
384	0.0101						60.14	0.79		
385	0.0104						180.07	1.287		
386	0.0102						360.17	2.312		
548	0.0104	10	10	2500	0.045	550	7.25	0.5874	0.32	0.00013
399	0.0105						15.15	0.724		
388	0.0103						30.1	0.8256		
389	0.0101						60	1.296		
523	0.0097						180.14	2.162		
391	0.0105						360.18	3.59		
397	0.0103						180.17	2.97		
390	0.0104						183.32	1.219		
387	0.0101						15.27	0.598		
392	0.0252	10	10	4000	0.045	550	15.06	0.6548	0.45	0.00056
393	0.025						29.99	0.955		
394	0.0251						60.1	1.522		
395	0.0252						180	3.35		
396	0.0255						360.31	4.529		
403	0.0501	10	10	4000	0.045	550	15.42	0.3987	0.47	0.00066
404	0.0502						30.17	0.6291		
405	0.0507						60.21	1.387		
406	0.0502						180.23	3.403		
407	0.0503						360.04	4.623		

Table 4. continued-1

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
543	0.0103	10	10	4000	0.045	600	7.28	0.6891	0.64	0.00137
408	0.0101						15.28	0.9673		
409	0.0105						30.17	1.221		
511	0.0103						60.2	3.148		
512	0.0107						180.37	3.916		
412	0.0105						360.19	4.257		
509	0.0106						29.97	1.203		
411	0.0105						180.15	3.723		
410	0.0103						60	2.497		
540	0.0104	10	10	4000	0.045	500	7.45	0.8495	0.29	0.00064
413	0.0104						15.04	0.8978		
414	0.0106						30.33	1.329		
415	0.0101						60.48	1.749		
416	0.0106						180.3	3.003		
417	0.0105						360.3	4.069		
560	0.0107	10	15	4000	0.045	550	7.2	0.5756	0.41	0.00069
418	0.0104						15	0.8888		
419	0.0102						30.21	1.032		
420	0.0107						60.27	1.531		
421	0.0106						180.23	2.667		
422	0.0102						360.28	3.449		
557	0.0102	10	5	4000	0.045	550	7.27	0.7386	0.49	0.0015
423	0.103						15.43	1.25		
424	0.0107						30.03	1.66		
425	0.0105						60.35	2.316		
510	0.0103						180.14	3.957		
427	0.0104						360.38	5.078		
426	0.0103						180.25	4.484		
566	0.0107	10	10	4000	0.036	550	7.24	0.5678	0.34	0.00113
428	0.0105						15.33	0.8155		
429	0.0105						30.09	1.243		
430	0.01						60.23	1.903		
431	0.0105						180.47	3.1		
432	0.0101						360.2	4.345		
563	0.0103	10	10	4000	0.09	550	7.14	0.6372	0.38	0.0008
433	0.0105						15.27	0.8454		
434	0.0103						30.03	0.8072		
435	0.0101						60.13	1.637		
458	0.0101						180.1	3.213		
437	0.0104						360	4.197		
436	0.0103						180.14	4.664		

Table 4. Continued-2

Run #	Sorbent Amount, g	Hydrogen v%	Moisture v%	Hydrogen Sulfide, ppm	Space Time, s	Reaction Temperature, °C	Reaction Duration, s	Sulfur Absorption, w%	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s
551	0.0105	5	10	4000	0.045	550	7.27	0.5902	0.29	0.00067
438	0.0104						14.94	0.7302		
459	0.0108						30.01	1.076		
440	0.0103						60.3	1.681		
441	0.0104						180.1	2.698		
442	0.0101						360.36	3.699		
439	0.0102						30.2	1.497		
554	0.0103	20	10	4000	0.045	550	7.04	0.682	0.39	0.0011
443	0.0102						15.04	0.911		
444	0.0106						30.44	1.12		
445	0.01						59.97	1.927		
446	0.0107						180.34	3.361		
447	0.0106						360.15	4.454		
572	0.01	10	20	4000	0.045	550	4.06	0.7568	0.23	0.00025
573	0.0108						7.09	0.8035		
574	0.01						14.14	0.06285		
575	0.0106						30.27	0.8487		
576	0.0103						60.015	1.327		
577	0.0106						180.06	2.233		
578	0.0101						360.04	2.842		
620	0.0107	0	10	4000	0.045	550	4.14	0.6187	0.31	0.00085
621	0.0105						7.18	0.7066		
622	0.0103						15.27	0.8174		
623	0.0101						29.94	1.069		
624	0.0101						60.3	1.717		
625	0.0101						180.09	2.953		
626	0.0103						360.3	4.199		
627	0.0102						7200	7.31		
613	0.0104	10	0	4000	0.045	550	4.3	1.441	2.05	--
614	0.0104						7.34	0.7869		
615	0.0102						15.33	1.749		
616	0.0107						30.18	3.984		
617	0.0107						60.16	5.8		
618	0.0104						180.24	7.475		
619	0.0101						360.24	8.364		
628	0.0103						7200	9.359		
629	0.0106	10	10	4000	0.045	450	4.7	0.7709	0.99	0.00011
630	0.0104						8.05	0.8296		
631	0.0102						15.25	0.984		
632	0.0101						30.18	1.163		
633	0.0102						60.04	1.696		
635	0.0103						180.21	2.257		
636	0.0102						360.35	2.768		

THEORY

Levenspiel[1] described a reaction equation for a gas-solid reaction of spherical particles, using three reaction rate-controlling steps such as mass transfer of gaseous reactants through gaseous reaction mixtures, diffusion of reactants through porous solid reactants, and surface reaction of gaseous reactants with solid reactants (see Equation 1). Equation 1 was modified to obtain mass transfer rate of H_2S , intraparticle diffusivity of H_2S , and reaction rate of H_2S with the sorbent using the experimental data shown in Tables 2 and 3. This equation is developed under the assumptions that the shrinking core model and a quasi-steady state are valid.

$$\left(-\frac{d\left(\frac{r_c}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_s R^2}{C_g}\right) \left(\frac{1}{Rk_g} - \frac{1}{d}\right) \left(\frac{r_c}{R}\right) + \left(\frac{C_s R^2}{C_g d}\right) \left(\frac{r_c}{R}\right) + \left(\frac{C_s R}{C_g k_b}\right) \quad (1)$$

Equation 2 is obtained from Equation 1, when mass transfer rates are much higher than both diffusion rates of gaseous reactants and reaction rates of solid reactants. Equation 2 was applied to the experimental data shown in Table 3 to obtain both intraparticle diffusivity of H_2S and reaction rate of H_2S with the AHI-1 sorbent.

$$\left(-\frac{d\left(\frac{r_c}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_s R^2}{C_g}\right) \left(\frac{r_c}{R} - \left(\frac{r_c}{R}\right)^2\right) + \left(\frac{C_s R}{C_g k_b}\right) \quad (2)$$

Equations 3 and 6 are obtained from Equation 1, when both intraparticle diffusion controlling step and mass transfer controlling step of gaseous reactants are negligible. Intraparticle diffusion-controlling step is considered insignificant during initial absorption of H_2S into the sorbent. When Equation 6 was applied to the initial reaction data shown in Table 2, the reaction rate constants of H_2S with the MCRH-67 sorbent are obtained under various reaction conditions.

Equation 7 is obtained from Equation 1, when both surface reaction step and mass transfer controlling step of gaseous reactants are negligible. Equation 7 is applied to some experimental data in Table 3 to obtain intraparticle diffusivity values.

$$\left(-\frac{d\left(\frac{r_c}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_s R}{C_g k_b}\right) \quad (3)$$

$$t = \left(\frac{C_s R}{C_g k_b}\right) \left(1 - \frac{r_c}{R}\right) \quad (4)$$

$$\left(\frac{r_c}{R}\right) = (1 - x_B)^{1/3} \quad (5)$$

$$t = \left(\frac{C_s R}{C_g k_b'} \right) \left(1 - (1 - x_B)^{1/3} \right) \quad (6)$$

$$t = \left(\frac{C_s R}{C_g k_b'} \right) \left(1 - (1 - x_B)^{2/3} + 2(1 - x_B) \right) \quad (7)$$

where r_c : radius of an unreacted core k_g : mass transfer rate of gaseous reactant
 R : radius of spherical sorbent C_s : molar concentration of solid reactant
 t : reaction time $\mathbf{d}$: intraparticle diffusivity of gaseous reactant
 C_g : concentration of gaseous reactant k_b' : reaction rate constant
 x_B : conversion of solid reactant

RESULTS AND DISCUSSION

Experiments on absorption of hydrogen sulfide into the sorbents were carried out for 4 – 14400 seconds at 450 - 600°C (see Table 1) to evaluate effects of concentrations of H₂S, H₂ and moisture, temperature, sorbent amounts, and space time on initial dynamic absorption of hydrogen sulfide into the sorbents. A typical simulated coal gas mixture consists of 4000-ppm hydrogen sulfide, 10-vol % moisture, 10 vol % hydrogen, and nitrogen as remainder. A typical volumetric feed rate of a simulated coal gas mixture to the reactor is 500 cm³/min at room temperature and atmospheric pressure. The temperature of the reactor is controlled in the furnace oven at 450 - 550°C. The pressure of the reactor is maintained at 18 psia. The total capacities of the sorbents for absorption of H₂S are determined with the experimental data shown in Figure 2.

Figure 2. Effects of reaction duration on absorption of 4000-ppm H₂S on 0.01-g sorbent with 10-v% moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

Effects of Temperature on Initial Dynamic Absorption of H₂S

Experiments on initial absorption of H₂S into the sorbents were carried out for 4 – 360 seconds at 18 psia and 450 - 600°C to find effects of temperature on initial dynamic absorption of H₂S with the sorbents. The concentrations of both moisture and hydrogen are maintained at 10-vol percent. The concentration of hydrogen sulfide in the simulated coal gas mixture is maintained at 4000 ppm.

Initial absorption of H₂S into the MCRH-67 sorbent is affected with absorption temperature for short absorption duration of 4 - 60 seconds (see Figure 3). Equation 6 was applied to the experimental data to obtain surface reaction rate constants of H₂S with the sorbent (see Figure 4). The range of surface reaction rate constant is 1.75 – 2.76 cm/s (see Figure 5). These observations may indicate that reactivity of the MCRH-67 sorbent be independent of reaction temperature in the temperature range of 500 – 600°C. However, reactivity of the sorbent is much lower at 450°C than that at 500 – 600°C. These facts also suggest that the controlling step for the initial absorption of H₂S into sorbent particles is surface reaction of H₂S with reactive sites of sorbent particles.

Figure 3. Effects of temperature on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture at the space time 0.045 s.

Initial absorption of H₂S into the AHI-1 sorbent is affected with absorption temperature for short absorption duration of 4 - 60 seconds (see Figure 6). Equation 2 was applied to the experimental data to obtain surface reaction rate constants as well as intraparticle diffusivity of H₂S with the sorbent (see Figure 7). The range of surface reaction rate constant is 0.29 – 0.98 cm/s. The range of intraparticle diffusivity is 0.00011 – 0.00137 cm²/s. Both surface reaction rate constant and intraparticle diffusivity are affected by reaction temperature (see Figure 8). These observations may indicate that reactivity of the AHI-1 sorbent be dependent on reaction temperature. These facts also suggest that the controlling steps for the absorption of H₂S into sorbent particles are surface reaction of H₂S with reactive sites of sorbent particles and diffusion of H₂S through porous sorbent particles.

Figure 7. Effects of temperature on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v % H_2 and 10-v% moisture at the space time 0.045 s.

Figure 8. Effects of temperature on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at the space time 0.045 s.

Effects of Moisture on Initial Dynamic Absorption of H_2S

Experiments on initial absorption of H_2S into the sorbents were carried out for 4 – 360 seconds at 18 psia and 550°C to find effects of moisture concentrations on initial dynamic absorption of H_2S with the sorbents. The concentrations of H_2S and hydrogen are maintained at 4000 ppm and 10-vol %, respectively. The concentration range of moisture in the simulated coal gas mixture is 0 – 20 volume percent.

Initial absorption of H_2S into the MCRH-67 sorbent is not affected with concentrations of moisture for short absorption duration of 4 – 60 seconds (see Figure 9). These facts may indicate that moisture is inert for the reaction of H_2S with the MCRH-67 sorbent. Equation 6 was applied to the experimental data to obtain surface reaction rate constants of H_2S with the sorbent (see Figures 10). The range of surface reaction rate constant is 2.41 – 2.51 cm/s (see Figure 11). These observations may indicate that reactivity of the MCRH-67 sorbent be independent of moisture concentrations. These facts also suggest that the controlling step for initial absorption of H_2S into sorbent particles is surface reaction of H_2S with reactive sites of sorbent particles.

Figure 9. Effects of moisture on absorption of 4000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen at 550°C and the space time 0.045 s.

Figure 10. Effects of moisture on absorption of 4000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-volume % hydrogen at 550°C and the space time 0.045 s.

Figure 11. Effects of moisture on absorption of 4000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-volume % hydrogen at 550°C and the space time 0.045 s.

Initial absorption of H_2S into the AHI-1 sorbent is affected with concentrations of moisture for short absorption duration of 4 –60 seconds (see Figure 12). These facts may indicate that moisture is not inert for the reaction of H_2S with the AHI-1 sorbent. Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S with the sorbent (see Figure 13). The range of surface reaction rate constants is 0.23 – 2.05 cm/s, and the range of intraparticle diffusivity values is 0.00025 –0.0015

cm²/s (Figure 14). These observations may indicate that reactivity of the AHI-1 sorbent and intraparticle diffusivity decrease with increased moisture concentrations. These facts also suggest that the controlling steps for the absorption of H₂S into sorbent particles are surface reaction of H₂S with reactive sites of sorbent particles and diffusion of H₂S through porous sorbent particles in the presence of moisture.

Figure 12. Effects of moisture on absorption of 4000-ppm H₂S on 0.01-g AHI-1 sorbent with 10-volume % hydrogen at 550°C and the space time 0.045 s.

Figure 13. Effects of moisture on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H₂S into 0.01-g AHI-1 sorbent with 10-v % H₂ and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 14. Effects of moisture on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 15. Absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-volume % hydrogen in the absence of moisture at 550°C and the space time 0.045 s.

A series of absorption reaction of H_2S into the AHI-1 sorbent was carried out in the absence of moisture (see Figure 12). Equation 6 was applied to the experimental data to obtain the surface reaction rate constant (see Figure 15). The surface reaction rate constant is 2.05 cm/s . Initial absorption of H_2S into the sorbent in the presence of moisture is controlled by both the surface reaction step and the intraparticle diffusion control step. However, initial absorption of H_2S into the sorbent in the absence of moisture is controlled by the surface reaction step only. The total sulfur absorption capacity of the sorbent is 7.05 w% in the presence of moisture, whereas the total sulfur absorption capacity of the sorbent is 9.36 w% in the absence of moisture

(see Table 4). These observations also suggest that moisture poison reactive sites of the AHI-1 sorbent at the elevated temperature 550°C and affects mechanisms on absorption of H₂S into the sorbent.

Effects of Space Time on Initial Dynamic Absorption of H₂S

Experiments on effects of space (residence) time on initial dynamic absorption of H₂S into the sorbents were conducted for the reaction duration of 4 – 360 seconds at 550°C and the space-time of 0.03 – 0.09 s. The concentrations of both hydrogen and moisture were maintained at 10-v percent. The concentration of H₂S was maintained at 4000 ppm.

Space time does not affect significantly initial dynamic absorption of H₂S into the MCRH-67 sorbent in the space time range of 0.03 - 0.045 s (see Figure 16). These observations may suggest that the mass transfer-controlling step of H₂S through the gas mixture is negligible for adsorption of H₂S into the sorbent in the space time range of 0.03 - 0.045 s. However, space-time affect significantly initial dynamic absorption of H₂S into the MCRH-67 sorbent in the space time range of 0.045 – 0.09 s (see Figure 16). These observations may suggest that absorption of H₂S into the sorbent is significantly affected by the mass transfer of H₂S through the gas mixture in the space time range of 0.045 – 0.09 s. Equation 6 was applied to the experimental data to obtain surface reaction rate constants of H₂S with the sorbent (see Figure 17). The range of surface reaction rate constant is 1.57 – 2.57 cm/s (see Figure 18). These observations may indicate that reactivity of the MCRH-67 sorbent be significantly affected by space-time. These facts also suggest that the controlling step for the absorption of H₂S into sorbent particles is surface reaction of H₂S with reactive sites of sorbent particles in the 4 – 60 s initial reaction duration.

Figure 16. Effects of space time on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen and 10 v% moisture at 550°C.

Figure 17. Effects of space time on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-v% moisture and 10-v% hydrogen at 550°C.

Figure 18. Effects of space time on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-volume % moisture and 10-v% hydrogen at 550°C.

Space-time does not affect significantly initial dynamic absorption of H₂S into the AHI-1 sorbent in the space time range of 0.036 - 0.09 s (see Figure 19). These observations may suggest that the mass transfer-controlling step of H₂S through the gas mixture is negligible for adsorption of H₂S into the sorbent in the space time range of 0.036 - 0.09 s. Equation 6 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H₂S with the sorbent (see Figure 20). The range of surface reaction rate constant is 0.34 – 0.53 cm/s, and the range of intraparticle diffusivity values is 0.0006 – 0.0011

cm^2/s (see Figure 21). These observations may indicate that reactivity of the AHI-1 sorbent is slightly affected by space-time. These data also indicate that intraparticle diffusivity decrease drastically with increased space time in the range of 0.036 – 0.045 s and is slightly affected by space time in the range of 0.045 – 0.09 s.

Figure 19. Effects of space time on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-v% hydrogen and 10 v% moisture at 550°C .

Figure 20. Effects of space time on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C .

Figure 21. Effects of space time on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C .

Effects of Concentration of H_2S on Initial Dynamic Absorption of H_2S

Experiments on effects of concentration of H_2S on initial dynamic absorption of H_2S into the sorbents were conducted for the reaction duration of 4 – 360 seconds at 550°C and the space-time of 0.045 s. The concentrations of hydrogen and moisture were maintained at 10-volume percent, respectively

Concentrations of H_2S affect significantly initial dynamic absorption of H_2S into the MCRH-67 sorbent in the H_2S concentration range of 1000 – 4000 ppm (see Figure 22). Equation 6 is applied to the experimental data. Equation 6 fits well the experimental data obtained at the 4000-ppm H_2S concentration, but Equation 6 does not fit well the experimental data obtained at the H_2S concentration of 1000 – 2500 ppm (see Figure 23). The reaction rate constants and the intraparticle diffusivity values in the H_2S concentration range of 1000 – 2500 ppm were obtained with Equation 2 (Figure 25). The range of surface reaction rate constant is 2.57 – 2.84 cm/s , and the range of intraparticle diffusivity values is 0.0074 – 0.0079 cm^2/s . The reaction rate constants of the sorbent, obtained from Equations 2 and 6, decrease slightly with increased H_2S concentration (see Figure 24). These observations may indicate that the chemical reaction of H_2S with the sorbent controls initial adsorption of H_2S into the sorbent at relatively high H_2S concentrations. These facts may indicate that both chemical reaction of H_2S with the sorbent and the intraparticle diffusivity of H_2S through the porous solvent control initial adsorption of H_2S into the sorbent at relatively low H_2S concentrations.

Figure 22. Effects of H₂S concentration on absorption of H₂S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 23. Effects of H₂S concentration on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-v% moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

Figure 24. Effects of H₂S concentration on absorption of 4000-ppm H₂S on 0.01-g MCRH-67 sorbent with 10-volume % moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

Figure 25. Effects of H₂S concentration on intraparticle diffusivity and reaction rate constant in the adsorption of H₂S into MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Concentrations of H₂S affect significantly initial dynamic absorption of H₂S into the AHI-1 sorbent in the H₂S concentration range of 1000 – 4000 ppm (see Figure 26). Equation 2 is applied to the experimental data. Equation 2 fits well the experimental data obtained at the 4000-ppm H₂S concentration, but Equation 6 does not fit well the experimental data obtained at the H₂S concentration of 1000 – 2500 ppm. Equation 7 was applied to the low-concentration data to obtain intraparticle diffusivity values in the H₂S concentration range of 1000 – 2500 ppm (see Figure 27). The reaction rate constants in the H₂S concentration range of 1000 – 2500 ppm were obtained with Equation 3. The range of surface reaction rate constant is 0.24 – 0.53 cm/s,

and the range of intraparticle diffusivity values is $0.00013 - 0.00058 \text{ cm}^2/\text{s}$. The reaction rate constants of the sorbent, obtained from Equations 2 and 3, increase with increased H_2S concentration (see Figure 28). The intraparticle diffusivity values of H_2S through porous sorbents increase drastically with increased H_2S concentrations in the H_2S concentration range of 2500 – 4000 ppm. These observations may indicate that the chemical reaction of H_2S with the sorbent as well as the intraparticle diffusivity of H_2S through the porous sorbent controls initial adsorption of H_2S into the sorbent at relatively high H_2S concentrations. These facts may indicate that the intraparticle diffusivity of H_2S through the porous sorbent controls initial adsorption of H_2S into the sorbent at relatively low H_2S concentrations.

Figure 26. Effects of H_2S concentration on absorption of H_2S on 0.01-g AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 27. Effects of H_2S concentration on intraparticle diffusivity in the adsorption of H_2S into AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 28. Effects of H₂S concentration on intraparticle diffusivity and reaction rate constant in the adsorption of H₂S into AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 29. Effects of sorbent amount on absorption of 4000-ppm H₂S on MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Effects of Sorbent amounts on Initial Dynamic Absorption of H₂S

Experiments on effects of sorbent amounts on initial dynamic absorption of H₂S into the sorbents were conducted for the reaction duration of 4 – 360 seconds at 550°C and the space-time of 0.045 s. The concentrations of both hydrogen and moisture were maintained at 10-v percent. The concentration of H₂S was maintained at 4000 ppm.

Amounts of the MCRH-67 sorbent affect significantly initial dynamic absorption of H_2S into the sorbent in the sorbent amount range of 0.005– 0.05 g (see Figure 29). Equation 6 was applied to the experimental data to obtain surface reaction rate constant of H_2S with the sorbent (see Figure 30). The range of the surface reaction rate constant is 1.52 – 3.89 cm/s. The reaction rate constants decrease with increased sorbent amounts (see Figure 31). Initial absorption of H_2S into the sorbent increases with decreased amounts of the sorbent (see Figure 29). These observations may suggest that hydrodynamics of gas mixtures in the fluidized differential reactor affects significantly initial adsorption of H_2S into the sorbent.

Figure 30. Effects of sorbent amount on absorption of 4000-ppm H_2S on MCRH-67 sorbent with 10-v% moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

Figure 31. Effects of sorbent amount on absorption of 4000-ppm H_2S on MCRH-67 sorbent with 10-v% moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

Amounts of the AHI-1 sorbent affect slightly initial dynamic absorption of H_2S into the sorbent in the sorbent amount range of 0.01– 0.05 g (see Figure 32). Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S (see Figure 33). The range of the surface reaction rate constant is 0.47 – 0.53 cm/s , and the range of the intraparticle diffusivity values is 0.00058 – 0.00066 cm^2/s . The reaction rate constants decrease slightly with increased sorbent amounts, and the intraparticle diffusivity values increase slightly with increased sorbent amounts (see Figure 34).

Figure 32. Effects of sorbent amount on absorption of 4000-ppm H_2S on AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 33. Effects of sorbent amount on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v % H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

Figure 34. Effects of sorbent amount on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v % H_2 and 10-v% moisture at $550^\circ C$ and the space time 0.045 s.

Effects of Hydrogen Concentration on Initial Dynamic Absorption of H_2S

Experiments on effects of hydrogen concentrations on initial dynamic absorption of H_2S into the sorbents were conducted for the reaction duration of 4 – 360 at $550^\circ C$ and the space-time of 0.045 s. The concentration of moisture was maintained at 10-volume percent. The concentration of H_2S was maintained at 4000 ppm.

Figure 35. Effects of hydrogen on absorption of 4000-ppm H_2S into 0.01-g MCRH-67 sorbent with 10-v% moisture at $550^\circ C$ and the space time 0.045 s.

Concentrations of hydrogen do not affect significantly initial dynamic absorption of H_2S into the MCRH-67 sorbent in the hydrogen concentration range of 5 – 20 v% (see Figure 35). Equation 6 was applied to the experimental data to obtain initial surface reaction rate constants (see Figure 36). The range of the initial surface reaction rate constant is 2.44 – 2.57 cm/s (see Figure 37). These facts may indicate that hydrogen is inert for the reaction of H_2S with the sorbent.

Figure 36. Effects of hydrogen on absorption of 4000-ppm H_2S on 0.01-g sorbent with 10-volume % moisture at 550°C and the space time 0.045 s.

Figure 37. Effects of hydrogen on absorption of 4000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-volume % moisture at 550°C and the space time 0.045 s.

Concentrations of hydrogen affect slightly initial dynamic absorption of H_2S into the AHI-1 sorbent in the hydrogen concentration range of 0 – 20 v% (see Figure 38). Equation 2 was applied to the experimental data to obtain initial surface reaction rate constants and intraparticle diffusivity values (see Figure 39). The range of the initial surface reaction rate constant is 0.29 – 0.53 cm/s, and the range of the intraparticle diffusivity values is 0.00058 – 0.00101 cm^2/s (see Figure 40). Surface reaction rate constant increases with hydrogen concentration. These facts may indicate that hydrogen affect both surface reaction of H_2S with the sorbent and intraparticle diffusivity of H_2S through porous sorbents. Intraparticle diffusivity of hydrogen sulfide through porous sorbent decreases drastically with increased hydrogen concentration in the hydrogen concentration range of 0 – 10 volume percent (see Figure 40).

Figure 38. Effects of hydrogen on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-volume % moisture at 550°C and the space time 0.045 s.

Figure 39. Effects of hydrogen on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% moisture at 550°C and the space time 0.045 s.

Figure 40. Effects of hydrogen on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H₂S into 0.01-g AHI-1 sorbent with 10-v% moisture at 550°C and the space time 0.045 s.

CONCLUSIONS

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

- Initial reactivity of the MCRH-67 sorbent appears to be independent of reaction temperature in the temperature range of 500 – 600°C. The controlling step for the initial absorption of H₂S into MCRH-67 sorbent particles is surface reaction of H₂S with reactive sites of sorbent particles.
- Initial reactivity of the AHI-1 sorbent is dependent on reaction temperature. The controlling steps for the absorption of H₂S into AHI-1 sorbent particles are both surface reaction of H₂S with reactive sites of sorbent particles and diffusion of H₂S through porous sorbent particles.
- Initial reactivity of the MCRH-67 sorbent appears to be independent of moisture concentrations, whereas both initial reactivity of the AHI-1 sorbent and intraparticle diffusivity decrease with increased moisture concentrations.
- Initial absorption of H₂S into the AHI-1 sorbent in the presence of moisture is controlled by both surface reaction step and intraparticle diffusion control step. However, initial absorption of H₂S into the sorbent in the absence of moisture is controlled by the surface reaction step only. The total sulfur absorption capacity of the sorbent is 7.05 w% in the presence of moisture, whereas the total sulfur absorption capacity of the sorbent is 9.36 w% in the absence of moisture. These observations also suggest that moisture poison reactive

sites of the AHI-1 sorbent at the elevated temperature 550°C and affect mechanisms on adsorption of H₂S into the sorbent.

- Initial reactivity of the MCRH-67 sorbent appears to be dependent on space-time. Initial reactivity of the AHI-1 sorbent is slightly affected by space-time.
- Chemical reaction of H₂S with the MCRH-67 sorbent controls initial adsorption of H₂S into the sorbent at relatively high H₂S concentrations. Chemical reaction of H₂S with the sorbent and intraparticle diffusivity of H₂S through the porous solvent control initial adsorption of H₂S into the sorbent at relatively low H₂S concentrations.
- Both chemical reaction of H₂S with the AHI-1 sorbent and intraparticle diffusivity of H₂S through the porous sorbent control initial adsorption of H₂S into the sorbent at relatively high H₂S concentrations. Intraparticle diffusivity of H₂S through the porous sorbent controls initial adsorption of H₂S into the sorbent at relatively low H₂S concentrations.
- Reaction rate constants of the MCRH-67 sorbent decrease with increased sorbent amounts. Initial absorption of H₂S into the sorbent increases with decreased amounts of the sorbent.
- Hydrogen appears to be inert for the reaction of H₂S with the MCRH-67 sorbent, whereas hydrogen affects both surface reaction of H₂S with the AHI-1 sorbent and intraparticle diffusivity of H₂S through porous AHI-1 sorbents.

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PUBLICATIONS

“Reactivity of Sorbents with Hot Hydrogen Sulfide in the Presence of Moisture and Hydrogen”, presented at the Eleventh Symposium on Separation Science and Technology for Energy Applications, Park Vista Hotel & Convention Center, Gatlinburg, Tennessee, October 17 -21, 1999.

“Reactivity of Metal Oxide Sorbents in the Removal of Hot Hydrogen Sulfide”, will be presented at Spring AIChE National Meeting, March 5-9, 2000, Atlanta, GA.