ENERGY

Kinetics of Hot-Gas Desulfurization Sorbents for Transport Reactors

Annual Technical Progress Report for the Period
October 1, 2000 to September 30, 2001

F
O
S
S
I
L

By
K. C. Kwon
Tel: (334) 727-8976, Fax: (334) 724-4188

January 2002

Work Performed Under Contract No
DE-FG26-98FT40145

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

By
Tuskegee University
Tuskegee, Alabama 36088

Kinetics of Hot-Gas Desulfurization Sorbents for Transport Reactors

Annual Technical Progress Report
for the Period October 1, 2000 to September 30, 2001

K. C. Kwon
Tel: (334) 727-8976, Fax: (334) 724-4188

January 2002

Work Performed Under Contract No.: DE-FG26-98FT40145

For
U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
P.O. Box 10940
Pittsburgh, PA 15236-0940

By
Tuskegee University
Tuskegee, Alabama 36088

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES Continued-1

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, 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 was examined in this report. This sorbent was obtained from the Research Triangle Institute (RTI). The sorbent in the form of 130 μm particles are reacted with 18000-ppm hydrogen sulfide at 350 –525^{o}C. The range of space time of reaction gas mixtures is 0.069 – 0.088 s. The range of reaction duration is 4 – 180 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.

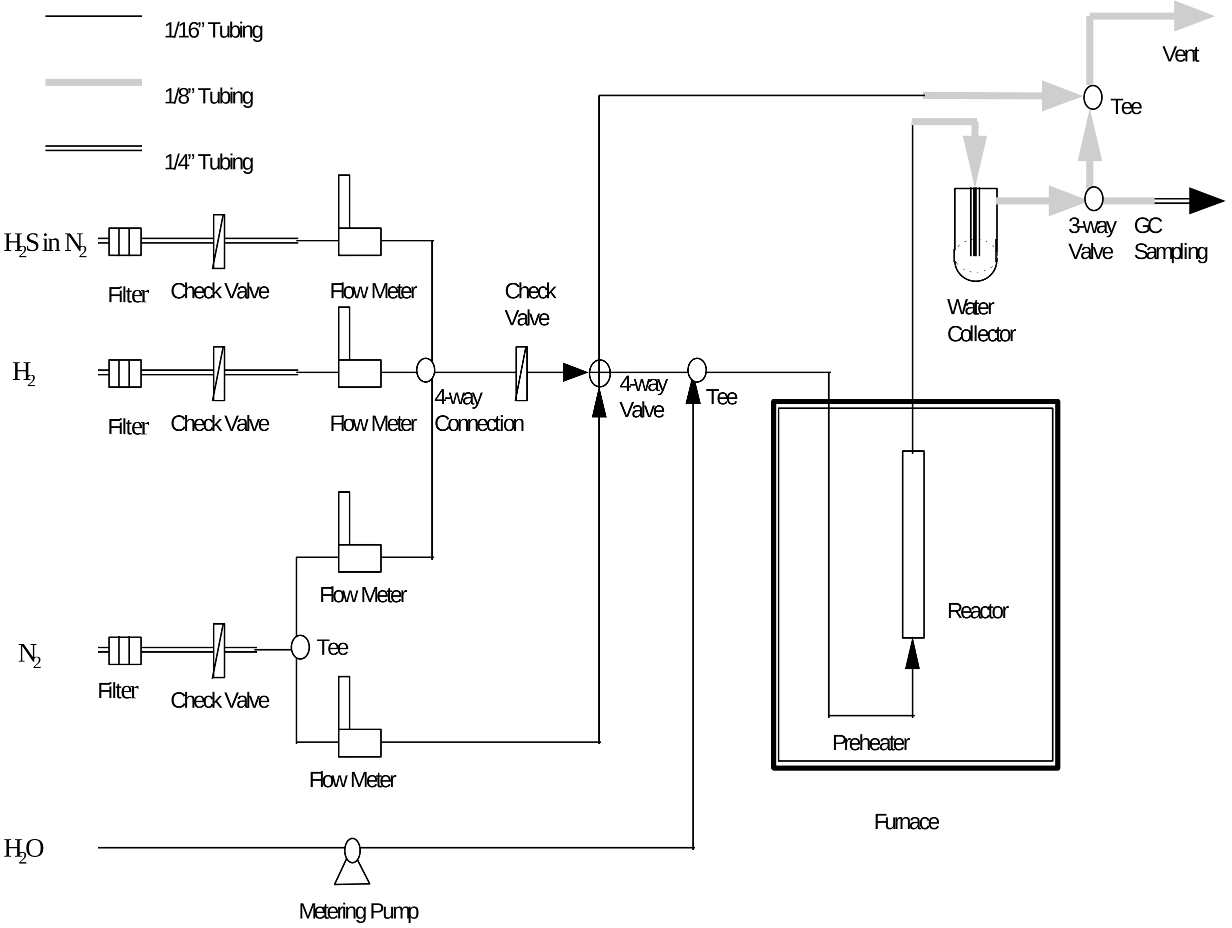
Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. The minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, 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-67 sorbent in the form of 130-μm spherical particles were examined. These sorbent particles were reacted with simulated coal gases containing hydrogen sulfide in the differential micro reactor for 4 – 180 seconds at 350 – 525°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 0.069 – 0.088 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 ¼-inch titanium grade-2 tubing and two ¼-inch external column end fittings. The preheater is made of 1/16-inch Hastelloy C tubing. The reactor was loaded with 130 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, ^oC:	350 – 525
Reaction Pressure, psia	40.7
Reaction Time, s:	4 –180
Space Time under the absorption conditions, s:	0.069 – 0.088
Mean Particle Size, μm	130
Amount of Sorbent, g	0.005 – 0.02
Gas Flow Rate, cc/min at room temperature and 1 atm	750
Hydrogen, vol %	5 – 27
Moisture, vol %:	5 – 20
Concentration of H_2S, ppm	18000
Nitrogen, vol %	Remainder

Table 2. Properties of the MCRH-67 sorbent from the Research Triangle Institute (RTI).

BET Area, m^2/g	81.8
Avg. Pore Diameter, Å, based on volume	207
Density, g/cm^3	2.7671
Pore Volume, cm^3/g	0.2167
Mean Particle Size, μm	130
Composition	15% ZnO 5% CO 5% Ni

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	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, ^{o}C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm^{2}/s
678	0.01	7200 s	9.089	550	4000	10	10			
1279	0.0102	4.1	1.742	450	18000	10	10	0.076	0.3971	0.001412
1280	0.0108	8	2.561							
1281	0.0104	12.18	3.457							
1282	0.0103	15.97	4.576							
1283	0.0099	19.89	4.218							
1284	0.0105	25.1	5.326							
1285	0.01	30.26	5.642							
1286	0.0105	60.24	6.178							
1287	0.01	180.38	7.681							
1288	0.0102	4.13	1.335	500	18000	10	10	0.071	0.4683	0.001662
1289	0.0105	8.15	3.695							
1290	0.0101	12.24	3.906							
1291	0.0109	16.09	4.425							
1292	0.0104	19.95	4.595							
1293	0.0102	25.19	5.272							
1294	0.0102	30.06	5.674							
1295	0.0105	180.04	7.641							
1296	0.104	60.04	6.67							
1297	0.0105	4.03	1.203	400	18000	10	10	0.081	0.2428	0.000740
1298	0.0100	180.23	6.896							
1299	0.0105	7.97	2.388							
1300	0.0104	29.48	4.443							
1301	0.0106	12.01	3.149							
1302	0.0106	16.11	2.913							
1303	0.0101	20.16	3.349							
1304	0.0102	25.16	4.032							
1305	0.0108	60.34	5.136							
1306	0.0102	4.24	1.405	425	18000	10	10	0.079	0.3511	0.001028
1307	0.0107	8.19	2.566							
1308	0.0102	12.17	3.656							
1309	0.0106	16.09	3.649							
1310	0.0103	20.1	4.233							
1311	0.0105	25.2	4.634							
1312	0.0103	30.2	4.981							
1313	0.0103	60	5.891							
1314	0.0106	180.22	7.061							
1315	0.0103	4.33	1.184	475	18000	10	10	0.073	0.4323	0.001553
1316	0.0102	8.28	2.888							
1317	0.0107	12.17	3.895							
1318	0.0105	16.18	4.443							
1319	0.0102	20.09	4.733							
1320	0.0107	25.37	5.165							

Table 3. continued-1

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, ºC	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm^2/s
1321	0.0105	30.12	5.661							
1322	0.0108	60.33	6.348							
1323	0.0101	180.15	7.442							
1324	0.0104	4.29	0.7294	525	18000	10	10	0.069	0.5536	0.002504
1325	0.01	8.02	2.76							
1326	0.011	12	4.104							
1327	0.01	16.01	4.902							
1328	0.0102	20.17	5.177							
1329	0.0103	25.28	5.759							
1330	0.0101	30.11	6.387							
1331	0.01	60.23	6.761							
1332	0.0107	180.42	7.636							
1333	0.0102	4.45	1.326	375	18000	10	10	0.085	0.2110	0.000592
1334	0.0104	8.27	1.345							
1335	0.0106	12.36	1.867							
1336	0.0104	16.37	2.341							
1337	0.0104	20.07	3.035							
1338	0.0108	25.41	3.44							
1339	0.0106	30.18	3.761							
1340	0.0106	60.28	4.258							
1341	0.0104	180.44	6.015							
1342	0.0106	4.3	0.5834	350	18000	10	10	0.088	0.1787	0.000358
1343	0.0106	8.31	0.8748							
1344	0.0106	12.21	1.146							
1345	0.0104	20.27	1.852							
1346	0.0108	16.25	1.447							
1347	0.0106	25.37	1.967							
1348	0.0104	30.16	2.619							
1349	0.0105	60.12	3.713							
1350	0.0107	179.93	5.078							
1351	0.0105	4	0.9707	450	18000	10	20	0.076	0.3358	0.001390
1352	0.0108	8.11	2.191							
1353	0.0103	11.94	4.46							
1354	0.0109	16.4	3.775							
1355	0.0105	20.17	4.29							
1356	0.0103	25.07	4.526							
1357	0.0104	30.16	4.938							
1358	0.0108	60.35	5.784							
1359	0.0104	180.08	6.844							
1360	0.01	4.32	0.9634	450	18000	10	5	0.076	0.4128	0.001740
1361	0.0108	8.03	3.191							
1362	0.0102	12.01	4.367							
1363	0.01	16.14	4.721							
1364	0.0103	20.19	5.277							
1365	0.0105	25.18	5.368							
1366	0.01	30.1	5.498							
1367	0.0105	60.14	6.471							

Table 3. continued-2

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, ºC	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm^2/s
1368	0.0102	180.23	7.244							
1369	0.0105	4.29	1.246	450	18000	10	15	0.076	0.3669	0.001401
1370	0.0107	8.17	3.883							
1371	0.0104	12.35	3.292							
1372	0.0104	16.27	4.444							
1373	0.0106	20.12	4.626							
1374	0.0107	25.17	5.09							
1375	0.0108	30.17	5.312							
1376	0.0104	60.43	6.202							
1377	0.0107	180.34	7.312							
1378	0.0208	4.16	1.316	450	18000	10	15	0.076	0.4804	0.001401
1379	0.0205	8.23	2.53							
1380	0.0203	12.11	3.619							
1381	0.0207	16.33	3.729							
1382	0.0204	20.25	4.271							
1383	0.0209	25.31	4.907							
1384	0.0207	30.1	5.203							
1385	0.0209	59.99	6.651							
1386	0.211	179.93	7.097							
1387	0.0057	4.28	1.903	450	18000	10	15	0.076	0.3431	0.001343
1388	0.0053	8.4	2.622							
1389	0.0052	12.01	3.704							
1390	0.0051	16.02	4.523							
1391	0.0057	20	4.783							
1392	0.0055	25.41	5.355							
1393	0.0051	30.11	4.662							
1394	0.0054	60.16	60.16							
1395	0.0055	180.19	7.072							
1396	0.0153	4.17	1.489	450	18000	10	15	0.076	0.4159	0.001364
1397	0.0152	8.01	2.342							
1398	0.0152	12.1	3.088							
1399	0.0151	15.99	4.141							
1400	0.0153	20.33	4.66							
1401	0.0153	25.32	4.871							
1402	0.0153	30.71	5.356							
1403	0.0152	59.91	6.174							
1404	0.0155	179.98	7.332							
1405	0.0097	4.17	1.378	450	18000	5	10	0.076	0.3833	0.001298
1406	0.0105	8.14	2.981							
1407	0.0101	12.2	3.821							
1408	0.0102	16.2	4.463							
1409	0.0103	20.37	4.746							
1410	0.0103	25.44	4.711							
1411	0.0106	30.27	5.279							
1412	0.0107	60.17	6.212							
1413	0.0108	180.42	7.27							

Table 3. continued-3

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, ^{o}C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm^2/s
1414	0.0105	4.3	1.679	450	18000	15	10	0.076	0.4034	0.001333
1415	0.0105	8.24	3.275							
1416	0.0108	16.19	4.351							
1417	0.0106	12.2	4.085							
1450	0.0103	20.16	3.961							
1451	0.0106	25.2	4.104							
1452	0.0107	30.35	4.802							
1418	0.0106	20.09	4.976							
1419	0.0104	25.23	4.99							
1420	0.0107	30.04	5.042							
1421	0.0104	60.04	6.567							
1422	0.0101	180.23	7.599							
1423	0.0101	4.3	1.352	450	18000	27	10	0.076	0.4160	0.001504
1424	0.0109	8.09	2.995							
1425	0.0102	12.19	3.987							
1426	0.0108	16.06	4.454							
1427	0.0104	20.04	4.886							
1428	0.0103	25.12	5.184							
1429	0.0101	29.91	5.582							
1430	0.01	59.97	6.385							
1431	0.0103	179.96	7.467							
1441	0.0107	4.23	1.026	450	18000	20	10	0.076	0.3248	0.001433
1442	0.0109	8.34	3.147							
1443	0.0106	12.1	4.339							
1444	0.0107	16.2	4.679							
1445	0.0105	20.32	4.785							
1453	0.0106	25.17	4.238							
1446	0.0105	25.42	4.253							
1447	0.0107	30.43	5.128							
1448	0.0107	60.15	5.868							
1449	0.0108	180.25	6.866							
1450	0.0103	20.16	3.961	450	18000	15	10	0.076	0.3473	0.001460
1451	0.0106	25.2	4.104							
1452	0.0107	30.35	4.802							
1453	0.0106	25.17	4.238							
1454	0.0105	4.2	0.7630							
1455	0.0106	8.17	2.918							
1456	0.0106	12.45	3.884							
1457	0.0104	16.15	4.616							
1458	0.0104	20.1	5.060							
1459	0.0108	25.17	4.216							
1460	0.0106	29.43	4.732							
1461	0.0102	60.26	6.256							
1462	0.0105	180.24	7.291							

Table 4. Surface reaction rate constants and intraparticle diffusivity values calculated with initial absorption data and the reaction model.

Temperature, °C	Sorbent Amount, g	Pressure, psia	Concentration, v% H_2S	H_2	H_2O	Reaction Rate Constant cm/s	Intraparticle Diffusivity, cm/s^2
450	0.01	40.7	1.8	10	10	0.3971	0.001412
500	0.01	40.7	1.8	10	10	0.4683	0.001662
400	0.01	40.7	1.8	10	10	0.2428	0.000740
425	0.01	40.7	1.8	10	10	0.3511	0.001028
475	0.01	40.7	1.8	10	10	0.4323	0.001553
525	0.01	40.7	1.8	10	10	0.5536	0.002504
375	0.01	40.7	1.8	10	10	0.2110	0.000592
350	0.01	40.7	1.8	10	10	0.1787	0.000358
450	0.01	40.7	1.8	10	20	0.3358	0.001390
450	0.01	40.7	1.8	10	5	0.4128	0.001740
450	0.01	40.7	1.8	10	15	0.3669	0.001401
450	0.02	40.7	1.8	10	15	0.4804	0.001401
450	0.005	40.7	1.8	10	15	0.3431	0.001343
450	0.015	40.7	1.8	10	15	0.4159	0.001364
450	0.01	40.7	1.8	5	10	0.3833	0.001298
450	0.01	40.7	1.8	15	10	0.4034	0.001333
450	0.01	40.7	1.8	27	10	0.4160	0.001504
450	0.01	40.7	1.8	20	10	0.3248	0.001433
450	0.01	40.7	1.8	15	10	0.3473	0.001460

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 rearranged to obtain mass transfer rate of H_2S, intraparticle diffusivity of H_2S, and reaction rate of H_2S with the sorbent using the physical properties (see Table 2), and the experimental data (see Table 3). This equation is developed under the assumptions that the shrinking core model and a quasi-steady state are valid.

$$\left(-\frac{d\left(\frac{r_C}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_S R^2}{C_G}\right)\left(\frac{1}{Rk_g} - \frac{1}{d}\right)\left(\frac{r_C}{R}\right)^2 + \left(\frac{C_S R^2}{C_G d}\right)\left(\frac{r_C}{R}\right) + \left(\frac{C_S R}{C_G k_b'}\right) \qquad (1)$$

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 surface reaction rate constant and intraparticle diffusivity of H_2S with the MCRH-67 sorbent. Conversion of a sorbent is described in terms of the radius of an unreacted core, as shown in Eqution 3.

$$\left(-\frac{d\left(\frac{r_C}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_S R^2}{C_G d}\right)\left(\frac{r_C}{R}-\left(\frac{r_C}{R}\right)^2\right)+\left(\frac{C_S R}{C_G k_b^{'}}\right) \tag{2}$$

$$\left(\frac{r_C}{R}\right) = \left(1-x_B\right)^{1/3} \tag{3}$$

where r_c: radius of an unreacted core
R: radius of spherical sorbent
t: reaction time
C_G: concentration of gaseous reactant
x_B: conversion of solid reactant

k_g: mass transfer rate of gaseous reactant
C_S: molar concentration of solid reactant
d: intraparticle diffusivity of gaseous reactant
k_b': reaction rate constant

CALCULATIONS

Conversion of a sorbent, x_B, is calculated by dividing absorption of H_2S into the sorbent with the total absorption capacity of the sorbent (see Figures 2, 6, 9 and 12). Ratios of the radius of an unreacted core r_c to the radius of the sorbent R, r_c/R, are obtained with conversion values of the sorbent (see Equation 3). Values of r_c/R are plotted against corresponding absorption durations, and then values of $(-d(r_c/R)/dt)^{-1}$ in the left-hand side of Equation 2 are obtained from slope values of this plotted curve at various corresponding absorption durations.

Values of $(-d(r_c/R)/dt)^{-1}$ as a dependent variable and values of $(r_c/R-(r_c/R)^2)$ as an independent variable (see Equation 2) are plotted, as shown in Figures 3, 7, 10 and 13, and then are applied to the linear least squares method to find both the value of the slope and the value of the intercept of this linear curve.

The value of the slope, obtained from the linear least squares method, is equal to the value of $C_SR^2/(C_G$ä) , as shown in the first term of Equation 2. The value of intraparticle diffusivity ä can be computed by substituting the known value of the slope $C_SR^2/(C_G$ä) with the sorbent radius R, the H_2S concentration C_G, and the total absorption capacity of the sorbent C_S, as shown in Figures 4, 8, 11 and 14.

The value of the intercept, obtained from the linear least squares method, is equal to the value of $C_SR/(C_Gk_b')$, as shown in the second term of Equation 2. The value of surface reaction rate constant k_b' can be obtained by substituting the known value of the intercept $C_SR/(C_Gk_b')$ with the sorbent radius R, the H_2S concentration C_G, and the total absorption capacity of the sorbent C_S, as shown in Figures 4, 8, 11 and 14.

RESULTS AND DISCUSSION

Experiments on absorption of hydrogen sulfide into the MCRH-67 sorbent was carried out for 4 – 180 seconds at 350 - 500°C (see Table 1) to evaluate effects of concentrations of H_2 and moisture, temperature, and sorbent amounts on initial dynamic absorption of hydrogen sulfide into the sorbent. A typical simulated coal gas mixture consists of 18000-ppm hydrogen sulfide, 10-vol % moisture, 10-vol % hydrogen, and nitrogen as remainder. A volumetric feed rate of a simulated coal gas mixture to the reactor is 750 cm^3/min at room temperature and atmospheric pressure. The temperature of the reactor is controlled in the furnace oven at 350 - 525^oC. The pressure of the reactor is maintained at 40.7 psia. Most reaction of H_2S with the sobent appears to occur for the first 3-min reaction duration. The entire reaction experimental data for this report were obtained for the 3-min reaction duration.

Effects of Temperature on Initial Dynamic Absorption of H_2S

Experiments on initial absorption of H_2S into the sorbent were carried out for 4 – 180 seconds at 40.7 psia and 350 - 525^oC to find effects of temperature on initial dynamic absorption of H_2S with the sorbent. The concentrations of both moisture and hydrogen are maintained at 10-volume percent. The concentration of hydrogen sulfide in the simulated coal gas mixture is maintained at 18000 ppm.

Initial absorption of H_2S into the MCRH-67 sorbent is affected with absorption temperature for short absorption duration of 4 - 180 seconds (see Figure 2). Equation 2 was applied to the experimental data to obtain surface reaction rate constants of H_2S with the sorbent and intraparticle diffusivity values of H_2S through pores of the sorbent (see Figure 3). The range of surface reaction rate constant is 0.18 – 0.55 cm/s (see Table 4). The range of intraparticle diffusivity values of the sorbent is 0.0004 – 0.0025 cm^2/s. These observations may indicate that reactivity of the MCRH-67 sorbent be dependent on reaction temperature in the temperature range of 350 – 525^oC. Reactivity of the sorbent is lower at 350^oC than that at 525^oC over the reaction temperature range of 350 – 525^oC. These facts also suggest that the controlling steps for the initial absorption of H_2S into sorbent particles are surface reaction of H_2S with reactive sites of sorbent particles and intraparticle diffusivity through pores of the sorbent.

Figure 2. Effects of temperature on absorption of 18000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture.

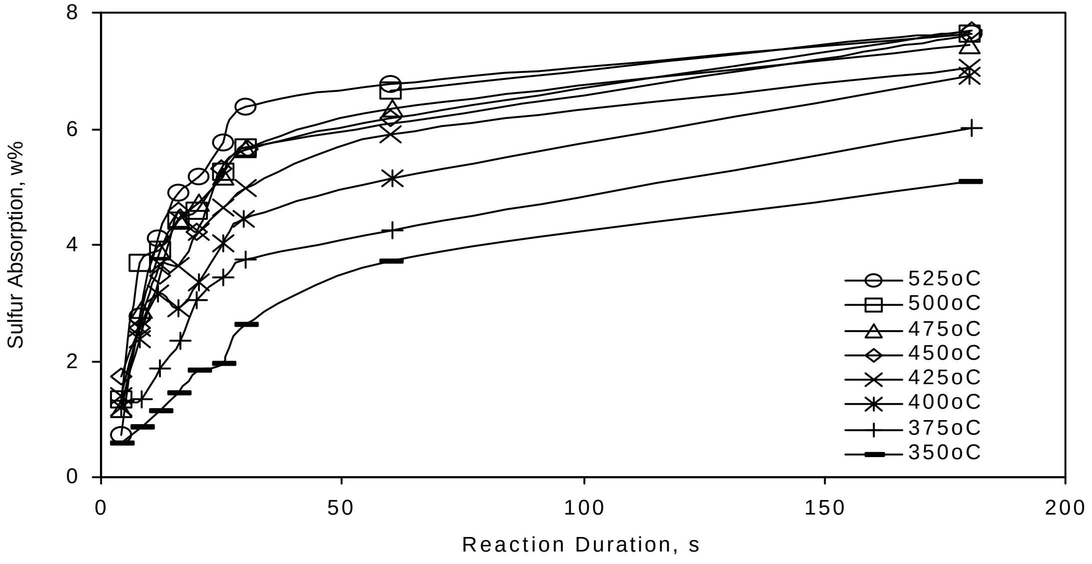


Figure 3. Effects of temperature on absorption of 18000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture, using the reaction model.

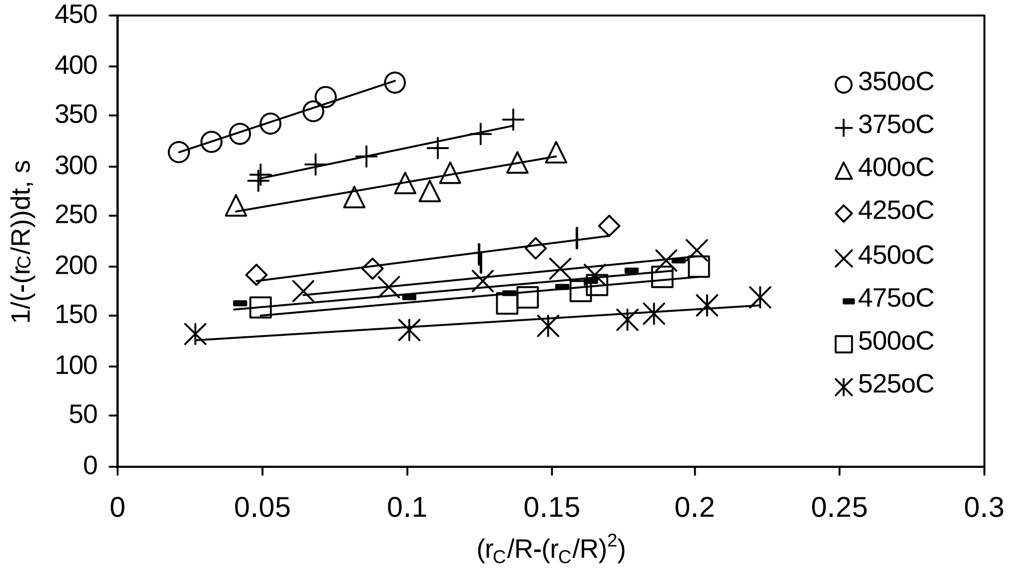
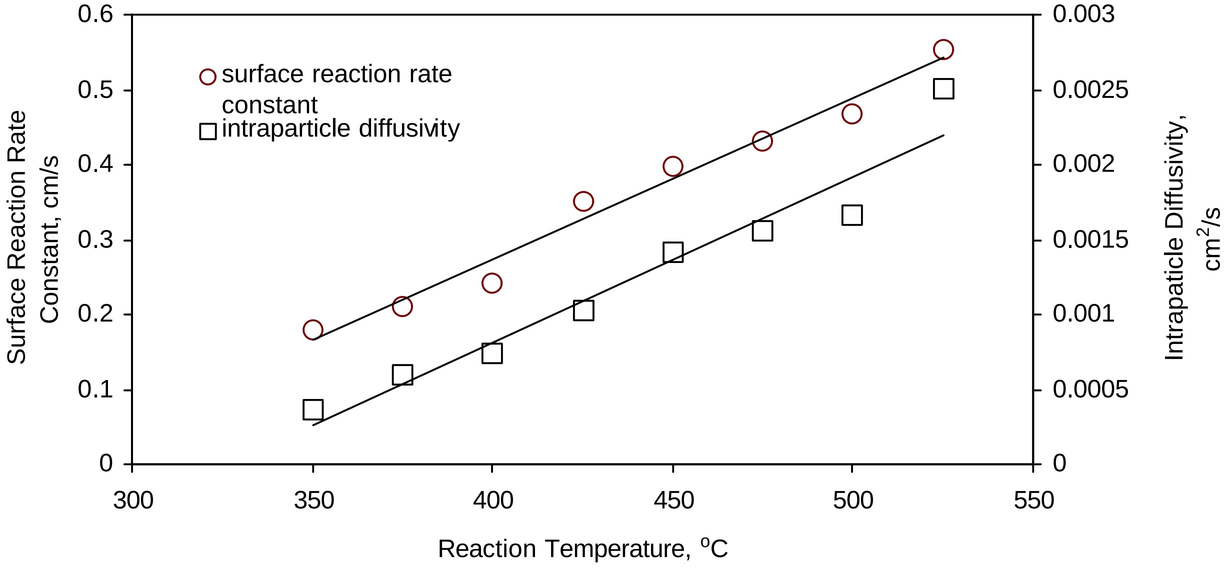
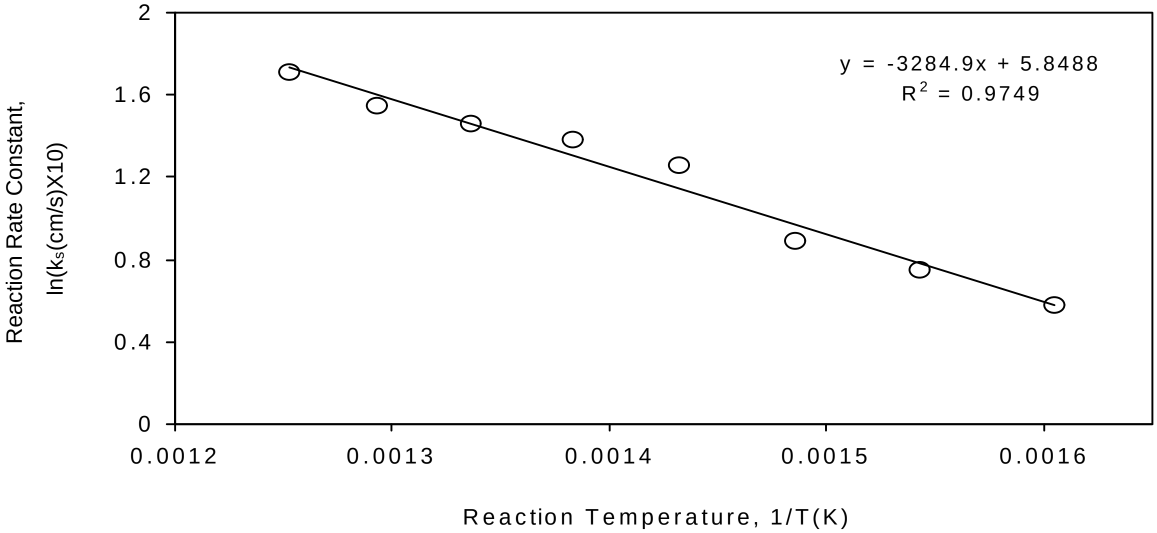


Figure 4. Effects of temperature on surface reaction rate constant and intraparticle diffusivity in the absorption of 18000-ppm H_2S into MCRH-67 sorbent with 10-v% H_2 and 10-v% moisture.



The surface reaction rate constant and the intraparticle diffusivity value increases with the reaction temperatures. The surface reaction rate constants, obtained from the reaction model, are applied to the Arrhenius equation (see Figure 5). The surface reaction rate constants appear to agree fairly with the equation in the temperature range of 350 – 525°C.

Figure 5. Effects of temperature on surface reaction rate constant in the absorption of 18000-ppm H_2S into MCRH-67 sorbent with 10-v% H_2 and 10-v% moisture, using the Arrhenius equation.



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 – 180 seconds at 40.7 psia and 450°C to find effects of moisture concentrations on initial dynamic absorption of H_2S with the sorbent. The concentrations of H_2S and hydrogen are maintained at 18000 ppm and 10-vol %, respectively. The concentration range of moisture in the simulated coal gas mixture is 5 – 20 volume percent.

Figure 6. Effects of moisture concentration on absorption of 18000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen at 450°C and the space time 0.076 s.

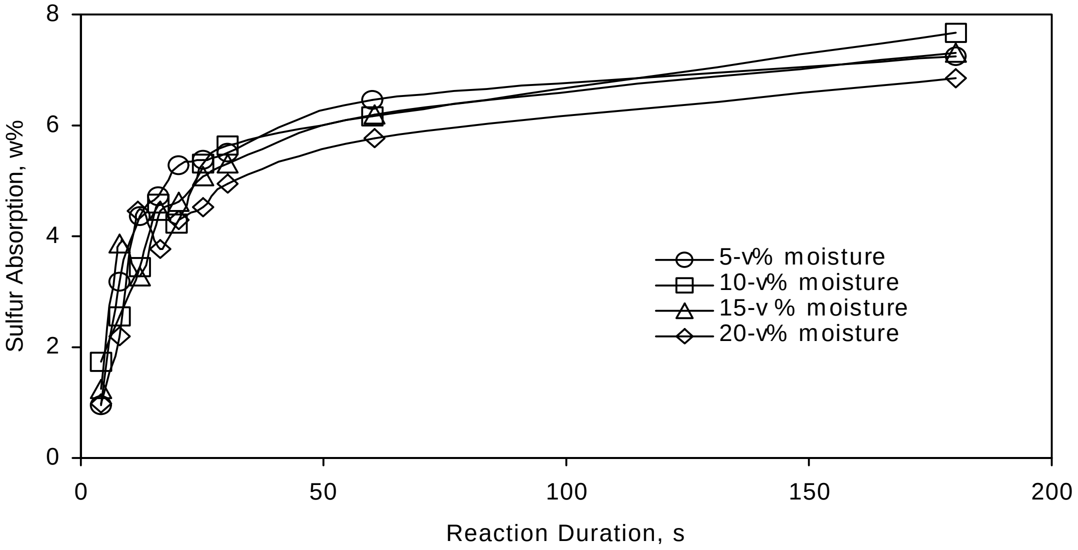
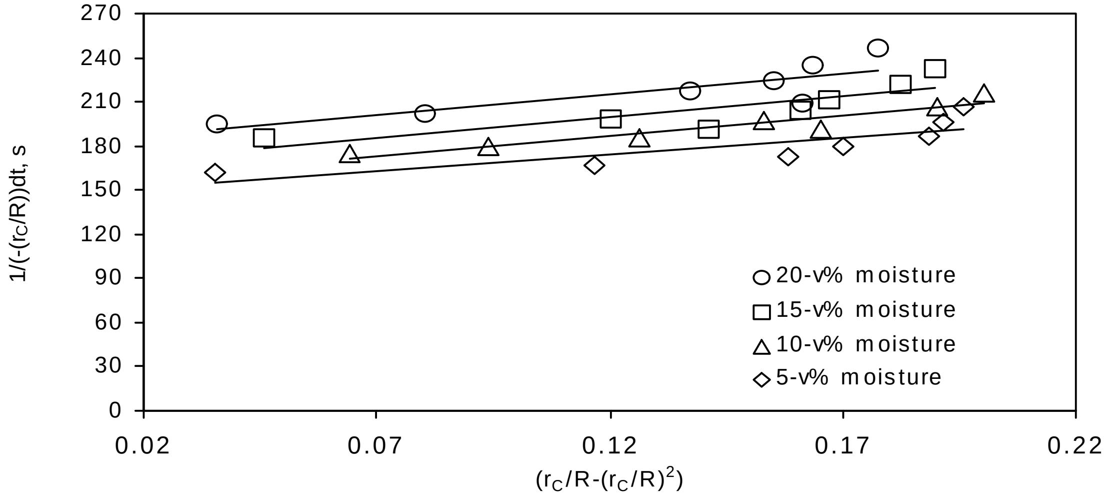
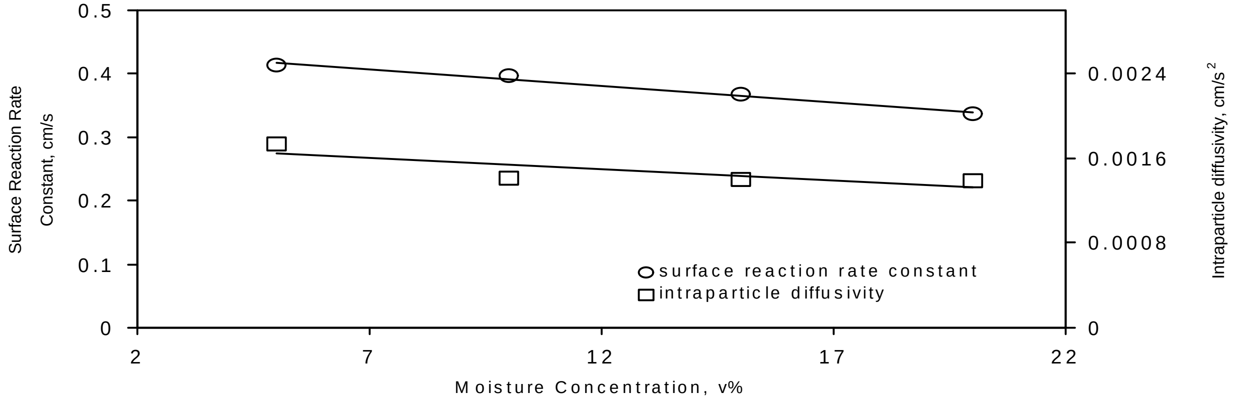


Figure 7. Effects of moisture concentration on absorption of 18000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% hydrogen at 450°C and the space time 0.076 s, using the reaction model.



Initial absorption of H_2S into the MCRH-67 sorbent is affected with concentrations of moisture for short absorption duration of 4 –180 seconds (see Figure 6). These facts may indicate that moisture is not inert for the reaction of H_2S with the MCRH-67 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 7). The range of surface reaction rate constants is 0.34 – 0.41 cm/s, and the range of intraparticle diffusivity values is 0.0014 –0.0017 cm^2/s (see Table 4). These observations may indicate that reactivity of the MCRH-67 sorbent and intraparticle diffusivity decrease slightly with increased moisture concentrations. These facts also suggest that the controlling steps for the absorption of H_2S into sorbent particles are surface reaction of H_2S with reactive sites of sorbent particles and diffusion of H_2S through porous sorbent particles in the presence of moisture.

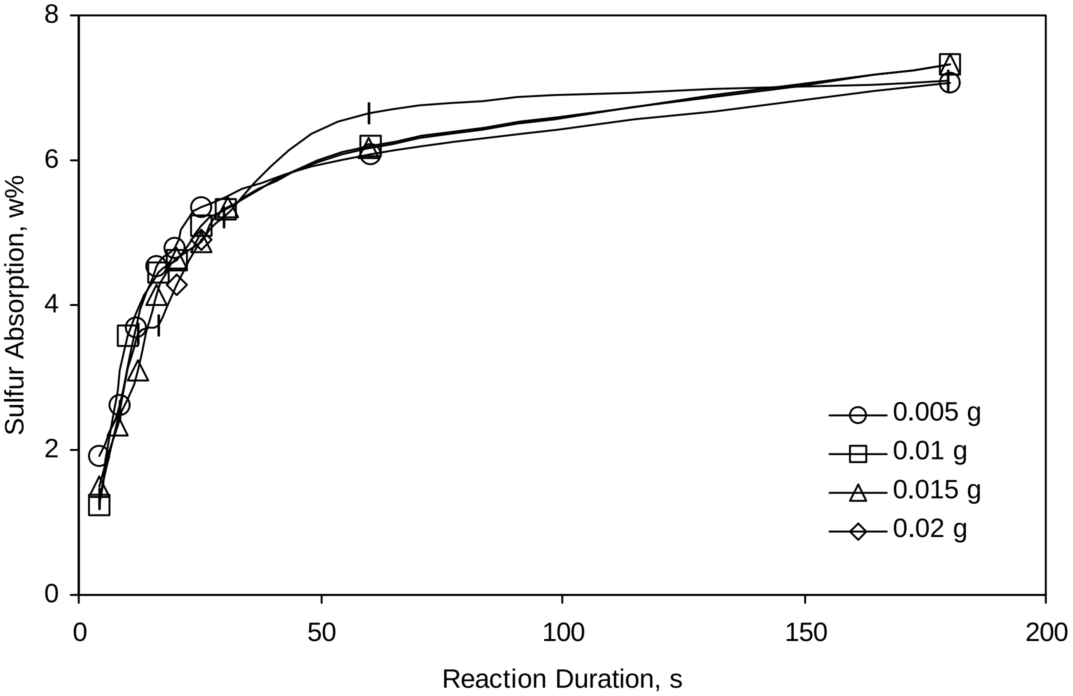
Figure 8. Effects of moisture concentration on surface reaction rate constant and intraparticle diffusivity in the absorption of H_2S into 0.01-g MCRH-67 sorbent with 10-v% H_2 at 450°C.



Effects of Sorbent amounts on Initial Dynamic Absorption of H_2S

Experiments on effects of sorbent amounts on initial dynamic absorption of H_2S into the sorbent were conducted for the reaction duration of 4 – 180 seconds at 450°C and the space-time of 0.076 s. Amounts of the MCRH-67 sorbent affect slightly initial dynamic absorption of H_2S into the sorbent in the sorbent amount range of 0.005– 0.02 g (see Figure 9). Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S (see Figure 10). The range of the surface reaction rate constant is 0.34 – 0.48 cm/s, and the range of the intraparticle diffusivity values is 0.0013 – 0.0014 cm^2/s. The concentrations of hydrogen and moisture were maintained at 10-v % and 15-v %, respectively. The concentration of H_2S was maintained at 18000 ppm. The surface reaction rate constant increase with increased amount of the sorbent. The intraparticle diffusity values do not change significantly with increased amount of the sorbent (see Figure 11). These observations may suggest that mass transfer of H_2S from the bulk gaseous phase to the surface of the solid sorbent affects somewhat the overall reaction of H_2S with the sorbent

Figure 9. Effects of sorbent amount on absorption of 18000-ppm H_2S on MCRH-67 sorbent with 10-v% hydrogen and 15-v% moisture at 450°C and the space time 0.076 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 sorbent were conducted for the reaction duration of 4 – 180 s at 450°C and the space-time of 0.076 s. The concentration of moisture was maintained at 10-volume percent. The concentration of H_2S was maintained at 18000 ppm.

Figure 10. Effects of sorbent amount on absorption of 18000-ppm H_2S on MCRH-67 sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s, using the reaction model.

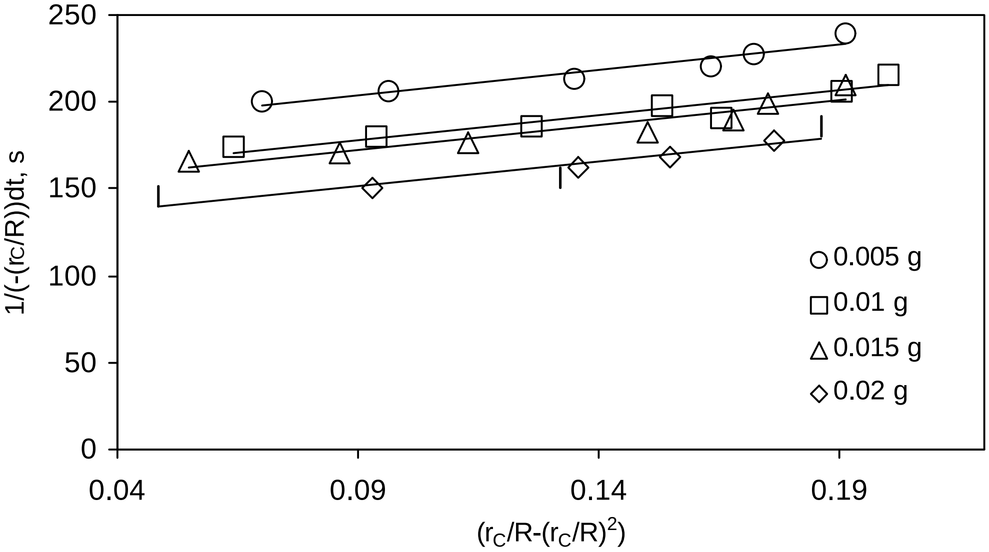


Figure 11. Effects of sorbent amount on surface reaction rate constant and intraparticle diffusivity in the absorption of 18000-ppm H_2S into MCRH-67 sorbent with 10-v% H_2 and 15-v% moisture at 450°C.

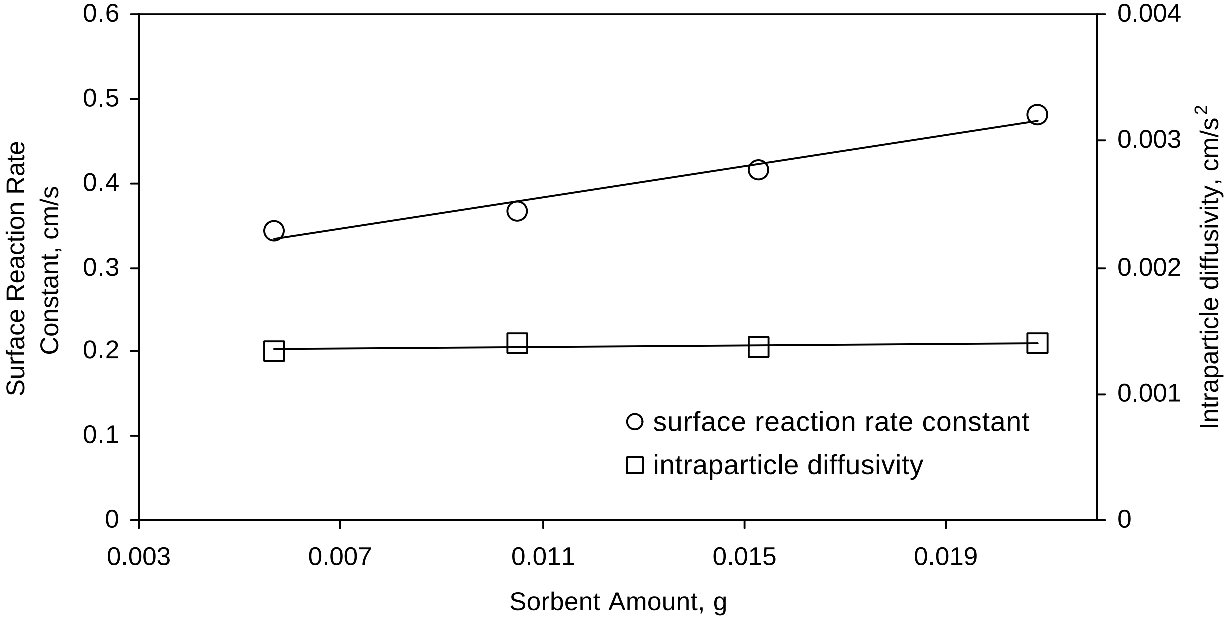


Figure 12. Effects of hydrogen concentration on absorption of 18000-ppm H_2S on 0.01-g MCRH-67sorbent with 10-v% moisture at 450°C and the space time 0.076 s.

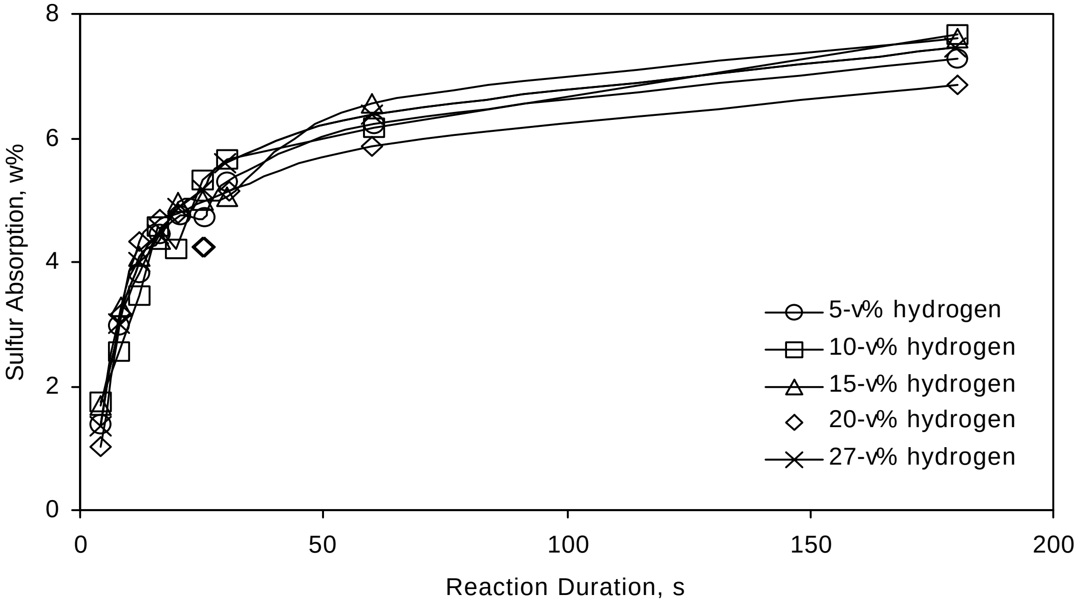


Figure 13. Effects of hydrogen concentration on absorption of 18000-ppm H_2S on 0.01-g MCRH-67 sorbent with 10-v% moisture at 450°C and the space time 0.076 s, using the reaction model.

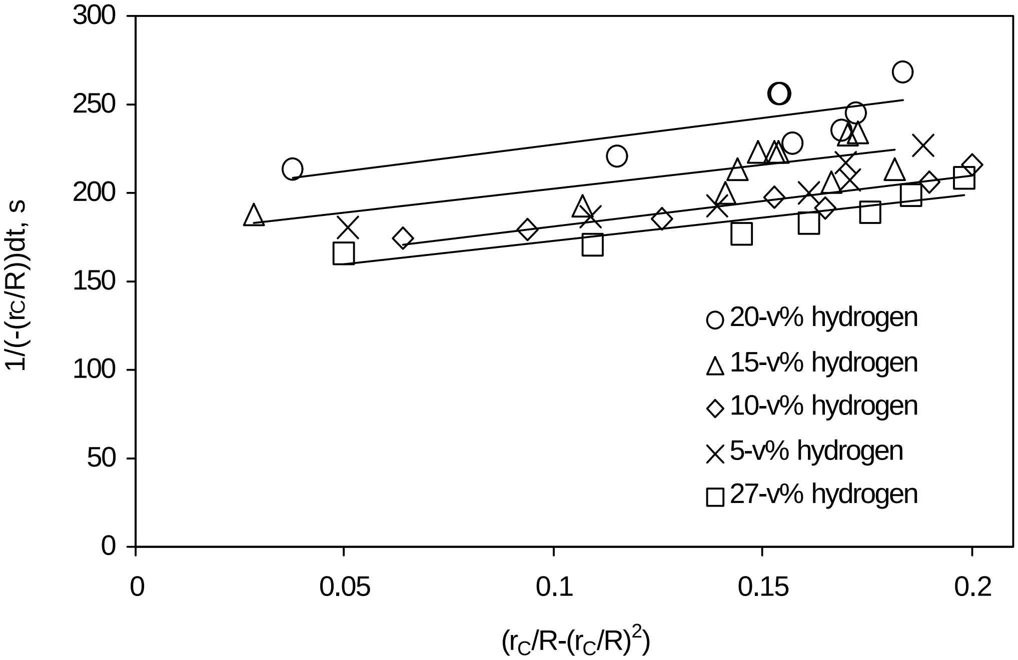
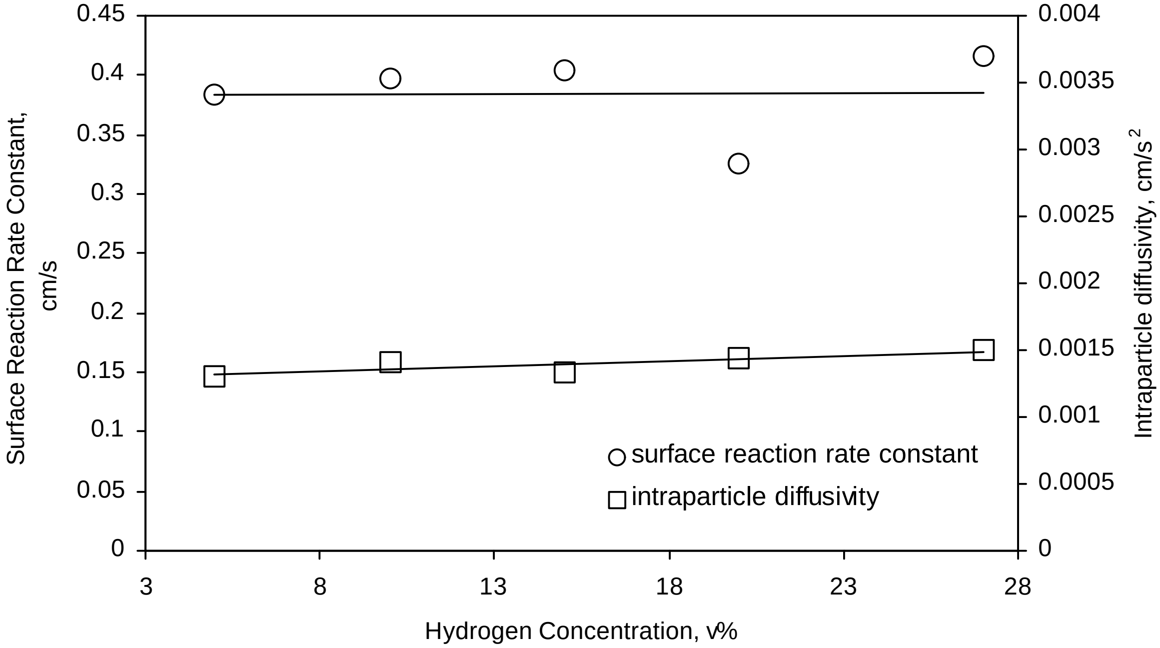


Figure 14. Effects of hydrogen concentration on surface reaction rate constant and intraparticle diffusivity in the absorption of H_2S into 0.01-g MCRH-67 sorbent with 10-v% moisture at 450°C.



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 – 27 v% (see Figure 12). Equation 2 was applied to the experimental data to obtain initial surface reaction rate constants and intraparticle diffusivity values (see Figure 13). The range of the initial surface reaction rate constant is 0.32 – 0.42 cm/s, and the range of the intraparticle diffusivity values is 0.0013 – 0.0015 cm^2/s (see Table 4). Surface reaction rate constant and intraparticle diffusivity slightly increase with hydrogen concentration. These facts may indicate that hydrogen does not affect significantly both surface reaction of H_2S with the sorbent and intraparticle diffusivity of H_2S through the porous sorbent (see Figure 14).

CONCLUSIONS

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

- Initial absorption of H_2S into the MCRH-67 sorbent is affected with absorption temperature for short absorption duration of 4 - 180 seconds. The range of surface reaction rate constant is 0.18 – 0.55 cm/s. The range of intraparticle diffusivity values of the sorbent is 0.0004 – 0.0025 cm^2/s. These observations may indicate that reactivity of the MCRH-67 sorbent be dependent on reaction temperature in the temperature range of 350 – 525°C. These facts also suggest that the controlling steps for the initial absorption of H_2S into sorbent particles are surface reaction of H_2S with reactive sites of sorbent particles and intraparticle diffusivity through pores of the sorbent.

- Initial absorption of H_2S into the MCRH-67 sorbent is affected with concentrations of moisture for short absorption duration of 4 –180 seconds. These facts may indicate that moisture is not inert for the reaction of H_2S with the MCRH-67 sorbent. The range of surface reaction rate constants is 0.34 – 0.41 cm/s, and the range of intraparticle diffusivity values is 0.0014 –0.0017 cm^2/s. These observations may indicate that reactivity of the MCRH-67 sorbent and intraparticle diffusivity decrease slightly with increased moisture concentrations.

- Amounts of the MCRH-67 sorbent affect slightly initial dynamic absorption of H_2S into the sorbent in the sorbent amount range of 0.005– 0.02 g. The range of the surface reaction rate constant is 0.34 – 0.48 cm/s, and the range of the intraparticle diffusivity values is 0.0013 – 0.0014 cm^2/s. Absorption of H_2S into the sorbent is almost independent of amount of the sorbent in the reactor. The surface reaction rate constant increase with amount of the sorbent. The intraparticle diffusity values is almost independent of amount of the sorbent. These observations may suggest that mass transfer of H_2S from the bulk gaseous phase to the surface of the solid sorbent affects somewhat the overall reaction of H_2S with the sorbent

- Concentrations of hydrogen affect slightly initial dynamic absorption of H_2S into the MCRH-67 sorbent in the hydrogen concentration range of 5 – 27 v%. The range of the initial surface reaction rate constant is 0.32 – 0.42 cm/s, and the range of the intraparticle diffusivity values is 0.0013 – 0.0015 cm^2/s. Surface reaction rate constant and intraparticle diffusivity slightly increase with hydrogen concentration. These facts may indicate that hydrogen affects slightly both surface reaction of H_2S with the sorbent and intraparticle diffusivity of H_2S through porous sorbents.

REFERENCES

1. Octave Levenspiel, Chemical Reaction Engineering, 3rd Edition, John Wiley & Sons, 1999
2. Gilbert F. Froment, Chemical Reactor Analysis and Design, 2nd Edition, John Wiley & Sons, 1990
3. James J. Carberry, Chemical and Catalytic Reaction Engineering, McGraw-Hill, 1976

PUBLICATIONS AND PRESENTATIONS

-“Reactivity of Formulated Metal Oxide Sorbents with Hot Hydrogen Sulfide”, Proceedings of 11th Symposium, Separation Science and Technology Volume 36, no. 5 & 6, PP 1375, 2001.

-“Reactivity of Sorbents with Hot Hydrogen Sulfide in the Presence of Moisture and Hydrogen”, submitted for publication in Separation Science and Technology.

-“Initial Reactivity of AHI-5 Sorbent with H_2S at High Temperatures”, submitted for publication in Advances in Environmental Research.

-“Initial Reaction Kinetics of Solid Sorbents with H_2S at High Temperatures”, presented at AIChE 2000

Annual Meeting, November 12-17, Los Angeles, CA.

Reactivity of AHI-5 Sorbent with Hot Hydrogen Sulfide in the Presence of Moisture and Hydrogen presented at the University Coal Research, Historically Black Colleges and Universities and Other Minority Institutions Contractors Review Conference, Pittsburgh
Marriott City Center, June 5 -6, 2001

STUDENT RESEARCH ASSISTANTS

Mr. Gaetan L. Tibere and Ms. Raushanah El-Amin, our Chemical Engineering students, worked for this research project. Mr. Gaetan L. Tibere is a graduate student of Arizona State University. Ms. Raushanah El-Amin is a graduate student of Tuskegee Univerisity.