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

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ABSTRACT

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 high pressures and high temperatures. Metal oxides such as zinc titanate oxides, zinc ferrite oxide, copper oxide, manganese oxide and calcium oxide, were found to be promising sorbents in comparison with other removal methods such as membrane separations and reactive membrane separations. Some metal oxide sorbents exhibited the quite favorable performance in terms of attrition resistance and sulfur capacity. Removal reaction of H_2S from coal gas mixtures with ZT-4 or other promising sorbents of fine solid particles, and regeneration reaction of sulfur-loaded sorbents will be carried on in a batch reactor or a continuous differential reactor.

The objectives of this research project are to find intrinsic initial reaction kinetics for the metal oxide-hydrogen sulfide heterogeneous reaction system, to obtain effects of concentrations of coal gas components such as hydrogen, carbon monoxide, carbon dioxide, nitrogen and moisture on equilibrium reaction rate constants of the reaction system at various reaction temperatures and pressures, to identify regeneration kinetics of sulfur-loaded metal oxide sorbents, and to formulate promising metal oxide sorbents for the removal of sulfur from coal gas mixtures. Promising durable metal oxide sorbents of high-sulfur-absorbing capacity will be formulated by mixing active metal oxide powders with inert metal oxide powders and calcining these powder mixtures, or impregnating active metal oxide sorbents on supporting metal oxide matrixes.

The Research Triangle Institute, a sub-contractor of this research project, will also prepare promising metal oxide sorbents for this research project, plan experiments on removal of sulfur compounds from coal gases with metal oxide sorbents as well as regeneration of sulfur-loaded metal oxide sorbents, and review experimental results.

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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 more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more 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. Coal 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 as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occurring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. In gasification process, coal is reacted with steam and air or 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 reduce all forms of pollutants released from a coal conversion process through a lower fuel consumption and from the use of more energy efficient high pressure and/or temperature unit operations for the removal of environmental pollutants. Among these options, integrated gasification combined cycles (IGCC) are relatively well developed.

Sulfur products in combustion of sulfur present in coal not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. Removal of hydrogen sulfide from hot coal gas produced in integrated gasification combined cycle power generation systems by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compound from coal gas products is investigated by using various metal oxide sorbents, and membrane separation methods. Current research results show that removal of sulfur with metal oxide sorbents appears to be the most promising method among others.

Main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles. Spalling of sulfur-loaded fixed-bed metal oxide sorbents occurs during the regeneration of sulfur-loaded metal sorbents. The main causes of spalling of sorbents appear to be temperature rises of sulfur-loaded sorbents due to tremendous exothermic heat of reaction, and sulfate formation during regeneration processes. Sulfate products occupy more space than sulfide products in pores of sorbents, and result in significant structural stresses of metal sorbents.

The main objectives of this research proposal are to formulate durable metal oxide sorbents of high-sulfur-absorbing capacity by a physical mixing method or an impregnation method, to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, and to study kinetics on regeneration of sulfided sorbents, using formulated promising metal oxide solid sorbents.

STATEMENTS OF RESEARCH OBJECTIVES

Experiments will be conducted in an isothermal stirred micro batch reactor or an isothermal continuous differential reactor to obtain kinetic data on both sulfidation of metal oxide sorbents and regeneration of sulfided metal oxide sorbents, and experimental data on mechanical/thermal stability of formulated metal oxide sorbents suitable for the design of bench-scale/pilot-scale transport reactors.

- (a) Metal-oxide sorbents with high reactivity/capacity and thermal/mechanical stability/durability will be formulated by a physical mixing method or an impregnation method.
- (b) Experimental procedures will be developed for both sulfidation and regeneration reactions of formulated metal oxide sorbents at high pressures and high temperatures.
- (c) Analytical procedures will be developed for the analysis of concentrations of both sulfur dioxide and hydrogen sulfide in a reaction product gas mixture.
- (d) Thermal/mechanical stability of formulated metal oxide sorbents from cyclic sulfidation/regeneration reactions will be investigated in the isothermal stirred batch reactor or the isothermal continuous differential reactor.

Effects of reaction variables on sulfidation/regeneration reaction kinetics will be investigated for formulated promising metal oxide sorbents. The reaction variables include concentrations of coal gas components, total pressures, reaction temperatures, space velocities of gases for continuous differential reactor operations, initial mass ratios of coal gases to sorbents for batch reactor operations, particle sizes of sorbents, and pore volumes of sorbents.

- (a) Effects of concentrations of coal gas components such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, and moisture on both sulfidation and regeneration reaction kinetics will be evaluated at various reaction temperatures and pressures, using a stirred batch reactor.
- (b) Effects of total pressures and reaction temperatures on sulfidation/regeneration reaction kinetics for formulated metal oxide sorbents will be determined in a stirred batch reactor or a continuous differential reactor.

- (c) Roles of initial mass ratios of sorbents to sulfidation/regeneration gas mixtures, particle sizes of sorbents, and pore volumes of sorbents will be found, using a stirred batch reaction system.
- (d) Roles of space velocities of regeneration gas mixtures, and particle sizes of sorbents, pore volumes of sorbents will be delineated, using a continuous differential reaction system.

EXPERIMENTAL APPROACH

The main objectives of this project are to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, using promising solid metal oxide sorbents, to study kinetics on the regeneration of sulfided sorbents, and to formulate promising durable metal oxide sorbents of high-sulfur-absorbing capacity.

Fresh metal oxide sorbent particles with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a batch reactor. The batch reactor, loaded with the fresh sorbent and the simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature. Fine metal oxide sorbents will be used to minimize effects of intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles. The batch reactor, loaded with a mixture of fresh sorbent and simulated coal gas mixtures, is shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is terminated at the desired reaction time. Conversions of sorbents are analyzed with an electronic balance and a gas chromatograph.

Experiments on the regeneration of sulfided sorbents will be conducted in the batch reactor. Effects of regeneration temperatures, regeneration pressures, and concentrations of regeneration gases such as oxygen, nitrogen, and moisture on regeneration rate will be investigated in the batch reactor.

Precise laboratory procedures will be developed for H_2S -sorbent heterogeneous reactions in a batch reactor at high pressures and high temperatures. This will involve developing procedures for a proper set-up of a batch reactor and a gas chromatograph for a reaction system. Experiments on intrinsic initial sulfidation kinetics for fresh/regenerated metal oxide sorbents for sulfur-loaded metal oxide sorbents as well as regeneration kinetics will be performed for metal-oxide sorbents- H_2S heterogeneous reaction systems.

STATUS OF THIS RESEARCH PROJECT

Research activities and efforts of this research project were concentrated on calibrating the recently-purchased gas chromatograph (GC) for the analysis of sulfur dioxide, using gas mixtures of compressed nitrogen and 4,000 ppm sulfur dioxide in nitrogen as standard gas samples, carrying out experiments on reactivity of hydrogen sulfide with the newly-fabricated 35-cm³ 316 SS batch reactor wall, investigating reactivity of ZT-4 sorbent with hydrogen sulfide, conducting experiments on reactivity of the 1/16" cylindrical rod TU-1 sorbent, which was reported in the Quarterly Progress Report for the period of January 1 to March 31, 1995, and examining durability of the ZT-4 sorbent as well as TU-1 sorbent. The ZT-4 sorbent was formulated and supplied by the Research Triangle Institute. The TU-1 sorbent was formulated at our laboratory, as described in the Quarterly Progress Report for the period of January 1 to March 31, 1995.

A chromatographic calibration curve for the analysis of sulfur dioxide was developed with a flame photometric detector (FPD), using various gas mixtures of 4,000 ppm sulfur dioxide in nitrogen and neat nitrogen (Table 1 and Figure 1). This calibration curve will be used to analyze concentrations of sulfur dioxide during regeneration of H₂S-loaded metal oxide sorbents. The FPD detector detects sulfur compounds only, and does not detect inert nitrogen gas. In this way, there is no inert key compound for the analysis of sulfur dioxide. The following linear relationships between concentrations of sulfur dioxide and chromatographic areas of sulfur dioxide for SO₂-N₂ gas mixtures, as shown in equations 1 through 3, were obtained with known concentrations of SO₂ and chromatographic responses. These relationships will vary with sensitivity of the detector, amounts of injected gas samples, and temperature programmings for the GC oven. These relationships were established by injecting 2 cm³ gas samples into the gas chromatograph, which was maintained at 50°C. The equation 1 was developed with the chromatography obtained in the morning of 7/25/1995, whereas the equation 2 was developed with the chromatography obtained in the afternoon of 7/25/1995. The equation 3 was developed with the chromatography obtained in the afternoon of 7/26/1995. Frequent calibration of the gas chromatograph may be required to analyze concentrations of SO₂, as shown in equations 1 through 3, since the calibration curves for the analysis of SO₂ are different, as shown in Figure 1.

$$y = 22.52\ln(x) - 191.01 \quad (1)$$

$$y = 30.02\ln(x) - 280.89 \quad (2)$$

$$y = 23.80\ln(x) - 220.73 \quad (3)$$

where y: concentration of SO₂, ppm
x: chromatographic area

Figure 1. Chromatographic calibration curves for SO₂-N₂ gas mixtures, using a FPD detector at 77°C.

Table 1. Chromatographic calibration data for H₂S-N₂ gas mixtures.

Concentration of SO ₂ , ppm	Chromatographic Area		
	7/25/95 afternoon	7/26/95 morning	7/26/95 afternoon
25	16992	25638	30861
25	16712	27555	29950
50	37662	58845	85459
50	39302	66692	93058
62.5	92486	90178	136311
62.5	85154	92054	153585

Experiments on reactivity of hydrogen sulfide with the 316 SS batch reactor wall, using the initial reaction gas mixture consisting of 9107-ppm hydrogen sulfide (0.005 g; 1 w%), 0.085-g water (15.84 w%), 0.0029-g hydrogen (0.58 w%), and 0.4046-g nitrogen (81.34 w%), were carried out, as shown in Tables 2 and 3, and Figure 2. Absorption of hydrogen sulfide on the reactor wall increases with absorption temperatures. Absorption of H₂S into the 316 SS wall increase with absorption time above 400°C. Absorption of H₂S into the 316 SS wall does not take place, and previously-absorbed H₂S appears to be released from the 316 SS wall at 350°C.

Table 2. Operation conditions for the reaction of hydrogen sulfide with 316 stainless steel wall in the presence of water, nitrogen and hydrogen at various temperatures.

Reactor Volume, cm ³ :	35
Temperature, °C:	350 - 500
Reaction Time, min:	5 - 60
Initial Partial Pressure of Hydrogen at 25°C, psia:	14.7
Initial Amount of Water, g:	0.085
Initial Concentration of H ₂ S, ppm	9107
Initial Partial Pressure of Nitrogen at 25°C, psia:	150

Compounds	Initial Weight %
H ₂ S	1
H ₂	0.58
H ₂ O	17.08
N ₂	81.34

Table 3. Reactivity of 316 stainless steel in the presence of 0.085-g moisture and the initial concentration 9107-ppm H₂S at various temperatures.

350°C			400°C			500°C		
Run #	Reaction Time, min	Concentration of H ₂ S, ppm	Run #	Reaction Time, min	Concentration of H ₂ S, ppm	Run #	Reaction Time, min	Concentration of H ₂ S, ppm
195	5	8760	145	5	8147	113	10	8497
	5	8580		5	8277		10	8631
194	10	8622	148	10	9609	117	20	7672
	10	9171		10	9779		20	7893
196	30	9065		10	9247	121	20	8324
	30	9637		10	9346		20	8209
193	60	9734	149	20	9045	123	20	7017
	60	10091		20	9402		20	7404
	60	10644		20	8503	124	20	6145
	60	9987		20	8782		20	5789
	60	10851		20	8277	118	30	7171
			147	30	9330		30	7438
				30	9379	114	40	7607
			146	60	8423		40	7431
				60	8739	120	50	6957
							50	7256
						112	60	7194
							60	7323

A series of experiments on effects of ZT-4 sorbent amounts on removal of H₂S were carried out for 10 min at 500°C (Tables 4 and 5, and Figure 3). Removal of H₂S increases with amounts of the sorbent, but appears to level off above 0.1-g sorbent.

Table 4. Operation conditions for the reaction of hydrogen sulfide with ZT-4 sorbent in the presence of water, nitrogen and hydrogen at various temperatures.

Reactor Volume, cm ³ :	35
Temperature, °C:	350 - 500
Reaction Time, min:	1 - 60
Particle Size	200 μ m or <200 mesh
Amount of Sorbent, g	0.1
Initial Partial Pressure of Hydrogen at 25°C, psia:	14.7
Initial Amount of Water, g:	0.085 - 0.120
Initial Concentration of H ₂ S, ppm	9107
Initial Partial Pressure of Nitrogen at 25°C, psia:	150

Table 5. Effects of ZT-4 sorbent amounts on removal of H₂S with the initial concentration 9107-ppm H₂S and 0.085-g moisture for 10 min at 500°C.

Run #	Amount of Sorbent, g	Concentration of H ₂ S, ppm
113	0	8497
	0	8631
115	0.05	3327
	0.05	3327
122	0.10	1991
	0.10	1962
125	0.15	2069
	0.15	2045

Reactivity of ZT-4 sorbent with H₂S was examined at various temperatures (Table 6 and Figure 4). Reactivity of the sorbent with H₂S increases with reaction temperatures. Equilibrium removal of H₂S increases with reaction temperatures, and requires longer reaction times with lower reaction temperatures.

Figure 4. Reactivity of 0.1-g ZT-4 sorbent with 0.085-g moisture and the initial concentration 9107-ppm H₂S at various temperatures.

Table 6. Reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H₂S and 0.085-g water at various temperatures.

350°C			400°C			500°C		
Run #	Reaction Time, min	Concentration of H ₂ S, ppm	Run #	Reaction time, min	Concentration of H ₂ S, ppm	Run #	Reaction time, min	Concentration of H ₂ S, ppm
172	1	4624	165	1	5048	128	5	1498
	1	4964		1	5118		5	1508
177	1	4499	141	3	4358	129	10	1675
	1	3983		3	4190		10	1633
178	3	6704	164	3	3984	127	20	1398
	3	6025		3	3966		20	1468
179	5	5821	140	5	3074		20	1433
	5	5543		5	3109	126	30	1234
173	7	5086	166	7	2651		30	1249
	7	4884		7	2367	133	40	1800
175	10	3377		7	2327		40	1793
	10	3492	170	7	2966	132	50	1660
181	15	2653		7	2977		50	1661
	15	2606	144	10	2287	130	60	1730
176	20	2712		10	2451		60	1728
	20	2781	169	10	2836			
180	40	3036		10	2762			
	40	2839	139	20	2081			
174	60	2598		20	2032			
	60	2727	168	20	2804			
				20	2736			
			167	30	2540			
				30	2578			
			143	30	2491			
				30	2666			
			142	40	2604			
				40	2674			
				40	2568			
			163	40	1837			
				40	1831			
			138	50	1969			
				50	1979			
			135	60	1671			
				60	1665			
				60	3696			
			171	60	3106			
				60	2942			

Effects of moisture on reactivity of ZT-4 sorbent with H₂S were investigated at 350°C (Tables 7 and 8, Figures 5 and 6). Increased moisture increases removal of H₂S below equilibrium absorption, as shown in Figure 5. Equilibrium absorption of H₂S appears to be independent of moisture amounts, as shown in Figure 6. This fact may indicate that moisture does not affect equilibrium absorption for the absorption of H₂S into ZT-4 sorbent at 350°C.

Table 7. Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H₂S for 3 min at 350°C.

Run #	Amount of Water, g	Concentration of H ₂ S, ppm
182	0.0489	6061
	0.0489	6006
178	0.0842	6704
	0.0842	6025
183	0.1172	4815
	0.1172	4638
	0.1172	3974

Table 8. Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H₂S at 350°C and various moisture contents.

0.085 g Moisture			0.12 g Moisture		
Run #	Reaction Time, min	Concentration of H ₂ S, ppm	Run #	Reaction Time, min	Concentration of H ₂ S, ppm
172	1	4624	192	2	3997
	1	4964		2	4172
177	1	4499	183	3	4815
	1	3983		3	4638
178	3	6704		3	3974
	3	6025	186	5	4306
179	5	5821		5	4364
	5	5543	184	7	4924
	7	5086		7	4839
173	7	4884	191	7	3702
175	10	3377		7	3342
	10	3492		7	3156
	15	2653		7	3198
181	15	2606	187	10	3726
176	20	2712		10	3633
	20	2781		10	3620
180	40	3036	190	15	2883
	40	2839		15	2803
174	60	2598	189	20	2872
	60	2727		20	2746
			185	40	2616
				40	2763
			188	60	2323
				60	2315

Figure 5. Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H₂S for 3 min at 350°C.

Figure 6. Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H_2S and various moisture amounts at 350°C.

Reactivity of TU-1 sorbent was tested at 350°C (Tables 9 and 10, and Figure 7). The 1/16"-cylindrical-rod TU-1 sorbent was briefly reported in the Quarterly Progress Report for the period January 1 to March 31, 1995. This sorbent, consisting mainly of zinc oxide and titanium oxide, were formulated with a physical mixing method. Absorption of H_2S into the sorbent also increases with absorption times below equilibrium absorption, as shown in Figure 7.

Table 9. Operation conditions for the reaction of hydrogen sulfide with TU-1 sorbent in the presence of water, nitrogen and hydrogen at various temperatures.

Reactor Volume, cm^3 :	35
Temperature, °C:	350 - 500
Reaction Time, min:	1 - 15
Particle Size	< 200 mesh
Amount of Sorbent, g	0.1
Initial Partial Pressure of Hydrogen at 25°C, psia:	14.7
Initial Amount of Water, g:	0.085
Initial Concentration of H_2S , ppm	9107
Initial Partial Pressure of Nitrogen at 25°C, psia:	150

Figure 7. Reactivity of 0.1-g TU-1 sorbent with the initial concentration 9107-ppm H_2S and 0.085-g moisture at 350°C and various reaction times.

Table 10. Reactivity of 0.1-g sorbent with 0.085-g moisture and the initial concentration 9107-ppm H_2S at 350°C

ZT-4 200 micron			ZT-4 200 mesh			1/16" rod TU-1		
Run #	Reaction Time, min	Concentration of H_2S , ppm	Run #	Reaction Time, min	Concentration of H_2S , ppm	Run #	Reaction Time, min	Concentration of H_2S , ppm
214	1	6900	206	1	6552	226	1	6799
	1	6808		1	6060		1	6700
213	2	6849	210	1	6259		1	6566
	2	6439		1	6102	225	2	6140
	2	6004	209	2	5496		2	5547
178	3	6704		2	5460		2	5510
	3	6025	200	3	4300		2	5891
212	4	5175		3	4533	224	4	5467
	4	5136	204	4	3803		4	4864
179	5	5821		4	4401		4	5113
	5	5543		4	4771	223	7	4861
218	5	3812	208	4	4403		7	4493
	5	3990		4	4603		7	4122
211	7	3884	198	5	3776	221	10	3909
	7	4054		5	3542		10	4112
217	7	4017		5	3814	229	15	3422
	7	3734	207	7	4060		15	2927
	7	3770		7	4118		15	3573
	7	3897		10	2794		15	3978
175	10	3377		10	3299			
	10	3492		10	3412			
216	10	3260		10	2606			
	10	3255		10	2996			
	10	3395		10	3462			
	10	3573		10	3262			
215	15	2186		10	2797			
215	15	2129		10	3009			
215	15	2260		10	2650			
215	15	2307		15	2420			
				15	2575			
				15	2438			
				15	2607			
				15	2487			

Effects of particle sizes of ZT-4 sorbent on removal of H_2S were examined at $350^\circ C$, as shown in Table 10 and Figure 8). The minus-200-mesh sorbent removes more H_2S than the 200- μm sorbent below equilibrium absorption. Equilibrium absorption of H_2S is not affected by particle sizes. This observations may suggest that intraparticle mass transfer of H_2S into pores of the sorbent is a limited step for absorption of H_2S into the sorbent at $350^\circ C$.

Reactivity of TU-1 sorbent was compared with that of ZT-4 sorbent at $350^\circ C$ (Table 10 and Figure 9). TU-1 sorbent removes less H_2S than ZT-4 sorbent, based on the experimental data generated from the 35 cm^3 batch reactor.

Durability of TU-1 sorbent as well as ZT-4 sorbent was monitored by weighting the spent sorbent after each experimental run (Table 11 and Figure 10). The batch reactor was shaken horizontally at 50 rpm to eliminate effects of transfer of H_2S from the bulk reaction gas mixture to the solid sorbent. Weight gain of ZT-4 sorbent increases with reaction times below equilibrium absorption, but weight gain of ZT-4 sorbent decreases with reaction times above equilibrium absorption. This fact may indicate that ZT-4 sorbent particles in the batch reactor were abraded by shaking the batch reactor for an extended reaction time.

Table 11. Durability of sorbents during reaction of sorbents with the initial concentration 9107-ppm H_2S in the presence of 0.085-g moisture and initial partial pressure 14.7-psia hydrogen at 350°C

ZT-4		
Run #	Reaction Time, min	Weight Gain %
213	2	1.7
178	3	1.6
212	4	3.3
211	7	4
215	15	4.4
180	40	4
174	60	3.3

TU-1		
Run #	Reaction Time, min	Weight Gain %
225	2	-0.5
224	4	-0.8
223	7	-2
221	10	-0.7
214	15	-3.1

PRESENTATION

The research paper, entitled "Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperatures and Pressures", was presented at the Ninth Symposium on SEPARATION SCIENCE AND TECHNOLOGY FOR ENERGY APPLICATIONS, Park Vista Hotel & Convention Center, Gatlinburg, Tennessee, October 22-26, 1995.

PLANS ON FUTURE EXPERIMENTS

Initial reaction kinetics on both sulfidation of sulfur-free sorbents and regeneration of sulfided sorbents will be conducted in the 35 cm³ 316 SS batch reactor, using sorbents impregnated on the Norton carriers as well as various sorbents formulated by a physical mixing method. A continuous differential reactor will be designed and fabricated, and tested. Durability of formulated sorbents will be examined.