

ENERGY

Kinetics of Hot-Gas Desulfurization Sorbents for Transport Reactors

Annual Technical Progress Report for the Period
October 1, 2001 to September 30, 2002

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February 2003

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

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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 H₂S into sorbents, and to evaluate effects of temperature and sorbent amounts on dynamic absorption of H₂S into sorbents. Experimental data on initial reaction kinetics of hydrogen sulfide with metal oxide sorbents were obtained with a 0.83-cm³ differential reactor. The reactivity of EX-SO₃ was examined in this report. This sorbent was obtained from the Research Triangle Institute (RTI). The sorbent in the form of 110 μm particles are reacted with 18000-ppm hydrogen sulfide at 350–550°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.

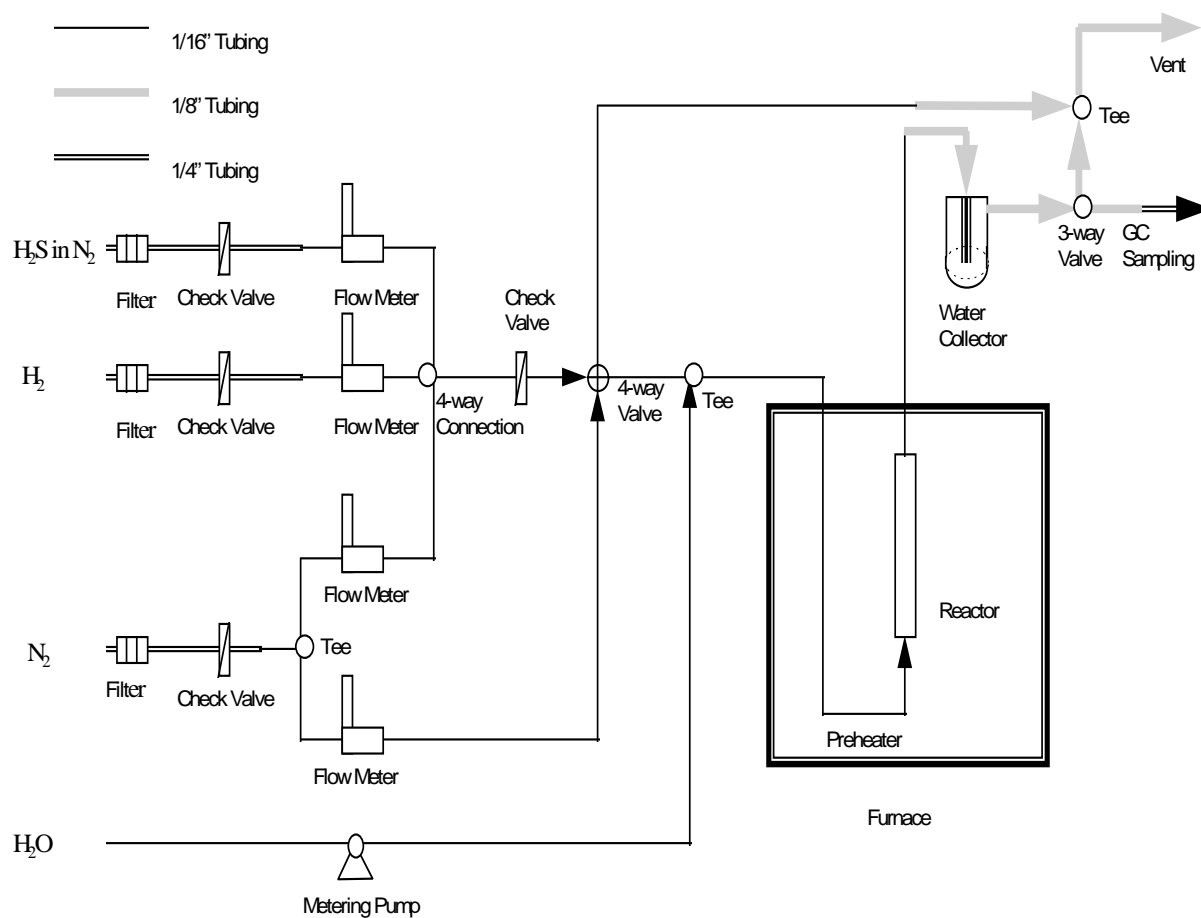
The removal of hydrogen sulfide from hot coal gas produced in the IGCC- based system by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. The removal of sulfur compounds from coal gas products is investigated by using various metal oxide 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 EX-SO3 sorbent in the form of $110\text{-}\mu\text{m}$ spherical particles was examined. These sorbent particles were reacted with simulated coal gases containing hydrogen sulfide in the differential micro reactor for 4 – 180 seconds at $350\text{--}550^\circ\text{C}$. 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 $0.069\text{--}0.088 \text{ s}$ 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 110 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 sorbent are shown in Table 2.

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

Reactor Volume, cm^3 :	0.83
Temperature, $^{\circ}\text{C}$:	350 – 550
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	110
Amount of Sorbent, g	0.005 – 0.02
Gas Flow Rate, cc/min at room temperature and 1 atm (sccm)	750
Hydrogen, vol %	5 – 30
Moisture, vol %:	5 – 20
Concentration of H_2S , ppm	4000 – 18,000
Nitrogen, vol %	Remainder

Table 2. Properties of the EX-SO₃ sorbent from the Research Triangle Institute (RTI).

BET Area, m^2/g	NA
Avg. Pore Diameter, Å , based on volume	NA
Particle Density, g/cm^3	2.8032
Pore Volume, cm^3/g	NA
Mean Particle Size, μm	110

Table 3. Absorption of hydrogen sulfide into EX-SO₃ sorbent in the presence of hydrogen and moisture at various absorption conditions.

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, °C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s x 10 ⁴
1463	0.0105	4.25	1.485	450	18000	10	10	0.076	0.0718	0.4493
1464	0.0102	8.24	1.233							
1465	0.0109	11.97	1.134							
1466	0.0108	22.40	1.475							
1467	0.0104	20.14	1.536							
1468	0.0107	25.20	1.865							
1469	0.0105	30.31	1.986							
1470	0.0105	60.10	2.567							
1471	0.0101	181.69	3.454							
1472	0.0108	4.27	0.5121	400	18000	10	10	0.081	0.0658	0.3879
1473	0.0102	8.56	0.8952							
1474	0.0107	12.13	1.131							
1475	0.0107	16.23	1.253							
1476	0.0104	20.22	1.385							
1477	0.0106	25.29	1.435							
1478	0.0106	30.10	1.492							
1479	0.0101	59.62	2.073							
1480	0.0106	180.97	2.876							
1481	0.0107	181.35	4.589	500	18000	10	10	0.071	0.1363	1.6330
1482	0.0101	60.98	3.392							
1483	0.01	31.11	2.986							
1484	0.0104	25.07	2.572							
1485	0.0104	20.87	2.076							
1486	0.0108	17.05	2.351							
1487	0.0106	12.63	2.072							
1488	0.0102	8.14	1.425							
1489	0.0107	4.69	0.6953							
1490	0.0106	180.29	6.171	550	18000	10	10	0.067	0.1873	2.2349
1491	0.0104	60.33	4.365							
1472	0.0105	30.7	2.915							
1493	0.01	25.7	2.962							
1494	0.0105	20.17	2.635							
1495	0.0104	16.59	2.552							
1496	0.0108	12.71	1.893							
1497	0.0106	8.77	1.644							
1498	0.0108	4.7	1.29							
1499	0.0107	181.1	2.112	350	18000	10	10	0.088	0.0192	0.1369
1500	0.0106	60.51	1.199							
1501	0.0104	34	1.118							
1502	0.0104	25.41	1.152							
1503	0.0106	20.12	0.9946							
1504	0.0108	16.71	0.8695							
1505	0.0109	12.84	0.9277							
1506	0.0108	8.2	0.7423							
1507	0.0107	4.72	0.6959							

Table 3. Continued – 1

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, °C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s x 10 ⁴
1508	0.0057	180.83	3.132	450	18000	10	10	0.076	0.1522	2.7805
1509	0.0057	60.32	4.9							
1510	0.0055	30.8	2.993							
1511	0.0055	25.17	4.853							
1512	0.0057	20.74	3.069							
1513	0.0053	16.2	3.244							
1514	0.0057	12.9	2.233							
1515	0.0059	8.2	2.246							
1516	0.0053	4.71	2.789							
1517	0.0151	180.85	3.38	450	18000	10	10	0.076	0.1006	0.4296
1518	0.0156	60	2.668							
1519	0.0157	30.79	1.777							
1520	0.0154	25.74	1.551							
1521	0.0154	20.62	1.59							
1522	0.0157	16.67	1.426							
1523	0.0153	12.82	1.292							
1524	0.0155	8.71	1.109							
1525	0.0156	4.69	0.86							
1532	0.0155	12.8	1.188							
1526	0.0207	180	3.95	450	18000	10	10	0.076	0.1012	0.8171
1527	0.0203	60.61	2.707							
1528	0.0207	30.38	2.085							
1529	0.0205	25.58	1.813							
1530	0.0202	20.82	1.701							
1531	0.0209	16.81	1.365							
1533	0.0203	12.11	1.196							
1534	0.0205	8.68	0.9866							
1535	0.0209	4.71	0.6834							
1536	0.0102	180	4.02	450	18000	10	5	0.076	0.0520	0.7775
1537	0.0103	180.8	4.059							
1538	0.0106	60.35	2.251							
1539	0.0101	30.85	2.128							
1540	0.01	25.67	2.219							
1541	0.0104	20.75	1.729							
1542	0.0103	16.86	1.68							
1543	0.0105	13.07	1.305							
1544	0.0106	8.19	1.487							
1545	0.0105	4.63	1.129							
1546	0.0101	180.34	3.598	450	18000	10	15	0.076	0.1064	0.8347
1547	0.0102	60.28	3.132							
1548	0.0107	30.34	1.972							
1549	0.0102	25.59	1.636							
1550	0.0103	20.64	2.142							
1551	0.0103	16.87	1.558							
1552	0.0105	12.44	1.354							
1553	0.0105	8.58	1.592							
1554	0.0107	4.87	0.8267							

Table 3. Continued - 2

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, °C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s x 10 ⁴
1555	0.0106	180.08	3.585	450	18000	10	20	0.076	0.0192	0.5386
1556	0.0107	60.43	2.755							
1557	0.0104	30.41	2.105							
1558	0.0105	25.11	6.023							
1559	0.01	20.8	1.656							
1560	0.0104	16.67	1.643							
1561	0.0106	12.14	1.371							
1562	0.0106	8.34	1.591							
1563	0.0101	4.1	0.9443							
1564	0.0108	180.43	3.772	450	15000	10	10	0.076	0.0639	1.5620
1565	0.0107	60.22	2.895							
1566	0.0105	30.25	2.024							
1567	0.0108	25.20	1.724							
1568	0.0107	21.00	1.766							
1569	0.0107	16.76	1.823							
1570	0.0106	12.16	1.249							
1571	0.0102	8.67	2.877							
1572	0.0103	4.88	1.971							
1573	0.0103	180.46	3.436	450	12000	10	10	0.076	0.0774	0.6634
1574	0.0108	60.73	2.697							
1575	0.0108	30.82	2.553							
1576	0.0106	25.15	1.985							
1577	0.0105	20.77	2.1							
1578	0.0103	16.32	2.486							
1579	0.0104	12.64	1.966							
1580	0.0105	8.53	2.097							
1581	0.0107	4.65	1.527							
1582	0.0106	180.77	3.651	450	9000	10	10	0.076	0.1697	1.3835
1583	0.0104	60.55	2.885							
1584	0.0104	30.27	2.188							
1585	0.0107	25.64	2.515							
1586	0.0107	20.74	2.02							
1587	0.0106	16.73	2.288							
1588	0.0106	12.87	1.441							
1589	0.0102	8.4	1.732							
1590	0.0107	4.83	1.257							
1591	0.0101	180.58	3.772	450	6000	10	10	0.076	0.1259	2.0428
1592	0.0106	60.83	2.246							
1593	0.0109	30.17	1.969							
1594	0.0105	25.59	1.456							
1595	0.0103	20.76	1.636							
1596	0.0106	16.00	1.487							
1597	0.0107	12.81	1.589							
1598	0.0108	8.84	1.19							
1599	0.0107	4.74	1.321							

Table 3. Continued - 3

Run #	Sorbent Amount, g	Reaction Duration, s	Sulfur Absorption, w%	Reaction Temperature, °C	Hydrogen Sulfide, ppm	Hydrogen v%	Moisture v%	Space Time, s	Reaction Rate Constant, cm/s	Intraparticle Diffusivity, cm ² /s x 10 ⁴
1600	0.0102	180.74	3.241	450	4000	10	10	0.076	0.1346	3.1213
1601	0.0109	60.42	1.938							
1602	0.0102	30.60	1.384							
1603	0.0101	25.77	1.591							
1604	0.0106	20.75	1.702							
1605	0.0106	16.75	1.290							
1606	0.0107	8.60	1.219							
1607	0.0106	4.64	1.105							
1608	0.0107	12.63	1.383							
1609	0.0108	181.10	4.000	450	18000	5	10	0.076	0.3931	0.3106
1610	0.0108	60.67	3.358							
1611	0.0102	30.80	2.978							
1612	0.0109	25.74	2.649							
1613	0.0103	20.64	2.163							
1614	0.0106	16.66	2.419							
1615	0.0104	12.75	2.032							
1616	0.0102	8.80	2.289							
1617	0.0104	4.87	1.706							
1618	0.0105	180.74	3.172							
1619	0.0103	180.37	4.147	450	18000	20	10	0.076	0.1030	1.0862
1620	0.0104	60.12	2.874							
1621	0.0102	30.17	3.304							
1622	0.0105	25.04	2.966							
1623	0.0104	20.22	2.188							
1624	0.0105	16.09	2.113							
1625	0.0105	12.10	1.953							
1626	0.0107	8.00	1.524							
1627	0.0102	4.15	1.193							
1628	0.0107	180.26	4.106	450	18000	30	10	0.076	0.1233	1.0595
1629	0.0107	60.42	3.590							
1630	0.0108	30.09	2.921							
1631	0.0104	25.18	2.012							
1632	0.108	20.34	1.867							
1633	0.0106	16.49	1.783							
1634	0.0106	12.97	2.323							
1635	0.0103	8.14	1.453							
1636	0.0105	4.20	1.439							

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%			Reaction Rate Constant cm/s	Intraparticle Diffusivity, cm ² /s x 10 ⁴
			H ₂ S	H ₂	H ₂ O		
450	0.0105	40.7	1.8	10	10	0.0718	0.4493
400	0.0108	40.7	1.8	10	10	0.0658	0.3879
500	0.0107	40.7	1.8	10	10	0.1363	1.6330
550	0.0106	40.7	1.8	10	10	0.1873	2.2349
350	0.0107	40.7	1.8	10	10	0.0192	0.1369
450	0.0057	40.7	1.8	10	10	0.1522	2.7805
450	0.0151	40.7	1.8	10	10	0.1006	0.4296
450	0.0207	40.7	1.8	10	10	0.1012	0.8171
450	0.0102	40.7	1.8	10	5	0.0520	0.7775
450	0.0101	40.7	1.8	10	15	0.1064	0.8347
450	0.0106	40.7	1.8	10	20	0.0912	0.5386
450	0.0108	40.7	1.5	10	10	0.0639	1.5620
450	0.0103	40.7	1.2	10	10	0.0774	0.6634
450	0.0106	40.7	0.9	10	10	0.1697	1.3835
450	0.0101	40.7	0.6	10	10	0.1259	2.0428
450	0.0102	40.7	0.4	10	10	0.1346	3.1213
450	0.0108	40.7	1.8	5	10	0.3931	0.3106
450	0.0103	40.7	1.8	20	10	0.1030	1.0862
450	0.0107	40.7	1.8	30	10	0.1233	1.0595

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). Mass transfer rate of H₂S, intraparticle diffusivity of H₂S, and reaction rate of H₂S are obtained from Equation 1. This equation is developed under the assumptions that the shrinking core model and a quasi-steady state are valid.

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

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 surface reaction rate constant and intraparticle diffusivity of H₂S with the EX-SO₃ sorbent. Conversion of a sorbent is

described in terms of the radius of an unreacted core, as shown in Equation 3.

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

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

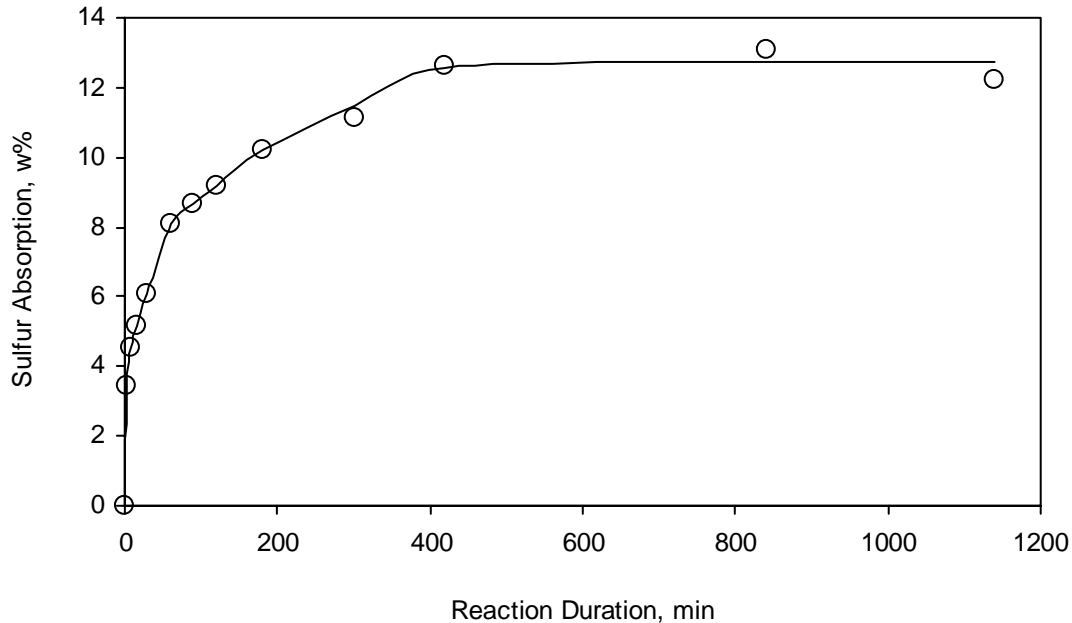
where	r_c : radius of an unreacted core	k_b' : mass transfer rate of gaseous reactant
	R : radius of spherical sorbent	C_s : molar concentration of solid reactant
	t : reaction time	δ : intraparticle diffusivity of gaseous reactant
	C_G : concentration of gaseous reactant	k_b' : reaction rate constant
	x_B : conversion of solid reactant	

RESULTS AND DISCUSSION

Experiments on absorption of hydrogen sulfide into the EX-SO₃ sorbent was carried out for 4 – 180 seconds at 350 - 550°C (see Table 1) to evaluate effects of concentrations of H₂S, H₂ 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 cm³/min at room temperature and atmospheric pressure. The temperature of the reactor is controlled in the furnace oven at 350 - 550°C. The pressure of the reactor is maintained at 40.7 psia. The entire reaction experimental data for this report were obtained for the 3-min reaction duration. Most experimental absorption data for the EX-SO₃ sorbent (see Tables 3) were obtained in the temperature range of 350-550°C and in the H₂S concentration 18,000 ppm.

The capacity of the sorbent for absorption of H₂S is determined with the experimental data shown in Figure 2. Experiments on reaction of 18,000-ppm H₂S with the sorbent in the presence of 10-v% moisture and 10-v% hydrogen were conducted up to 19 hours at 40.7 psia and 450°C to determine the absorption capacity of the sorbent for H₂S.

Figure 2. Effects of reaction duration on absorption of 18000-ppm H₂S on EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s



Effects of Temperature on Initial Dynamic Absorption of H₂S

Experiments on initial absorption of H₂S into the sorbent were carried out for 4 – 180 seconds at 40.7 psia and 350 - 550°C to find effects of temperature on initial dynamic absorption of H₂S into 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 H₂S into the EX-SO₃ sorbent is affected with absorption temperature for short absorption duration of 4 - 180 seconds (see Figure 3). Equation 2 was applied to the experimental data to obtain surface reaction rate constants of H₂S with the sorbent and intraparticle diffusivity values through pores of the sorbent (see Figure 4). The range of the surface reaction rate constants is 0.02 – 0.19 cm/s (see Table 4 and Figure 5). The range of the intraparticle diffusivity values of the sorbent is 0.14×10^{-4} – 2.23×10^{-4} cm²/s. These observations may indicate that reactivity of the EX-SO₃ sorbent be dependent on reaction temperature in the temperature range of 350 – 550°C. However, reactivity of the sorbent is much lower at 350°C than that at 550°C. These facts also suggest that the controlling steps for the initial absorption of H₂S into sorbent particles are surface reaction of H₂S with reactive sites of sorbent particles and intraparticle diffusivity through pores of the sorbent.

Figure 3. Effects of temperature on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture.

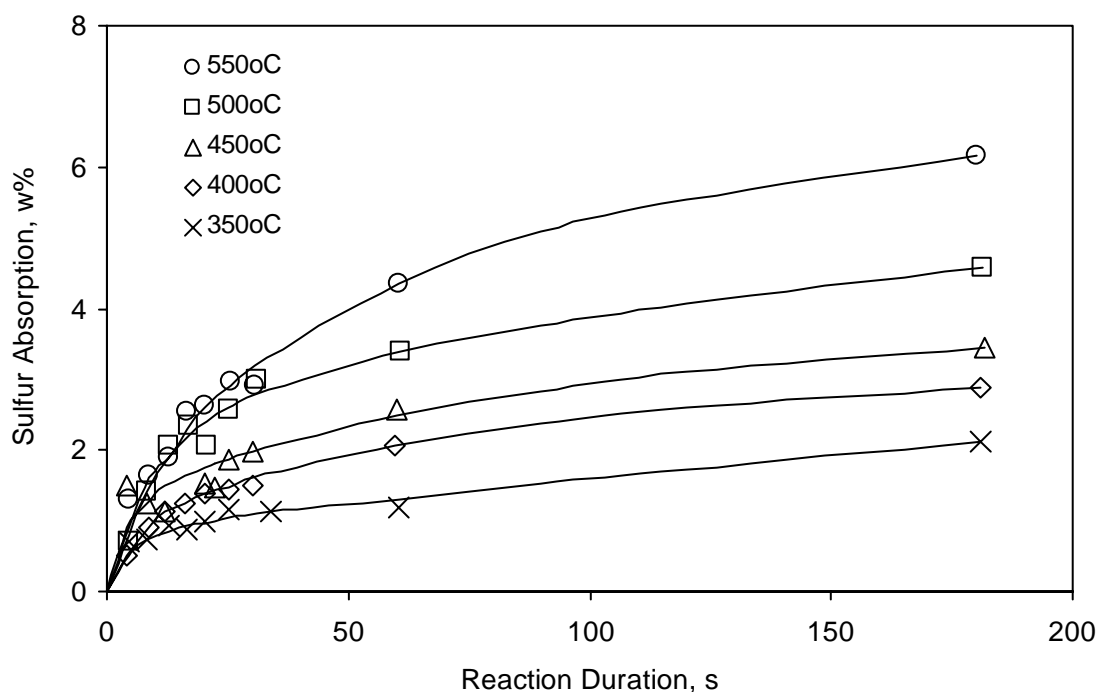
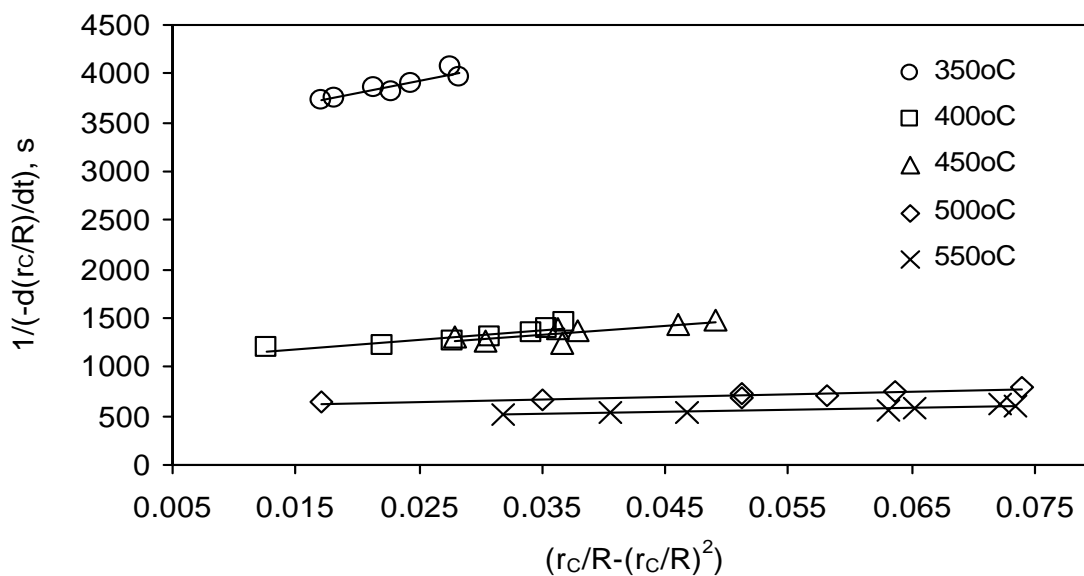


Figure 4. Effects of temperature on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture, using the reaction model.



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 6). The surface reaction rate constants appear to agree fairly with the equation in the temperature range of 350 – 550°C.

Figure 5. Effects of temperature on surface reaction rate constant and intraparticle diffusivity in the absorption of 18000-ppm H₂S into EX-SO₃ sorbent with 10-v% H₂ and 10-v% moisture.

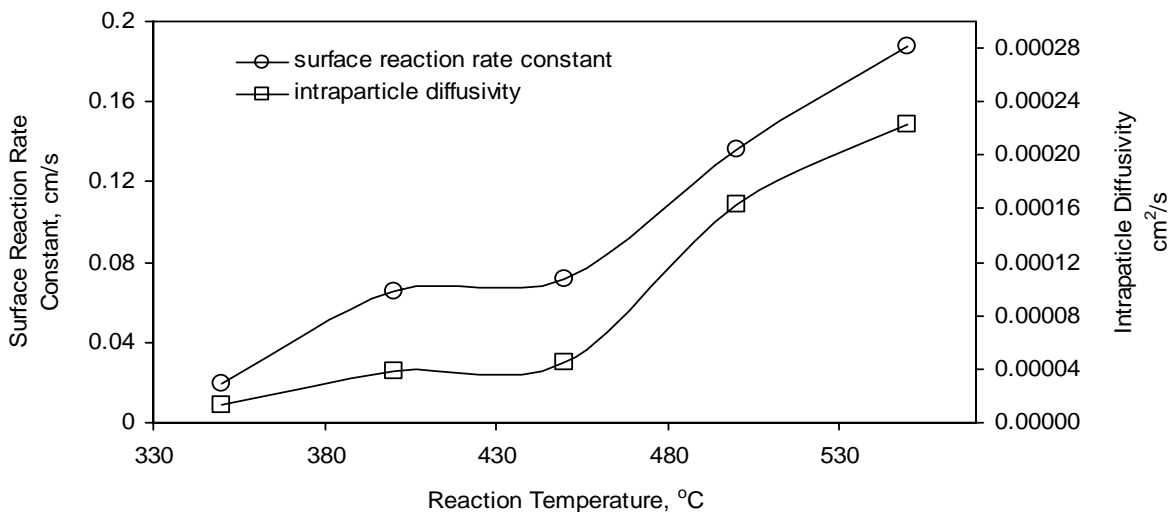
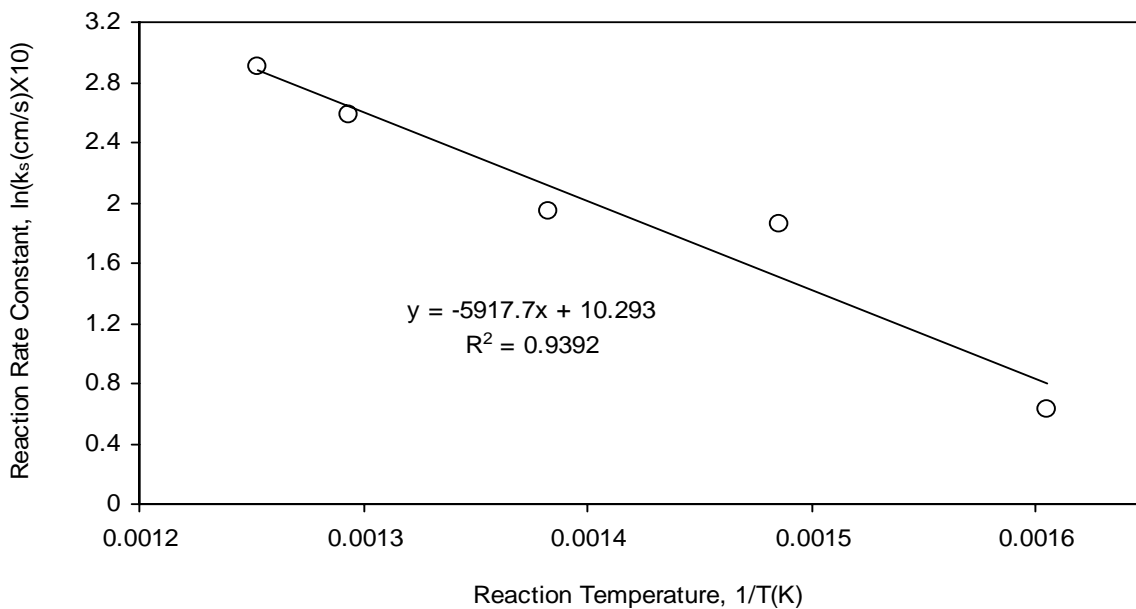


Figure 6. Effects of temperature on surface reaction rate constant in the absorption of 18000-ppm H₂S into EX-SO₃ sorbent with 10-v% H₂ and 10-v% moisture, using the Arrhenius equation.



Effects of Moisture on Initial Dynamic Absorption of H₂S

Experiments on initial absorption of H₂S into the sorbent 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 H₂S with the sorbent. The concentrations of H₂S and hydrogen are maintained at 18,000 ppm and 10-vol %, respectively. The concentration range of moisture in the simulated coal gas mixture is 5 – 20 volume percent.

Figure 7. Effects of moisture concentration on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen at 450°C and the space time 0.076 s.

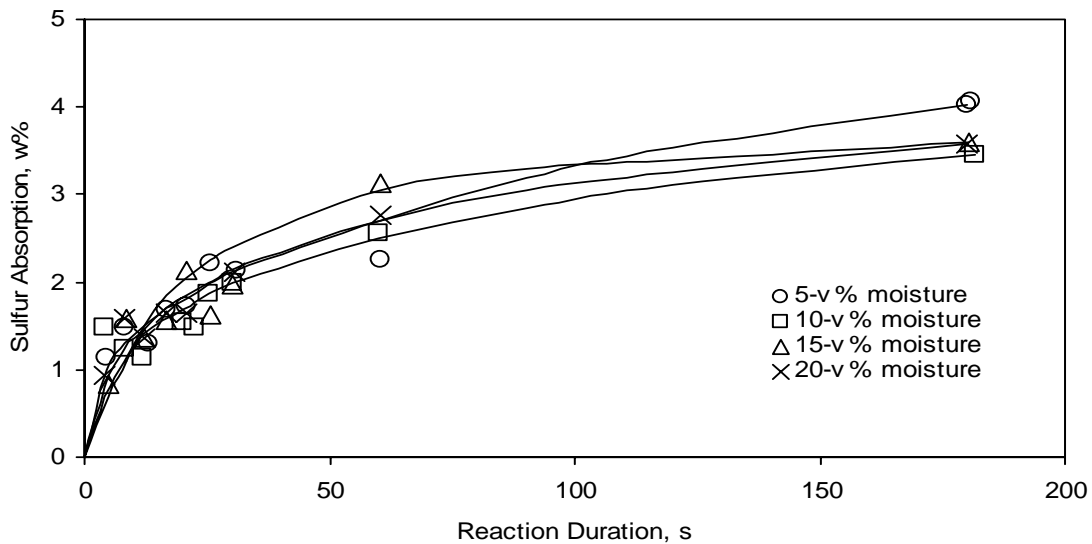
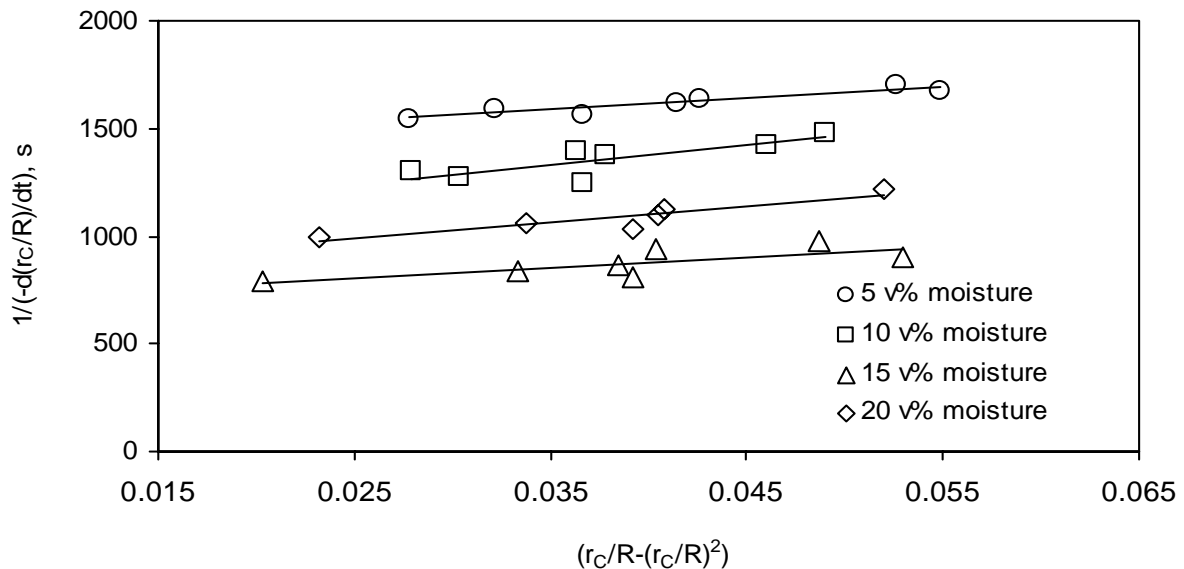
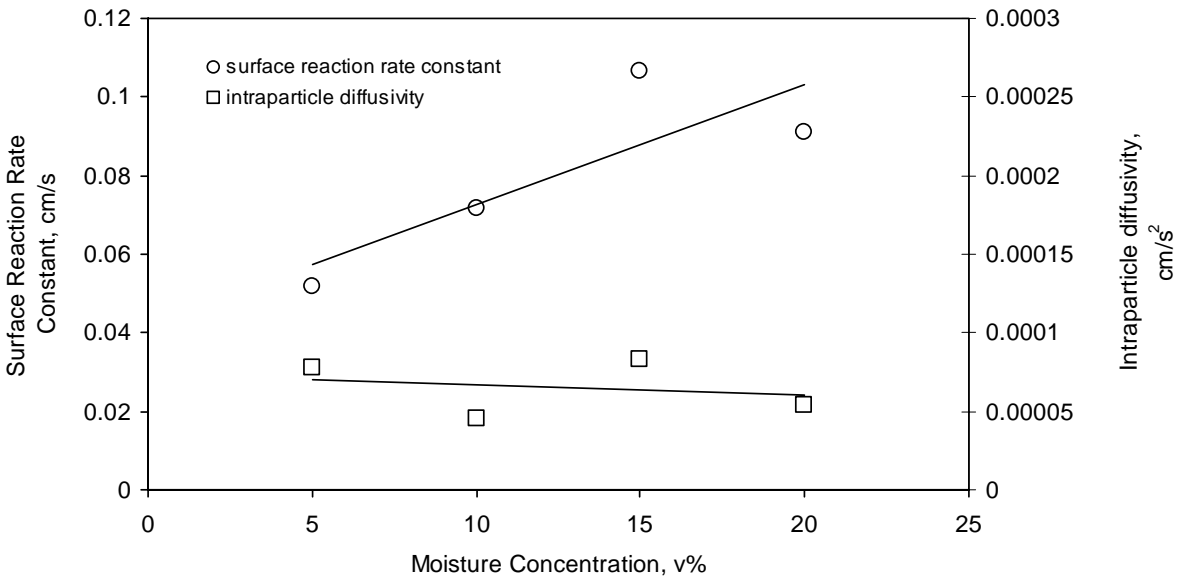


Figure 8. Effects of moisture concentration on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen at 450°C and the space time 0.076 s, using the reaction model.



Initial absorption of H₂S into the EX-SO₃ sorbent is affected with concentrations of moisture for short absorption duration of 4 –180 seconds (see Figure 7). These facts may indicate that moisture is not inert for the reaction of H₂S with the EX-SO₃ sorbent. Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H₂S with the sorbent (see Figure 8). The range of the surface reaction rate constants is 0.05– 0.11 cm/s, and the range of the intraparticle diffusivity values is 0.45×10^{-4} – 0.83×10^{-4} cm²/s (see Table 4 and Figure 8). These observations may indicate that reactivity of the EX-SO₃ sorbent increases with increased moisture concentrations, 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 9. Effects of moisture concentration on surface reaction rate constant and intraparticle diffusivity in the absorption of H₂S into 0.01-g EX-SO₃ sorbent with 10-v% H₂ at 450°C.



Effects of Sorbent amounts on Initial Dynamic Absorption of H₂S

Experiments on effects of sorbent amounts on initial dynamic absorption of H₂S 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 EX-SO₃ sorbent affect slightly initial dynamic absorption of H₂S into the sorbent in the sorbent amount range of 0.01– 0.02 g (see Figure 10). Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H₂S (see Figure 11). The range of the surface reaction rate constants is 0.07 – 0.10 cm/s, and the range of the intraparticle diffusivity values is 0.43×10^{-4} – 0.82×10^{-4} cm²/s. The concentrations of hydrogen and moisture were maintained at 10-v % and 10-v %, respectively. The concentration of H₂S was maintained at 18,000 ppm.

The surface reaction rate constant increases with increased amount of the sorbent. The intraparticle diffusivity values increase with increased amount of the sorbent (see Figure 12).

These observations may suggest attrition of the sorbent increases with sorbent amount in the fluidized bed of the micro reactor, thus changing particle distributions of the sorbent.

Figure 10. Effects of sorbent amount on absorption of 18000-ppm H₂S on EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s.

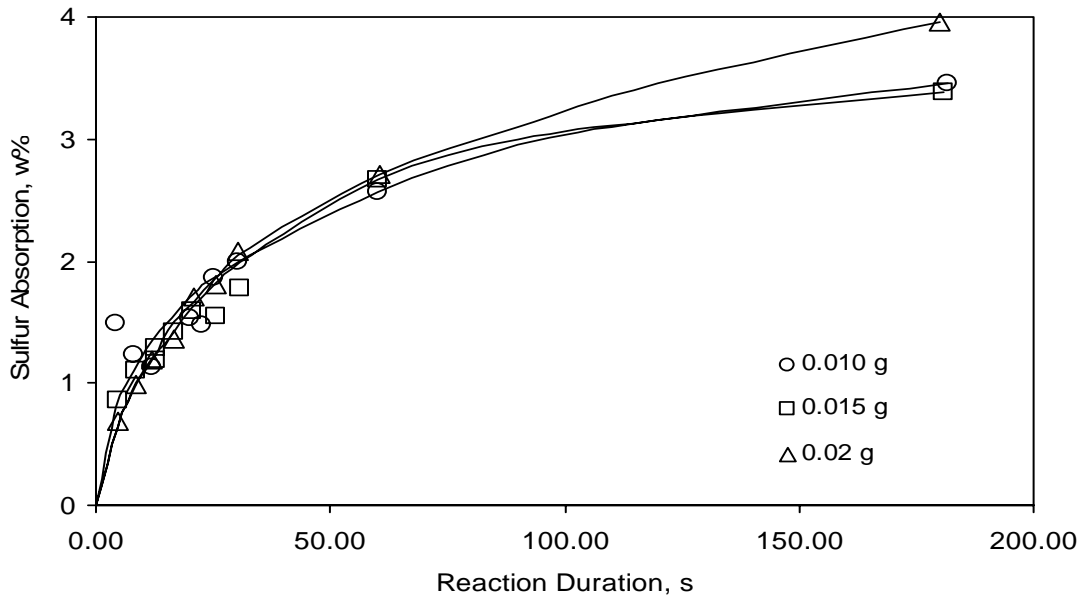


Figure 11. Effects of sorbent amount on absorption of 18000-ppm H₂S on EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s, using the reaction model.

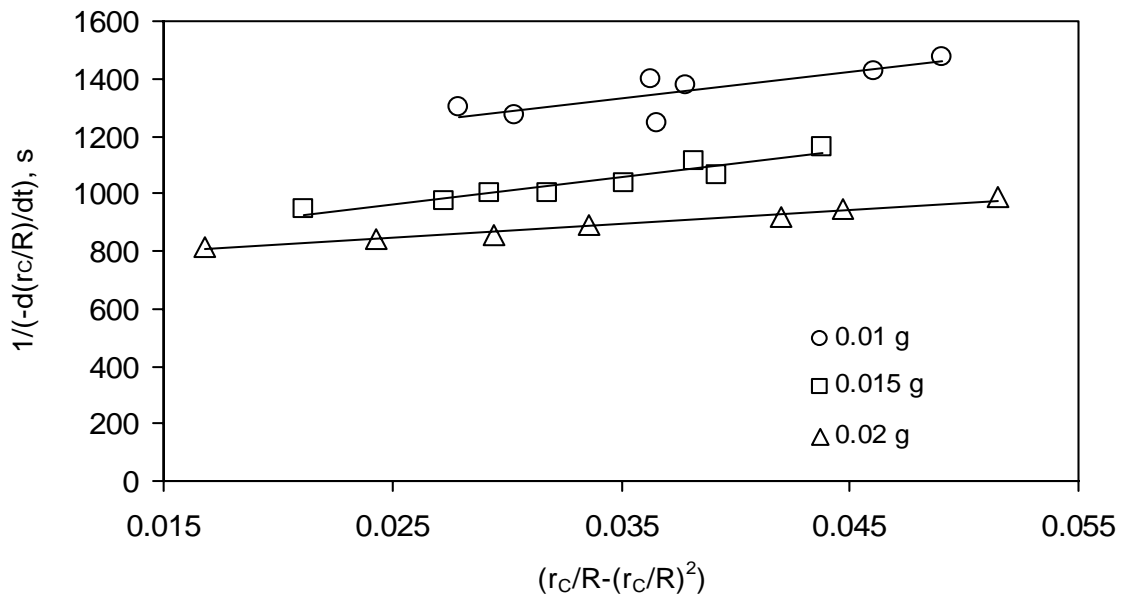
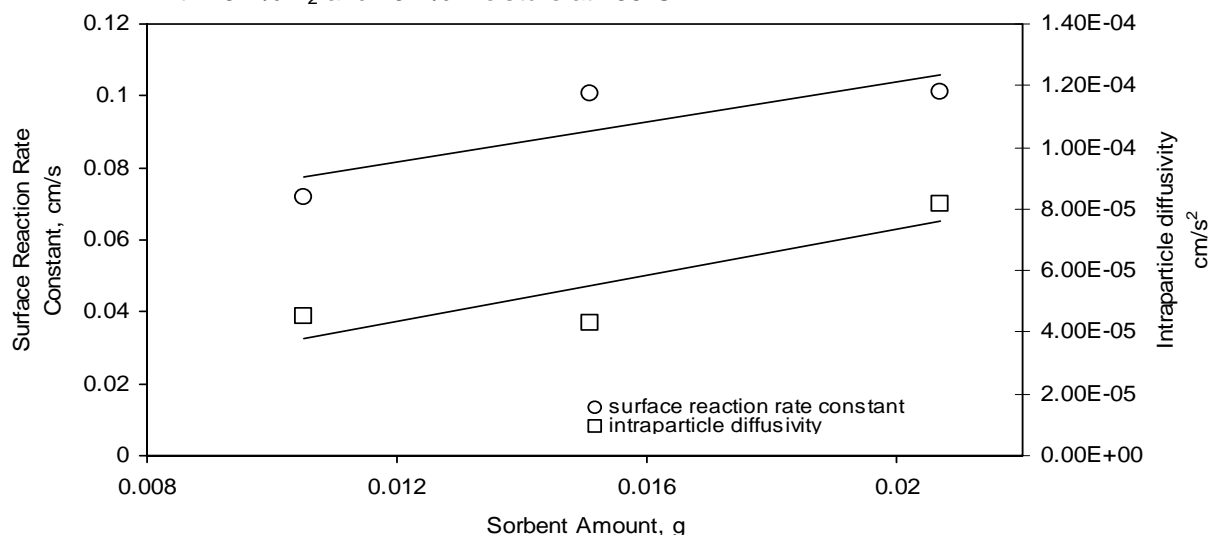


Figure 12. Effects of sorbent amount on surface reaction rate constant and intraparticle diffusivity in the absorption of 18000-ppm H₂S into EX-SO₃ sorbent with 10-v% H₂ and 10-v% moisture at 450°C.



Effects of Hydrogen Concentration on Initial Dynamic Absorption of H₂S

Experiments on effects of hydrogen concentrations on initial dynamic absorption of H₂S 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 H₂S was maintained at 18,000 ppm.

Figure 13. Effects of hydrogen concentration on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% moisture at 450°C and the space time 0.076 s.

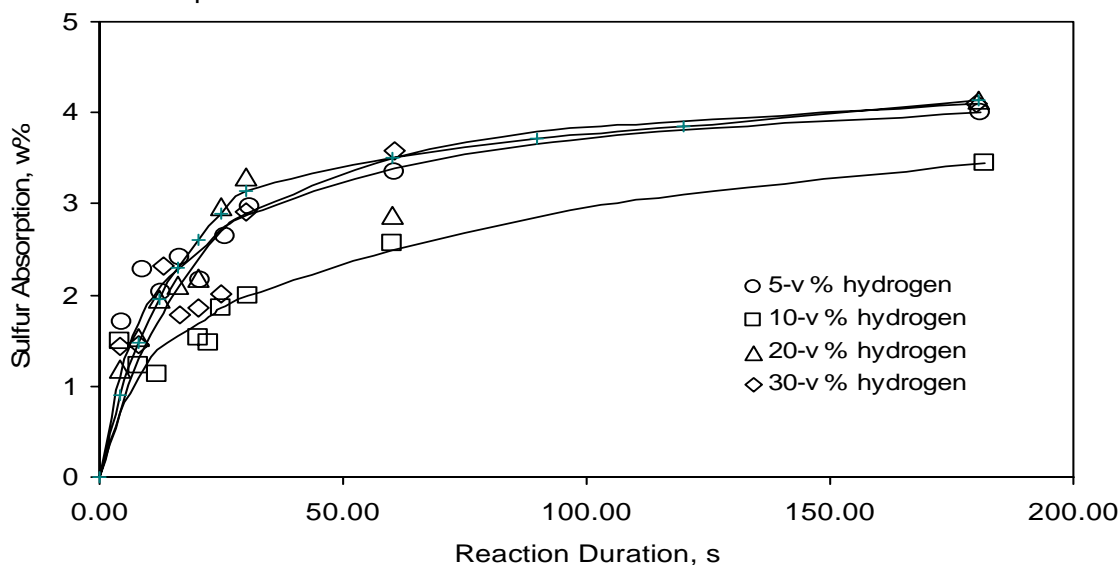
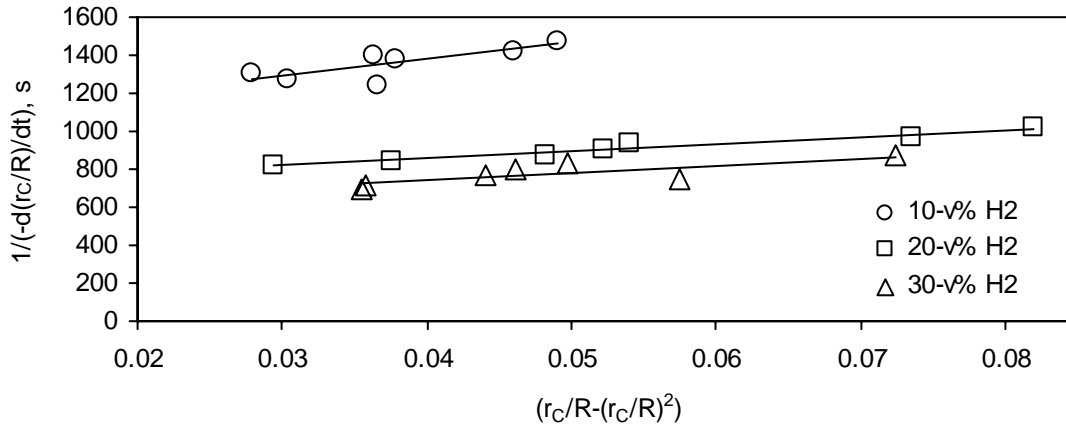
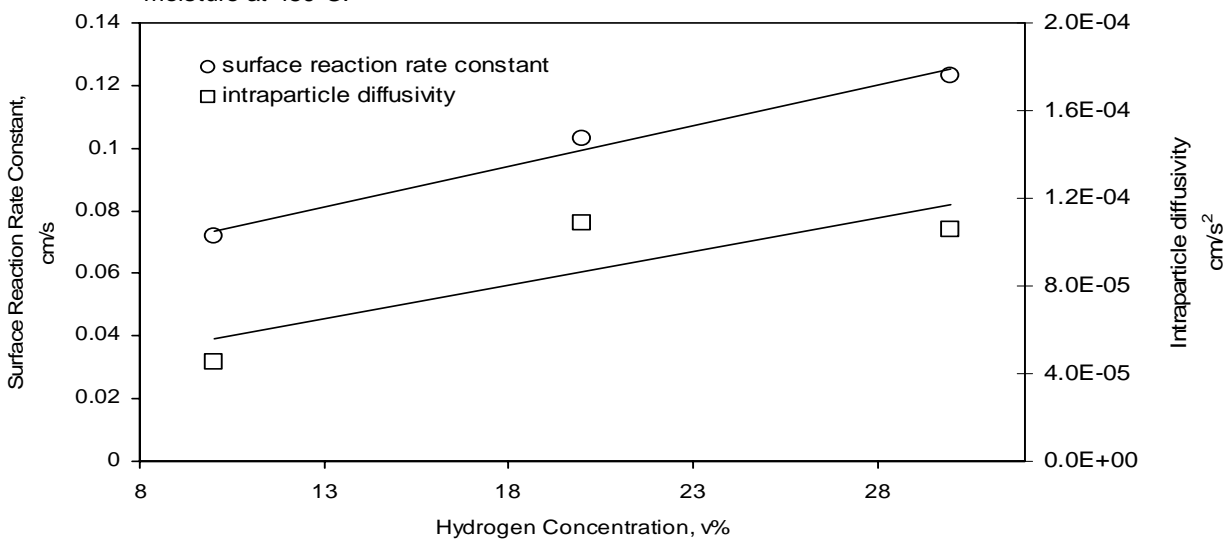


Figure 14. Effects of hydrogen concentration on absorption of 18000-ppm H₂S on 0.01-g EX-SO₃ sorbent with 10-v% moisture at 450°C and the space time 0.076 s, using the reaction model.



Concentrations of hydrogen affect initial dynamic absorption of H₂S into the EX-SO₃ sorbent in the hydrogen concentration range of 10 – 30 v% (see Figure 13). Equation 2 was applied to the experimental data to obtain initial surface reaction rate constants and intraparticle diffusivity values (see Figure 14). The range of the initial surface reaction rate constants is 0.07 – 0.12 cm/s, and the range of the intraparticle diffusivity values is 0.45×10^{-4} – 1.09×10^{-4} cm²/s (see Table 4). Surface reaction rate constant and intraparticle diffusivity increase with hydrogen concentration. These facts may indicate that hydrogen affects both surface reaction rate constants of H₂S with the sorbent and intraparticle diffusivity values of H₂S through the porous sorbent (see Figure 15).

Figure 15. Effects of hydrogen concentration on surface reaction rate constant and intraparticle diffusivity in the absorption of H₂S into 0.01-g EX-SO₃ sorbent with 10-v% moisture at 450°C.



Effects of H₂S Concentration of on Initial Dynamic Absorption of H₂S

Experiments on effects of H₂S concentrations on initial dynamic absorption of H₂S into the sorbent were conducted over the H₂S concentration range of 4,000 - 18000 ppm for the reaction duration of 4 – 180 s at 450°C and the space-time of 0.076 s. The concentration of moisture and the concentration of hydrogen were maintained at 10-volume percent.

Figure 16. Effects of H₂S concentration on absorption of H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s.

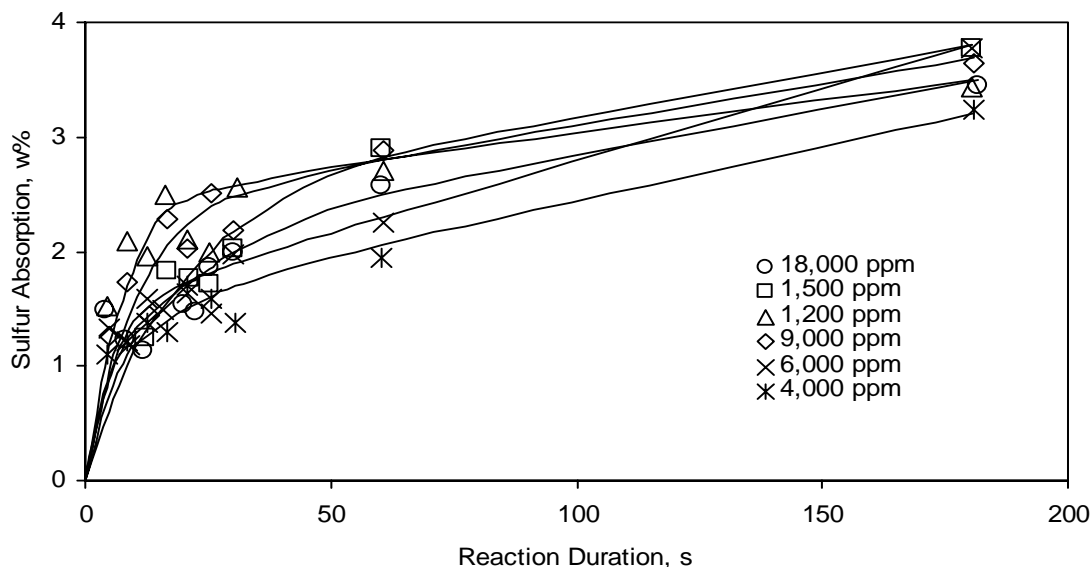
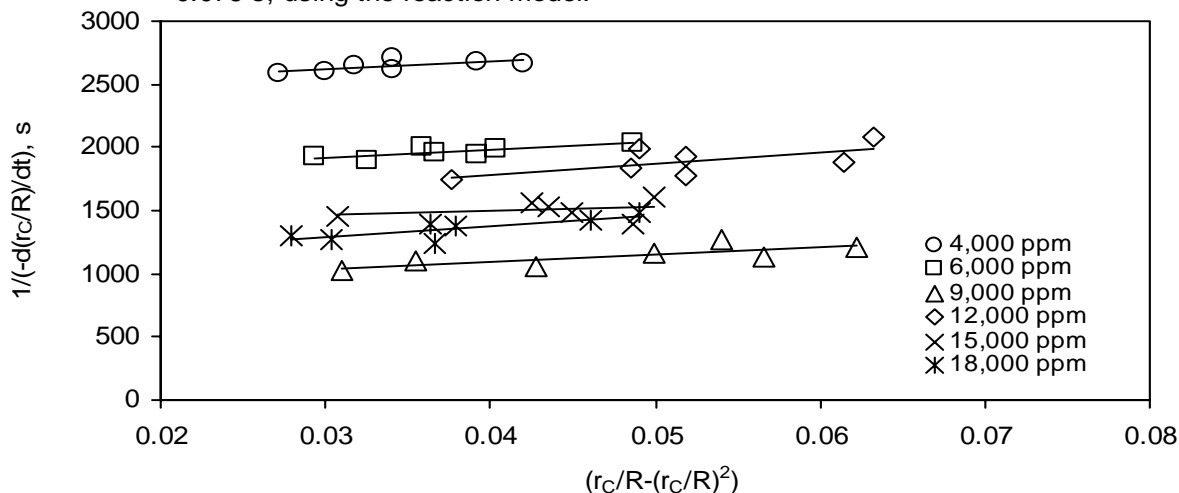
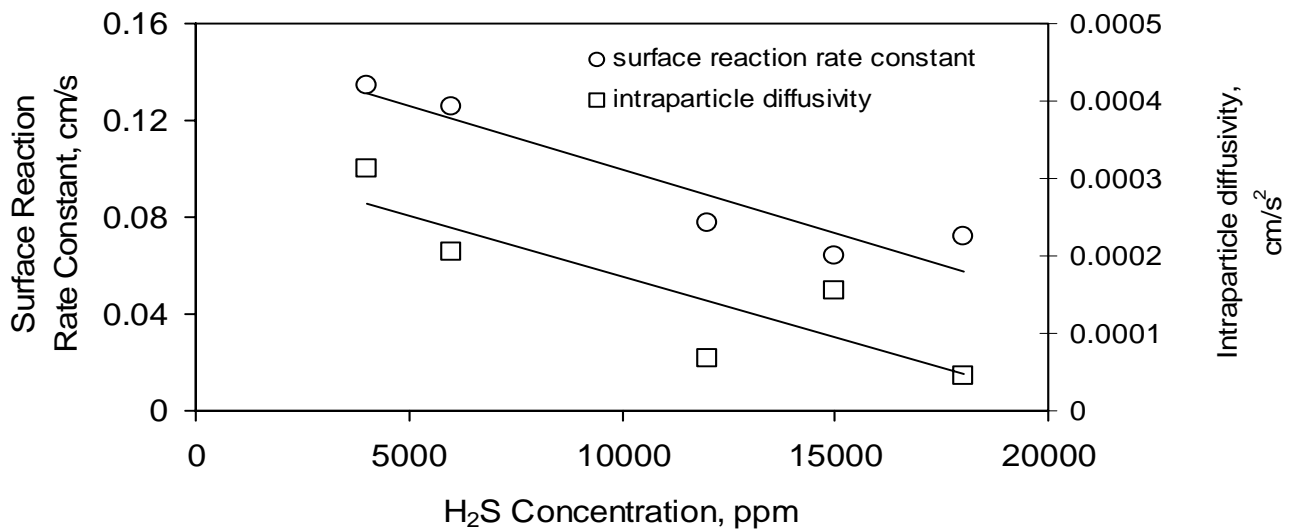


Figure 17. Effects of H₂S concentration on absorption of H₂S on 0.01-g EX-SO₃ sorbent with 10-v% hydrogen and 10-v% moisture at 450°C and the space time 0.076 s, using the reaction model.



Concentrations of hydrogen sulfide affect initial dynamic absorption of H₂S into the EX-SO₃ sorbent in the H₂S concentration range of 4,000 - 18000 ppm (see Figure 16). Equation 2 was applied to the experimental data to obtain initial surface reaction rate constants and intraparticle diffusivity values (see Figure 17). The range of the initial surface reaction rate constants is 0.06 – 0.13 cm/s, and the range of the intraparticle diffusivity values is 0.45×10^{-4} – 3.12×10^{-4} cm²/s (see Table 4). Surface reaction rate constant and intraparticle diffusivity increase with H₂S concentration. These facts may indicate that H₂S affects both surface reaction rate constants of H₂S with the sorbent and intraparticle diffusivity values of H₂S through the porous sorbent (see Figure 18).

Figure 18. Effects of H₂S concentration on surface reaction rate constant and intraparticle diffusivity in the absorption of H₂S into 0.01-g EX-SO₃ sorbent with 10-v% moisture at 450°C.



Surface Reaction Rate Constants and Intraparticle Diffusivity Values of H₂S for AHI-5 Sorbent, MCRH-67 Sorbent, and EX-SO₃ Sorbent

Experiments on absorption of hydrogen sulfide into the sorbents were carried out in the presence of 18,000-ppm hydrogen sulfide, 10-vol % moisture, 10 vol % hydrogen, and nitrogen as remainder for 4 – 180 seconds at 450°C and 40.7 psia, feeding a 750 cm³/min (sccm) gas mixture to compare surface reaction rate constants of H₂S in the absorption of H₂S with them and intraparticle diffusivity values of H₂S through their pore structures. The surface reaction rate constant and the intraparticle diffusivity value of H₂S are lowest for EX-SO₃ sorbent, while those are highest for AHI-5 sorbent, as shown in Figures 19 and 20.

Figure 19. Surface reaction rate constants in the absorption of 18000-ppm H₂S into 0.01-g sorbents with 10-v% H₂, 10-v% moisture, and 0.076-s space time at 450°C and 40.7 psia.

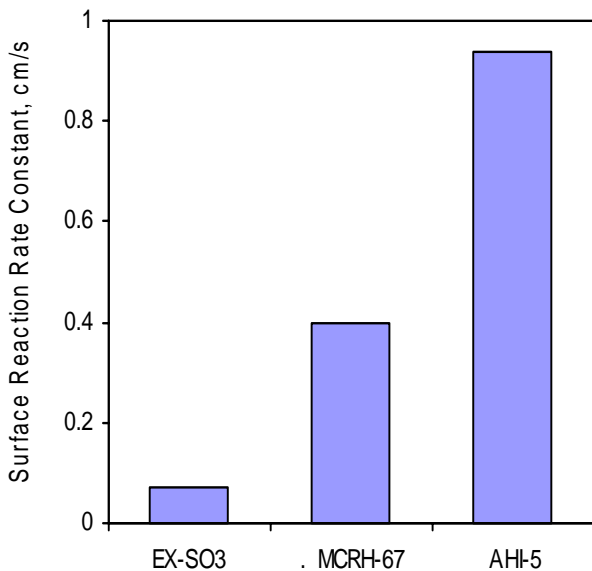
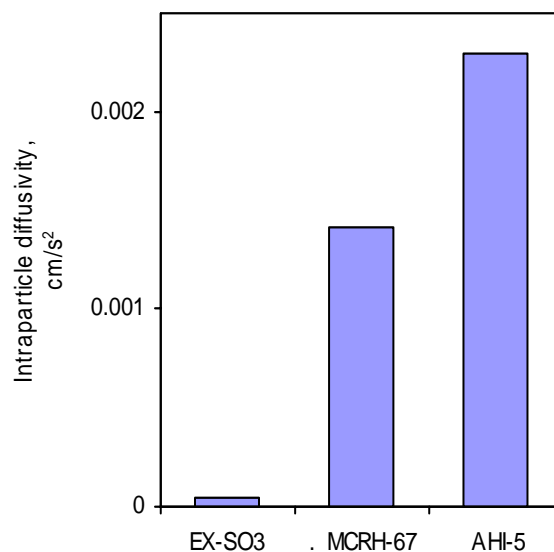


Figure 20. Intraparticle diffusivity values of sorbents in the absorption of 18000-ppm H₂S into 0.01-g sorbents with 10-v% H₂, 10-v% moisture, and 0.076-s space time at 450°C and 40.7 psia.



CONCLUSIONS

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

- Initial absorption of H₂S into the EX-SO₃ sorbent is affected with absorption temperature for short absorption duration of 4 - 180 seconds (see Figure 3). The range of the surface reaction rate constants is 0.02 – 0.19 cm/s (see Table 4 and Figure 5). The range of the intraparticle diffusivity values of the sorbent is 0.14×10^{-4} – 2.23×10^{-4} cm²/s. These observations may indicate that reactivity of the EX-SO₃ sorbent be dependent on reaction temperature in the temperature range of 350 – 550°C. The surface reaction rate constants and the intraparticle diffusivity values increase with the reaction temperatures. The surface reaction rate constants appear to agree fairly with the Arrhenius equation in the temperature range of 350 – 550°C (see Figure 6).
- Initial absorption of H₂S into the EX-SO₃ sorbent is affected with concentrations of moisture for short absorption duration of 4 –180 seconds (see Figure 7). These facts may indicate that moisture is not inert for the reaction of H₂S with the EX-SO₃ sorbent. The range of surface reaction rate constants is 0.05– 0.11 cm/s, and the range of intraparticle diffusivity values is 0.45×10^{-4} – 0.83×10^{-4} cm²/s (see Table 4 and Figure 8). These observations may indicate that reactivity of the EX-SO₃ sorbent increases with increased moisture concentrations, and intraparticle diffusivity decrease with increased moisture concentrations.

- Amounts of the EX-SO₃ sorbent affect slightly initial dynamic absorption of H₂S into the sorbent in the sorbent amount range of 0.01– 0.02 g (see Figure 10). The range of the surface reaction rate constants is 0.07 – 0.10 cm/s, and the range of the intraparticle diffusivity values is $0.43 \times 10^{-4} - 0.82 \times 10^{-4} \text{ cm}^2/\text{s}$. The concentrations of hydrogen and moisture were maintained at 10-v % and 10-v %, respectively. Surface reaction rate constants and intraparticle diffusivity values increase with increased amount of the sorbent (see Figure 12). These observations may suggest that attrition of the sorbent increases with sorbent amount in the fluidized bed of the micro reactor, thus changing particle distributions of the sorbent.
- Concentrations of hydrogen affect initial dynamic absorption of H₂S into the EX-SO₃ sorbent in the hydrogen concentration range of 10 – 30 v% (see Figure 13). The range of the initial surface reaction rate constants is 0.07 – 0.12 cm/s, and the range of the intraparticle diffusivity values is $0.45 \times 10^{-4} - 1.09 \times 10^{-4} \text{ cm}^2/\text{s}$ (see Table 4). Surface reaction rate constant and intraparticle diffusivity increase with hydrogen concentration. These facts may indicate that hydrogen affects both surface reaction rate constants of H₂S with the sorbent and intraparticle diffusivity of H₂S through the porous sorbent (see Figure 15).
- Concentrations of hydrogen sulfide affect initial dynamic absorption of H₂S into the EX-SO₃ sorbent in the H₂S concentration range of 4,000 - 18000 ppm (see Figure 16). The range of the initial surface reaction rate constants is 0.06 – 0.13 cm/s, and the range of the intraparticle diffusivity values is $0.45 \times 10^{-4} - 3.12 \times 10^{-4} \text{ cm}^2/\text{s}$ (see Table 4). Surface reaction rate constant and intraparticle diffusivity increase with H₂S concentration. These facts may indicate that H₂S affects both surface reaction rate constant of H₂S with the sorbent and intraparticle diffusivity of H₂S through the porous sorbent (see Figure 18).
- Experiments on absorption of hydrogen sulfide into AHI-5 sorbent, MCRH-67 sorbent, and EX-SO₃ sorbent were carried out in the presence of 18,000-ppm hydrogen sulfide, 10-vol % moisture, 10 vol % hydrogen, and nitrogen as remainder for 4 – 180 seconds at 450°C and 40.7 psia, feeding a 750 cm³/min (sccm) gas mixture to compare surface reaction rate constants of H₂S in the absorption of H₂S with them and intraparticle diffusivity values of H₂S through their pore structures. The surface reaction rate constant and the intraparticle diffusivity value of H₂S are lowest for EX-SO₃ sorbent, while those are highest for AHI-5 sorbent, as shown in Figures 19 and 20

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PUBLICATIONS AND PRESENTATIONS

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Kyung C. Kwon, Santosh K. Gangwal, Kamalendu Das, and Gaetan L. Tibere, Initial Reactivity of AHI-5 Sorbent with H₂S at High Temperatures”, revising in progress for publication in Advances in Environmental Research

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K. C. Kwon , Santosh K. Gangwal, and Jennifer T. Pinder, Initial Reaction Kinetics of Solid Sorbents with H₂S at High Temperatures, presented at the 2000 AIChE Annual Meeting, November 12-17, Westin Bonaventure/Marriott Downtown Los Angeles, CA

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