DOE CONTRACT NUMBER DE-AC21-94MC31089 ADVANCED SORBENT DEVELOPMENT PROGRAM

Topical Report

Task 6. Topical Report

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Program Objective

The overall objective of this program was to develop regenerable sorbents for use in the temperature range of 343° to 538° C (650° to 1000° F) to remove hydrogen sulfide (H₂S) from coal-derived fuel gases in a fluidized-bed reactor.

The goal was to develop sorbents that are capable of reducing the H_2S level in the fuel gas to less than 20 ppmv in the specified temperature range and pressures in the range of 1 to 20 atmospheres, with chemical characteristics that permit cyclic regeneration over many cycles without a drastic loss of activity, as well as physical characteristics that are compatible with the fluidized bed application.

Background Information

U.S. coals have a very variable sulfur content; low in the eastern (Appalachian) fields and in the western sub-bituminous deposits and too high in the mid-western basin deposits. The major reserves that are most readily accessible to industry and population centers are the mid-western coals of Illinois, Western Kentucky, Indiana, and Iowa. Unfortunately, these coals have sulfur levels that are too high for direct utilization. Therefore, sulfur removal must be accomplished prior to combustion, during combustion, or by postcombustion processing of the exhaust stream. With the ever-increasing limitations on SO_2 emissions, even most low sulfur coals will eventually require some treatment at sometime in their utilization. The sulfur in coal is typically about equally divided between its occurrence as the mineral component (pyrite-FeS₂) or as a sulfur-containing compound in the organic portion. Of these, the inorganic component is most readily removed via fine grinding, for liberation and separation via physical techniques. Current coal gasification technology relies on removal of some of the relatively easy inorganic fraction during coal cleaning (ash removal) and anticipates that the major removal will occur during or after gasification.

Coal gas desulfurization to sufficiently low levels at elevated temperatures is now recognized as crucial to efficient and economic coal utilization in Integrated Gasification-Combined Cycle (IGCC) systems. The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials that have high sulfur capacity and can efficiently remove H_2S (from several thousand ppmv levels down to a few ppmv) over many cycles of sulfidation/regeneration. Structural stability and good mechanical strength are also desirable features in a sorbent. Not surprisingly, only a few metal oxides can meet these stringent requirements.

The research and development for high-temperature desulfurization of fuel gases has been sponsored primarily by the Federal Energy Technology Center (FETC) of the United States Department of Energy (U.S. DOE). Over the last decade a number of studies have been reported on high-temperature H₂S removal, primarily using various transition metal oxides as regenerable sorbents.¹⁻⁵ The sorbent most intensively studied is iron oxide, which yields equilibrium H₂S concentrations in the few hundred ppm range for a composition representative of low Btu coal-derived gas and temperatures of above 500°C. While the sulfidation kinetics of iron oxide are very good³, this sorbent cannot be used for single-stage coal gas desulfurization to reduce the H₂S content of the fuel gas down to a few ppm of sulfur.

Zinc oxide has been used as a non-regenerable sorbent in "guard beds" protecting catalyst beds from trace sulfur impurities. More recently, zinc oxide has also been investigated as a regenerable sorbent.⁴⁻⁸ The thermodynamic equilibrium for sulfidation of ZnO is quite favorable, yielding desulfurization down to a few ppmv H₂S. The sulfidation kinetics of ZnO, however, is slower⁹ compared to that of iron oxide, and the regenerability of ZnO is restricted by the loss of surface area at high temperatures and the formation of zinc sulfate at low regeneration temperatures.

Reduction and sulfidation take place simultaneously when the sorbent is contacted with the hot fuel gas. Regeneration can be conducted with air or air-steam mixtures. When reaction and diffusion rates are sufficiently rapid, the sorbent sulfur capacity and the extent of desulfurization are determined by thermodynamics alone. With many sorbents, however, the rates of reaction, pore diffusion, or diffusion in the product layer, limit sorbent capacity and the extent of cleanup under practical conditions. Such is the case with some commercial ZnO sorbents where the reported conversions at breakthrough have been less than 20% in packed-bed applications. The larger molar volume of the product solid (ZnS = 24.4 cm³/mol) compared to that of the reactant solid (ZnO= 14.4 cm³/mol) causes pore plugging, limiting access to the interior of the sorbent.

In recent years it has been shown that certain mixed oxides have superior properties compared to single oxides for hot gas cleanup.^{6-8,10-16} A compound of zinc and iron

oxides, zinc ferrite, ZnFe₂O₄, developed by DOE/FETC has reached pilot-stage (testing) for desulfurization of low-Btu gases.¹⁷⁻¹⁹ However, physical durability of the zinc ferrite sorbent in long-term testing appears to be inadequate for IGCC application.

Because of the apparent limitations of the zinc ferrite sorbent, many investigators have been conducting research to develop a superior mixed metal oxide sorbent.^{6-8,11-13,20-26} Work on zinc titanates such as ZnTiO₃, Zn₂TiO₄, and Zn₂Ti₃O₈^{6-8,24} has shown that titanium oxide is a better alternative to iron oxide additives in terms of the higher stability of the titanates over the ferrite compounds of zinc, and their similar sulfidation equilibria. With zinc titanates, the sulfidation temperature has been shown to extend to 700°C and sintering of the ZnO was greatly reduced. Although zinc titanate has been shown to have better attrition resistance than zinc ferrite in pilot tests, this sorbent also suffers from gradual loss of reactivity in long-term cyclic operation, resulting in high fresh sorbent makeup rate to maintain the desired level of desulfurization.^{27,28} Other mixed metal oxides such as copper-based and cobalt-based sorbents have also been investigated,²⁹⁻³² however, the research has been limited to laboratory-scale equipment.

Although higher temperature application offers better overall process efficiency, the stringent requirement for sulfur removal efficiency at temperatures above $538^{\circ}C$ (1000°F) limits the choice of sorbents to a few metal oxides (based on thermodynamic equilibrium), that have been shown to have other limitations, as described earlier. The thermodynamic equilibria of many metal oxides significantly improve as the temperature decreases, making many metal oxide sorbents suitable for hot gas cleanup applications in the temperature range of 343° to $538^{\circ}C$ (650° to $1000^{\circ}F$). Although the initial chemical reactivities of the sorbents generally decrease with decreasing temperature, the lower thermal stress incurred can lead to better sorbent reactivity after a large number of cycles. In general, the benefit to be gained by lower temperature application may outweigh the slight loss of efficiency due to lower temperature application, resulting in lower overall cost of electricity. However, no extensive study has been done on the development of advanced sorbents for the lower temperature application. This program aimed at the development of regenerable sorbents suitable for desulfurization of coal-derived gases in the temperature range of 343° to $538^{\circ}C$ (650° to $1000^{\circ}F$) in a fluidized-bed reactor.

Fluidized-Bed Application

Although the fixed-bed approach using metal oxides has been shown to reduce the H_2S content of the cleaned gas to very low levels, the operation is not continuous, suffers from operational problems, and requires large-scale high temperature valves. To overcome these problems, US DOE has sponsored fluidized-bed as well as moving-bed hot gas desulfurization research in recent years. The fluidized-bed approach offers advantages over the moving- and fixed-bed reactors because of its ability to control the reactor temperature, particularly during the highly exothermic regeneration step.

The key characteristic of concern in the fluidized-bed application is maintenance of the physical integrity of the sorbent during the chemical transformations associated with sulfidation and regeneration. Testing appears to verify that excessive sorbent attrition results primarily from the changes in composition during chemical transformation and not from mechanical forces.^{27, 28} The extreme temperature and severe chemical conditions of air/steam regeneration are deleterious to many inorganic support materials and sorbent compounds. A sorbent suitable for fluidized-bed application must, therefore, have both good thermodynamic equilibrium and initial chemical reactivity in the range of 343°-538°C, as well as acceptable long-term physical and chemical durability with a reasonable cost of production.

TECHNICAL PROGRESS

Task 1. Information Required for the National Environmental Policy Acts (NEPA)

Within thirty (30) days after contract award, IGT prepared and submitted to GE-CRD a draft report which provided the environmental information described in the "Information Required for the National Environmental Policy Act (NEPA)", of RFP NO. DE-RP21-94MC31089. This report allowed the DOE to prepare NEPA documentation for the project. IGT submitted a final report after review and approval of the draft report by GE-CRD/DOE.

Task 2. Sorbent Preparation and Characterization

A systematic approach was used to prepare a large number of sorbent formulations for evaluation in fixed-bed, as well as thermogravimetric analyzer (TGA) reactors, to ultimately identify the most promising sorbent formulation for high pressure fluidized-bed application in the temperature range of 343° to 538°C. Desirable characteristics of hot gas cleanup sorbents include:

- Favorable sulfidation equilibrium
- High sorbent capacity
- Good reactivity toward H₂S
- Ease of regenerability
- Good attrition resistance

Thermodynamic Calculations

The initial principal criteria used for sorbent formulation was based on thermodynamic equilibrium to limit the choice of the active sorbent metals to those that can meet the stringent requirement of removing H_2S to below 20 ppmv. The thermodynamic H_2S equilibrium concentrations in simulated fuel gases (U-GAS and Texaco) for a number of potential metal oxides were calculated at elevated temperatures (i.e., 350° - 550° C) and

pressure (20 bar). The metal oxides considered for this analysis included copper, zinc, iron, nickel, tin, cobalt, molybdenum, manganese, and tungsten. The number of moles of the fuel gas and the solid oxides were selected to correspond to 50% sorbent conversion during sulfidation. Based on the available data, certain restrictions were imposed on the formation of a number of species to better simulate the actual environment.

The results of these analyses are presented in Figures 1 and 2 for the U-GAS and Texaco fuel gases, respectively, indicating that the calculated H_2S equilibrium is not significantly affected by the fuel gas composition. Furthermore, because of the lower temperature range (e.g., $350^{\circ}-550^{\circ}C$), a large number of metal oxides are capable of reducing the H_2S level of the fuel gases to below 20 ppmv for IGCC application.

Phase stability diagrams for reducing gas atmospheres (i.e., coal gases) and oxidizing gas atmospheres (i.e., regeneration gases) have been constructed by GE-CRD using algorithms that predict the stability of chemical species based on minimization of the Gibbs free energy of the system. The phase stability of metals under regeneration gases containing SO₂ and O₂ is important because spalling and pellet deterioration occurs more often as a result of metal sulfate formation. Figure 3 shows the stability of copper and molybdenum as a function of the log partial pressure of O₂ and SO₂. For gas compositions containing approximately 0.02 atm of O2 and 0.5 to 0.1 atm SO2 (typical of atmospheric regeneration gases in the moving-bed system), the thermodynamically stable phase of copper is copper sulfate, while the thermodynamically stable form of molybdenum is the oxide. For most pure oxides, including zinc oxide, the metal sulfate is the stable form under oxidizing gas conditions at temperatures around 500-700 °C, depending on SO2 and O2 concentrations. Of course, thermodynamic predictions do not take into account the rate of approach to equilibrium (i.e., kinetic rates) and hence experimental data are still needed to confirm the extent of formation of the predicted species. Nevertheless, thermodynamics allows the investigator to determine if formation of certain compounds is favored.

Based on thermodynamic equilibria and phase stability calculations, as well as available experimental data, four metals (\underline{Zn} , \underline{Fe} , \underline{Mn} , \underline{Cu}) were selected as primary desulfurization species, six other metals (\underline{Mo} , \underline{Ni} , \underline{Mn} , \underline{Fe} , \underline{Cu} , \underline{Cr}) as secondary species (i.e., additives) for desulfurization, and four metal species (\underline{Ti} , \underline{Zr} , \underline{Al} , \underline{Si}) were selected as supports and structure stabilizers.

Sorbent Preparation

Although because of the more favorable thermodynamic equilibria at lower temperature, the extent of desulfurization for all metal oxides improve with decreasing temperatures, the reactivity of the sorbents are greatly reduced because the kinetic mechanisms for sulfidation experience an Arrhenius-type decrease with decreasing temperature. Therefore, a highly reactive sorbent is needed for these lower temperature applications.

A total of <u>167</u> sorbent formulations were prepared in this program. Each of these sorbent formulations consisted of at least one metal oxide as the reactive component (toward H_2S), at least one support material, minor additives, and binders. Each sorbent formulation represents a unique set of preparation conditions that includes sorbent composition and the subsequent thermal treatment procedures. The general breakdown of the sorbent formulations prepared, with respect to the main reactive metal oxide, is given in Table 1.

TABLE 1. BREAKDOWN OF SORBENT FORMULATIONS BY MAIN REACTIVE COMPONENT

Reactive Metal Oxide	No. of Formulations Prepared
CuO	40
Fe ₂ O ₃	22
Mn_2O_3	10
ZnO	95

Formulation parameters considered in preparing the sorbents included nature of the reactive metal oxide component, overall sorbent composition, preparation technique, and thermal treatment (i.e., induration) conditions. For each support material several different molar ratios of metal to support material, generally in the range of 0.5 to 1, was examined to determine the composition that offered the best compromise between chemical reactivity and physical strength. The amounts of additional additives (i.e., binders, porosity enhancers, etc.) were also varied to achieve the desired sorbent composition. The effect of sorbent induration (thermal treatment) condition on the crush strength or attrition resistance of the sorbent was also determined by employing different temperatures in a practical range for the specified formulation.

Although high theoretical sorbent capacity and high initial reactivity are desired, these factors are not deemed crucial in developing a sorbent that will have acceptable long-term physical and chemical durability, as well as sufficient effective sulfur capacity. This latter parameter is equal to the theoretical sorbent capacity times the sorbent conversion at breakthrough. A sorbent with a lower theoretical capacity for sulfur, but much higher reactivity, may have equivalent overall effective capacity to a sorbent with higher theoretical capacity, but considerably lower reactivity. Therefore, if the higher reactivity of a sorbent with a lower theoretical capacity can be maintained or stabilized over a very large number of cycles, then the fresh sorbent makeup rate in an actual desulfurization process can be reduced, thereby reducing the overall cost of hot gas cleanup.

Given the above considerations, initially in this program efforts concentrated on preparing sorbents with higher levels of reactive metal oxide dispersion that have higher and stable reactivity as well as higher mechanical strength and durability. This was accomplished by the use of refractory supports/dispersants that are themselves highly resistant to sintering and deterioration. These low theoretical capacity/highly dispersed metal oxide sorbent formulations were considered to have a higher probability for maintaining stability at elevated temperatures over a large number of sulfidation-regeneration cycles. Following the preparation of low capacity sorbents, efforts were directed toward increasing the metal loading (concentration) of the sorbents to obtain higher theoretical sulfur capacity, while maintaining high mechanical strength.

Sorbent Screening

The initial selection of suitable sorbent formulations for testing was based on mechanical strength; only those sorbents having sufficient strength were evaluated. The sorbent formulations having comparable strength to that of UCI-4169 zinc titanate sorbent were subjected to testing in the fixed-bed reactor and/or thermogravimetric analyzer (TGA) to evaluate their reactivities and sulfur sorption capacities. This commercial zinc titanate sorbent which had been extensively tested in IGT's bench-scale high-pressure/high-temperature reactor as well as Enviropower pilot-scale desulfurization units, was used as a basis to evaluate granular sorbent performance in attrition tests. If the mechanical strength of a prepared sorbent was not at least comparable to that of the UCI zinc titanate, the sorbent formulation was modified, usually by changing the sorbent thermal treatment (i.e., induration) procedure, and the above evaluation step was repeated.

Early in this program, a single-hole attrition test unit was used to measure the relative resistance of sorbents to attrition. In a typical test, the air flow is set to generate sonic velocity, thus creating a strong shearing effect and turbulence to provide measurable attrition between sorbent particles. After a specified period of time the test is terminated and the change in the particle size distribution is measured. It must be emphasized that all sorbents selected for testing exhibited better attrition resistance capability than UCI-4169 zinc titanate sorbent, leading to the expectation of superior performance in a commercial fluidized-bed reactor.

An Instrom Universal Testing Instrument (Model 1011) was used to perform mechanical tests on some of the sorbents that have been prepared in the form of spherical pellets. In a typical test, a pellet is loaded onto a loading frame and a moving crosshead applies a load to the pellet at a commanded speed, in accordance with ASTM procedures. A calibrated transducer in the moving crosshead then measures the applied load at breakage. This load is known as the crush strength and is given in force divided by contact length (i.e., N/mm of pellet diameter). The average from 10 to 15 pellets is taken in this program as a representative value of the sorbent crush strength.

Preliminary sorbent testing included determination of the sulfidation reactivity and effective capacity of the sorbents prepared above to identify potential candidate sorbents for high pressure fluidized-bed application. Sorbent sulfidation-regeneration testing was carried out in a quartz fixed-bed reactor system at approximately one atmosphere pressure and temperatures of $350^{\circ}-550^{\circ}$ C using a simulated coal derived-fuel gas mixture (Table 2) at a space velocity of 2000 hr⁻¹. The average particle size of the sorbents tested is in the range of 180 to 425microns. Sulfided sorbents were regenerated using nitrogen- air mixtures at temperatures of $650^{\circ}-750^{\circ}$ C (800° C for Mn-based sorbents). The extent of

desulfurization was determined by analyzing the reactor exit gas for H₂S and SO₂ with a dedicated gas chromatograph.

<u>Component</u>	Composition, mol%		
H_2S	0.15-2		
H_2	10		
CO	20		
CO_2	10		
H_2O	10		
N_2	48-49.85		

Initial testing included two bulk copper-chromite sorbents (CuCr-1 and CuCr-2) and the UCI-4169 (also designated as UCI-4) sorbent which were tested at IGT and were shown (in earlier programs supported by the Illinois Clean Coal Institute and Enviropower, Inc.) to be highly efficient desulfurization sorbents at higher temperatures (550°-850°C). The CuCr-1 and CuCr-2 sorbents were previously prepared at IGT using a general method for synthesizing highly porous bulk mixed oxides. CuCr-1, a chromium-rich and CuCr-2, a copper-rich copper chromite, contain about 10 % and 25 % copper, respectively.

The H₂S breakthrough curves for the CuCr-1 and CuCr-2 sorbents are shown in Figures 4 and 5. Sorbent conversion is based on the assumption that the active sulfide phase produced during sulfidation is the one that is the most thermodynamically stable (i.e., Cu₂S or ZnS). Conversions greater than a value of one indicate the presence of other sulfided species. The desulfurization data for CuCr-1 and CuCr-2 at 750 °C, obtained in a previous program, were included in these figures to extend the temperature range for comparison purposes. The pre-breakthrough H₂S exit gas concentrations range from less than 1 to about 5 ppmv and are significantly lower than those predicted for the elemental Cu-H₂S equilibrium. These lower levels generally correspond to the copper oxide-H₂S equilibrium, suggesting that the copper in the compound oxide was not completely reduced to elemental copper by the fuel gas during the sulfidation stage. It is believed that this is probably due to either chemical and/or physical mechanisms, whereby compound formation, such as surface spinels or surface adsorption, may retard the complete reduction to metallic copper.

The rate of sulfidation of sorbents in the form of compounds, such as the copper chromite spinels used here, is generally expected to be lower compared to the rate of sulfidation of pure metal oxides. However, the sharp rise in the H_2S breakthrough curves and the high sorbent conversions observed in these tests indicate that the overall reaction rate involving copper chromite compound is sufficiently high at temperatures above $450^{\circ}C$.

The H_2S pre-breakthrough levels for the higher theoretical sulfur capacity UCI-4169 sorbent (Figure 6), ranging from about 10-20 ppmv, are considerably higher than those

obtained with the copper chromite sorbents. The gradually increasing H_2S prebreakthrough levels and very low sorbent conversions indicate a much lower reactivity compared to the lower capacity sorbents.

The maximum effective conversion as a function of temperature for the CuCr-1, CuCr-2 and UCI-4169 sorbents is summarized in Figure 7. The effective maximum conversion of the CuCr-2 sorbent is lower than that of the CuCr-1 sorbent throughout the entire temperature range studied, clearly indicating the beneficial effects of dispersion on enhancing reactivity. The effective conversion of the zinc titanate sorbent is lower than that of the copper chromite sorbents and decreases with decreasing temperature at about the same rate as that of the CuCr-2 sorbent.

Another indication of the higher reactivity of the highly dispersed copper chromite sorbent is shown in Figure 8, which shows the effect of temperature on the maximum space velocity. At 500°C, the CuCr-1 sorbent is capable of reducing the H_2S content of the fuel gas to below 20 ppmv at space velocities as high as 15,000 hr⁻¹, which is significantly higher than the maximum space velocity for the CuCr-2 and UCI-4169 sorbents.

Figure 9, which shows the effect of temperature on the maximum effective sulfur capacity, indicates that, although the chromium-rich copper chromite sorbent has a much lower theoretical sulfur capacity than that of the CuCr-2 or UCI-4169 zinc titanate sorbents, it has comparable effective sulfur capacities at temperatures around 450°C. Neither of the copper chromite sorbents appeared to have sufficient mechanical durability for fluidizedbed application. Therefore, no further testing of these sorbents was undertaken.

Based on the results of the above three sorbents, a number of well dispersed copper-based sorbents were prepared and their sulfidation reactivities were evaluated in a packed-bed reactor. These sorbent formulations generally had low sulfur capacity (about 2-3%), but they all have good mechanical strength. The regenerability of those sorbent formulations that achieved high levels of conversion during the first cycle were each evaluated in a $1\frac{1}{2}$ cycle test.

Among the initial sorbent formulations prepared in this program, the IGTSS-1 appeared to have the highest reactivity toward H₂S at 350°C. Therefore, a series of 15-cycle test was conducted with the IGTSS-1 at 350°C. As indicated in Figure 10, high levels of sorbent conversions were obtained at 350°C in the first 10 cycles for sorbent IGTSS-1. The H₂S breakthrough profiles for this sorbent (Figure 11) also indicate very high levels of desulfurization (<10 ppmv H₂S). The very sharp rise in the H₂S breakthrough curves at high levels of sorbent utilization indicates that the reactivity of this sorbent towards H₂S is very high. However, reactivity of the sorbent significantly decreased after the 10th cycle. An examination of the sorbent after the 15th cycle revealed that it had disintegrated which may explain the rapid decline in the sorbent reactivity.

Based on the performance of IGTSS-1 during the initial 10 cycles, a stronger version of this sorbent, IGTSS-11, was tested. The sorbent conversions are relatively high and

constant over the 13 cycles tested at 450° C, as shown in Figure 12. The H₂S breakthrough curves (Figure 13) indicate that this sorbent can reduce H₂S to below 10 ppmv. No loss of strength was observed after 13 cycles.

The results of 16 sulfidation/regeneration cycles conducted with IGTSS-6 are shown in Figures 14 and 15, indicating that the reactivity of this sorbent did not decrease during the 16 cycles tested. This series of tests was conducted at 350 °C, at a space velocity of 2000 hr⁻¹. In cycle 16, the sorbent was exposed to a reducing gas for an extended period before H_2S was added to fuel gas. As shown in Figures 14 and 15, the results indicate that possible sorbent pre-reduction, does not adversely affect the performance of the sorbent. The high level of fractional conversions obtained in this series of tests indicate that this sorbent is highly reactive toward H_2S and that the high level of reactivity of the results is maintained during the first 16 cycles.

Following the favorable results of the low capacity sorbents, attempts were made to improve the sulfur capacity of the sorbents, using the same sorbent preparation technique. However, most of the sorbent formulations prepared with this approach, lacked sufficient strength and/or reactivity toward hydrogen sulfide. Two sorbent formulations, namely, IGTSS-5 and IGTSS-55 appeared to have sufficient machanical strength, sulfur capacity, and reactivity to be evaluated in the packed-bed reactor. The results of packed bed tests conducted with these sorbents are shown in Figure 16. IGTSS-5, which was tested at 450°C, showed a marked reduction in conversion after the first cycle, but a more stable performance in the next five cycles. Although IGTSS-55 did not exhibit sufficient reactivity at 450°C, a conversion of about 35% was achieved with this sorbent after 3 cycles at a temperature of 538°C.

Because none of the sorbents prepared by the initial sorbent preparation technique exhibited acceptable characteristics in all the required attributes (i.e., mechanical strength, sulfur reactivity, regenerability, and long term durability), further testing of these sorbents was not pursued.

As indicated earlier, higher level of dispersion generally results in lower capacity and higher reactivity, while higher concentrations of the active compounds generally lead to higher theoretical sorbent capacity and lower reactivity. The key factors in the development of suitable sorbents are the stability of the sorbents through the cyclic process and the effective sulfur capacity of the sorbent (i.e., theoretical capacity x sorbent conversion). In order to achieve sorbent stability at the highest possible effective sorbent capacity and mechanical strength. This was accomplished by extending the application of a pelletization technique previously developed for the formulation of spherical pellets (dia.=3-5 mm)³⁴ to the preparation of highly attrition resistant granular (dia. = 100 to 850 μ m) sorbents. This sorbent manufacturing technique has been applied to prepare over 100 formulations of copper-, iron-, manganese-, and zinc-based sorbents suitable for fluidized-bed applications at lower temperatures, i.e., T ≤ 550°C. A number of these formulations had mechanical strength equal to or better than that of the UCI-4169 zinc

titanate sorbent. In the case of sorbents prepared in the form of larger spherical pellts, such as IGTSS-179 and IGTSS-057, for example, crush strength values, as determined according to the procedure described above, were 43.5 and 22.5 N/mm, respectively. Table 3 lists crush strength values reported by other investigators and serves as a basis for comparison with one of the sorbents studied in this program.

Reference No./Sorbent	Crush Strength Reported,
	N/mm
35	17
36	12 - 32
37	36
38	73
39	23.8
IGTSS-179 (this study)	43.5

 Table 3. CRUSH STRENGTH COMPARISONS

All sorbents that meet minimum mechanical strength requirement were evaluated for H_2S removal efficiency and effective sulfur capacity. Rigorous testing was undertaken to determine the sulfidation reactivity and effective sulfur capacity of prepared sorbents to identify potential candidates for further evaluation in the bench-scale high pressure fluidized-bed reactor unit in Task 4.

During this study, it was determined that, because of the high attrition resistance of the sorbents prepared, most of these sorbents (specially zinc-based sorbents) required an "activation step" to improve their reactivities at lower temperatures. A series of tests was conducted in the thermogravimetric analyzer reactor (TGA) to determine the optimum activation method. This finding is illustrated in Figure 17 for a zinc-based sorbent, after applying different activation methods. The results indicate that both sorbent reactivity and sulfur capacity increase substantially upon activation by Method C.

These results appear to suggest that the sorbent activation technique developed may be a major parameter in the development of attrition resistant sorbents for lower temperature (i.e., $T \le 550^{\circ}C$) applications. As reported in Table 1, sorbent development work in this projest has focused on zinc-based sorbents to a large extent. A comparison of the performance of several sorbent formulations in the TGA reactor unit at 450°C, following activation, are presented in Figure 18. The preliminary sorbent evaluation was used to identify promising sorbents for further testing in the fixed-bed reactor. Generally, those sorbents achieving a weight gain greater than 3% were further tested in the packed bed reactor. The relevant physical properties of the sorbent formulations exhibiting acceptable sulfur capacity in the packed bed tests are given in Table 4. The UCI-4169 sorbent was included for the purpose of comparison. With the exception of IGTSS-057 and IGTSS-057 and the Cu-based IGTSS-179 have the highest surface area and exhibited

very high reactivities toward H_2S and did not require an activation step, as will be discussed later.

Sorbent	Main	Hg Bulk	Apparent (Skeletal)	Porosity	Total Pore Surface
Designation	Reactive	Density ρ_b ,	Density, ρ_a (g/cm ³)	$\left(\% ight)^{*}$	Area (m^2/g)
	Metal	(g/cm^3)			
IGTSS-057	Mn	1.6170	4.6936	65.55	9.2085
IGTSS-122	Zn	2.3783	4.5425	47.64	3.9135
IGTSS-135	Zn	1.4825	2.6864	44.81	0.3457
IGTSS-139	Zn	1.7841	4.6872	61.94	1.6040
IGTSS-179	Cu	3.0573	4.1724	26.73	5.2273
IGTSS-189	Zn	2.5930	4.9111	47.20	2.0690
IGTSS-314B	Zn	2.2658	4.4787	49.42	3.3383
IGTSS-325A	Zn	1.9319	4.5468	57.51	2.5935
UCI-4169	Zn	1.3795	3.1409	56.08	0.7205

Table 4. PHYSICAL CHARACTERISTICS OF SELECTED SORBENTS (FRESH)

Calculated as $(1 - \rho_b/\rho_a)$ *100, or equivalently as ρ_b *(Total Intrusion Volume)*100

The results of three cycles of packed bed testing with the baseline UCI-4169 sorbent at 450°C are presented in Figure 19, indicating that this sorbent could achieve a sulfur loading in the range of 5-6 % at 450°C. The sulfur loading of IGTSS-122 at 450°C, after activation, is presented in Figure 20, reaching a level of 6%. However, the sulfur loading of the sorbent prior to activation was less than 1%. The IGTSS-135, IGTSS-139, and IGTSS-189 achieved sulfur loadings of less than 4%, after activation, indicating lower reactivities compared to the UCI-4169 sorbent.

The sulfur loadings for the IGTSS-314B in four (4) successive cycles, without activation, are shown in Figure 21, indicating that the reactivity of this sorbent gradually improved in the cyclic process. The sulfur loading of this sorbent during the first cycle is more than twice that of IGTSS-122 suggesting that this sorbent is more reactive than IGTSS-122 sorbent. Although the 6% sulfur loading of IGTSS-314B is similar to the UCI-4169, the very low level of H_2S pre-breakthrough and the sharp breakthrough curve are indicative of higher reactivity of IGTSS-314B sorbent. The results obtained with the IGTSS-325A sorbent in four successive cycles are presented in Figure 22, indicating that a much higher

sulfur loading of 10-12% was achieved with this sorbent, which is twice the sorbent loading achieved with the baseline UCI-4169 sorbent.

A manganese-based, high sulfur capacity sorbent, IGTSS-057, achieved a total prebreakthrough time of about six (6) hours in the second sulfidation cycle at 450°C, as shown in Figure 23. This time corresponds to a total sorbent conversion of nearly 47%, at a H₂S breakthrough level of 20 ppmv, and to an effective sulfur capacity of approximately 20 g S/100 g sorbent. This increase in capacity over that seen in the first cycle is likely due to structural changes during sulfidation-regeneration, leading to improved sorbent performance. Also, as shown in Figure 23, IGTSS-057 sorbent, in its fresh condition, performed comparably well at 350°C.

To reduce the cycle time during testing of IGTSS-057 sorbent, the sulfidation gas space velocity was increased to 6000 hr^{-1} . The results from several cycles are reported in Figure 24. As indicated in this figure, IGTSS-057 performed consistently well even at this higher sulfidation gas space velocity, achieving effective sulfur capacities ranging from 10 to 12 g S/100 g sorbent. The regeneration tests were carried out at 800°C.

The IGTSS-179, one of a number of copper-based sorbents recently developed at IGT in an on-going research program sponsored by the Illinois Clean Coal Institute (ICCI), appears to hold significant promise for fuel gas desulfurization in the temperatures range of 350° to 550°C. As shown in Figure 25, limited multi-cycle testing in the fixed-bed reactor at 450°C indicated that this sorbent has excellent H_2S removal efficiency and an effective sulfur capacity approximating 7 grams of sulfur per 100 grams of sorbent. This effective sulfur capacity corresponds to a sorbent conversion of 70% at breakthrough. Therefore, given the high mechanical strength of this sorbent, this significant conversion is indicative of its high reactivity at 450°C. It must also be pointed out that despite its significantly high crush strength (see Table 4), IGTSS-179 copper-based sorbent did not require an activation step to enhance its reactivity at the lower temperature. Furthermore, the sulfidation performance of IGTSS-179 sorbent at 350°C is essentially comparable to that at 450°C.

Based on the results of the packed bed tests, the IGTSS-057, IGTSS-179, IGTSS-314B, and IGTSS-325A were selected for further evaluation. The attrition resistance of the selected sorbent were determined by the ASTM D5757-95 method.

The standard ASTM D5757–95 is a test method for the determination of the relative attrition characteristics of powdered catalysts by air jets. This test method is capable of providing reliable information concerning the ability of a powdered material to resist particle size reduction during use in a fluidized environment. Strictly speaking, this method is applicable to spherically or irregularly shaped particles ranging in size between 10 and 180 μ m and having skeletal densities between 2.4 and 3.0 g/cm.³ Nevertheless, the information it provides can be particularly valuable for research and development efforts in the area of sorbent development for fluidized-bed as well as transport reactor applications where sorbent durability during mutli-cycling is essential.

During this test a representative sample of dry powder (approximately 50 grams) is subjected to attrition by means of three high velocity jets of air. The fines generated are continuously removed from the attrition zone by elutriation into a fines collection assembly. The percent attrition loss after five (5) hours is known as the Air Jet Index (AJI) and is calculated from the elutriated fines to give a relative estimate of the attrition resistance of the powdered catalyst as may be observed in commercial use.

The apparatus for the air jet attrition system consists of an attriting tube, a settling chamber, a fines collection assembly, and a circular orifice plate containing 3 holes and attached to the bottom of the vertical attriting tube within an air delivery manifold. The overall arrangement of the attrition unit and dimensions, as arranged at IGT, are as indicated on the schematic diagram shown in Figure 26.

During a typical test, the system is first reassembled without the fines collection assembly. Air supply is turned on and the flow adjusted to 10.00 L/min at standard temperature and pressure (273.15 K and 101.325 kPa), resulting in a back pressure in the range of 179 to 203 kPa. This is an indication that the air jet nozzles are clean and that there are no leaks in the apparatus connections.

Two fines collection assemblies are then prepared and weighed. With the air flowing at 10 L/min and the fines collection assembly off, 50 g of the material to be tested is charged through the top of the settling chamber. The first fines collection assembly is then quickly secured to the apparatus and the timekeeping started. After exactly 1 hour from the start, the first fines collection assembly is replaced with the second one. After exactly 5 hours from the start, the second fines collection assembly is removed, the attrition unit disassembled, and the sample from the attriting tube and settling chamber recovered and weighed.

The results of an inter-laboratory study conducted by Akzo Nobel Research Facility (Pasadena, Texas), on the measurement of AJI of a fresh FCC catalyst in 3 separate tests conducted at 4 different laboratories are presented in Figure 27, to demonstrate the expected variation in the values of AJI of a selected material. These results indicate an average five-hour loss due to attrition of 20.36% with a standard deviation of 3.6%.

To verify the performance of IGT's attrition unit four different materials were evaluated for attrition resistance by both IGT and Akzo Nobel Research Facility. These materials included FCC catalyst, dolomite 245, limestone 246, and UCI-4169. The results obtained with these four materials at IGT and Akzo, are presented in Figure 28, indicating that the results obtained using the IGT attrition unit are well within the experimental error of the experiment.

Following the verification of IGT's test unit and experimental procedure, the attrition characteristics of the selected sorbents were determined. The results of the ASTM attrition tests are shown in Figure 29, indicating that the expected attrition loss of the

zinc-based sorbents is about four times higher than the FCC catalyst. The attrition losses of the IGTSS-057 and IGTSS-179 were 39% and 10%, respectively, corresponding to about 1/2 and 1/7 of the commercial zinc titanate sorbent evaluated.

Given the results obtained in this task, two zinc-based sorbents (IGTSS-314B, IGTSS-325A), one manganese-based sorbent (IGTSS-057), and one copper-based sorbent (IGTSS-179) were selected for the bench-scale fluidized-bed tests in Task 4 described below.

Task 3. Provisions of the Bench-Scale Test Unit.

An existing state-of-the-art bench-scale high-pressure/high-temperature batch fluidizedbed/fixed-bed reactor (HPTR) was used to carry out bench-scale testing in Task 4. A schematic diagram of the test unit is shown in Figure 30. The test unit includes simulated hot coal-derived gas feed systems, an absorption/regeneration reactor, and associated process instrumentation and control devices.

This is a flexible reactor system that is capable of operating either in a fluidized-bed reactor mode or in a fixed-bed reactor mode. This unit can be operated as a 2-inch or 3-inch batch fluidized-bed/fixed-bed reactor at conditions that are expected in the hot gas desulfurization process. The design of the reactor is based on a double-shell balanced pressure system. All the H_2S wetted parts of the reactor are constructed of quartz or ceramic material to prevent corrosion and loss of sulfur.

The gas feed system is capable of delivering simulated gas mixtures containing CO, CO_2 , H_2 , H_2O , H_2S , N_2 , and CH_4 with different compositions representing various gasifiers. The gas feed system has been set up to deliver the desired simulated fuel gas compositions through six independently controlled gas streams, as well as a liquid (water) stream to deliver gas mixtures with widely different compositions.

Some important design aspects of this system are as follows:

- The HPTR vessel is a pressure-balanced system. A nitrogen purge prevents the H₂S and other corrosive gases from contacting metal surfaces such as the pressure-retaining vessel wall, reactor heater assembly, and insulation.
- Reactor materials that contact H_2S containing gases are constructed of quartz or ceramic material to prevent corrosion and loss of H_2S . This is crucial to accurate measurement of the sorbent performance.
- The exit gas is sampled in the disengaging zone of the fluidized-bed reactor using a ceramic probe.
- Feed gases (dry gas and the steam feed) are preheated within the reaction vessel. H₂S and other corrosive gases are fed directly to the bottom of the quartz HPTR

where it mixes with the wet hot gases before entering the fluidized-bed/fixed-bed reactor.

- The HPTR unit is internally heated using a diffusion-type heater divided into four temperature-control zones.
- Thermocouples used to measure heater, fluidized-bed/fixed-bed (five thermocouples) and preheat zone temperatures are protected by quartz/ceramic thermowells.

The pressure-retaining vessel houses the 2- or 3-inch O.D. quartz reactor insert, the reactor heater assembly, metal liners, ceramic tubes, and thermowells. Dry feed gases enter at the bottom of the reactor vessel through a distribution ring. De-ionized water is pumped to the bottom of the reactor vessel and into a stainless steel coil wrapped around the lower section of the outer liner. The water is vaporized in the coil and superheated. The steam produced mixes with the dry feed gases at the exit of the coil in the bottom of the reactor vessel. The annular space between the two metal liners is used as an annular heat exchanger to preheat the feed gases and super heat the steam. The hydrogen sulfide and other corrosive gases enter at the bottom of the reactor vessel and flow up through a small quartz tube.

The bulk of the exit gas leaves the reactor top through a ceramic tube. A separate gas stream that is used for gas sampling leaves through a second, smaller ceramic tube. A ceramic thermowell, extending down from the top of the reactor vessel, contains five thermocouples to monitor the fluidized-bed/fixed-bed temperatures at various levels in the reactor and the exit gas temperature.

A quartz reactor insert is used to contain the sorbent. The quartz insert consists of a flange, disengaging section, reactor bed, gas inlet sections, and a fritted ceramic gas distribution plate. The quartz reactor insert was fabricated with a flange at the top of the reactor for ease of removal and replacement.

The exit gas is sampled in the disengaging zone of the quartz reactor insert using a ceramic probe. The sampling gas stream is cooled immediately after leaving the reactor. The gas is sent directly to a dual-column gas chromatograph for analysis. The composition of the reactor exit gas is measured with a dual column gas chromatograph that is currently equipped with a flame photometric detector (FPD), a thermal conductivity detector (TCD) and auto-samplers. The FPD is used to detect low levels (0-100 ppm) of H_2S and COS while the TCD can be used to detect the sulfur dioxide (SO₂) in the exit gas.

Task 4. Bench-Scale Testing

As indicated earlier in this report, based on the results obtained in Task 2, two zinc-based sorbents (IGTSS-314B and IGTSS-325A), one manganese-based sorbent (IGTSS-057), and one copper-based sorbent (IGTSS-179) were selected for the bench-scale fluidized-

bed tests in this task. The operating conditions for evaluation of the selected sorbents are given in Table 5. The simulated coal gas composition used in these tests was similar to that reported in Table 2. The H₂S content of the feed gas in all the tests conducted in this task was 1500 ppmv. The sulfided sorbents were regenerated with a N_2/O_2 mixture containing 2-3% oxygen.

Table 5. OPERATING CONDITIONS FOR EVALUATION OF THE SORBENTS

Parameter	Condition		
Sorbent Formulations	4		
Mode of Operation	Bubbling fluidized bed		
Sulfidation Temperature	450°C		
Regeneration Temperature	650°C (850°C for IGTSS-057)		
Pressure	10 atm		
Particle Size	180-425 microns		
Bed Height	5 cm		
L/D ratio	1		
Superficial Gas Velocity	20 cm/s		

It should be noted that the operating condition used in this task corresponds to a very shallow bubbling fluidized bed with a very short gas residence time of about 0.25 seconds. Therefore, the sulfur loading obtained with the sorbents in these tests in much lower than the expected loadings in commercial reactors, where the fluidized-bed height and gas residence time are significantly higher. To provide a basis for comparison of the sorbent, prior to testing of the four selected sorbents, one sulfidation test was conducted with the UCI-4169 zinc titanate sorbent at the same operation conditions.

The H_2S breakthrough curve for the UCI-4169 is presented in Figure 31, indicating a sulfur loading of about 0.5% at the test condition. The H_2S breakthrough curve for the two zinc-based sorbents developed in this program (i.e., IGTSS-314B and IGTSS-325A) are presented in Figures 32 and 33, indicating that their effective sulfur loading is generally similar to the UCI-4169 sorbent.

Significantly higher sulfur loading was achieved with the IGTSS-057 sorbent, as shown in Figure 34. Although, the manganese-based IGTSS-057 sorbent achieved a very high sulfur loading, the relatively high H_2S pre-breakthrough concentration, and a much higher temperature of 850°C required for successful regeneration of this sorbent are undesirable characteristics of this sorbent.

A sulfur loading of 4-6% was achieved with the copper-based IGTSS-179 sorbents in cycles 2 through 5, as shown in Figure 35. Fluidization of this sorbent in the reducing environment at elevated temperature (i.e., above 450° C) proved to be difficult because of relatively strong attractive interparticle forces, leading to defluidization of the bed. To improve the fluidization behavior of the IGTSS-179 sorbent, this sorbent was mixed with the IGTSS-135 (which has been shown to have very low reactivity toward H₂S). As

shown in Figure 35, the reactivity of the IGTSS-179 sorbent appears to be improving with the cyclic process, and the H_2S pre-breakthrough concentration is well below 20 ppmv. The high reactivity of the IGTSS-179 sorbent, coupled with the very high attrition resistance, indicates that the IGTSS-179 is the best sorbent formulation developed in this program.

Compared to the UCI-4169 baseline sorbent, the IGTSS-179 is at least seven times more reactive, and seven times more attrition resistant. Therefore, further evaluation of this sorbent in the optional task 8 is recommended to determine the chemical stability and physical durability of the sorbent in a "life-Cycle" Test.

Task 5. Sorbent Cost Assessment

To assess the fluidized-bed sorbent cost, several different commercial sorbent manufacturers were contacted, of which, the United Catalyst Inc., and Contract Materials Processing, Inc., were interested to discuss possible future manufacturing of the IGTSS-179 sorbent. According to these sorbent manufacturers, given the nature of the metal oxides and the support materials in the IGTSS-179 sorbent, the sorbent cost is expected to be similar to that of the commercial zinc titanate sorbents.

Task 6. Topical Report

This draft topical report which covers tasks 1 through 5 is being submitted to GE-CRD and DOE/FETC to provide the information necessary to decide whether to opt for long-term testing. If the decision is made in favor of Task 8, then the IGTSS-179 sorbent shall be tested for long-term (at least 100 cycles) durability and chemical reactivity in the bench-scale unit. The topical report will be reviewed by GE-CRD and DOE. IGT will revise the report to accommodate the recommended changes requested (if any) by GE-CRD and DOE. If the option is not exercised, the topical report will be submitted as the final report for this project.

Task 7. Market Plan

If the decision is made in favor of Task 8, IGT shall develop a detailed marketing plan including, but not limited to, commercialization of the product, scale-up considerations for preparation of the formulations of the fluidized-bed sorbent on a commercial scale, teaming/licensing approach developed, and benefit to IGCC technologies.

Task 8. Long-Term Testing (Optional)

If the decision is made in favor of Task 8, then the IGTSS-179 sorbent will be tested for long-term (at least 100 cycles) durability and chemical reactivity in the bench-scale unit.

IGT shall thoroughly analyze the data collected under this Task l. The analysis shall include the characterization of the sulfided and regenerated sorbents to determine the changes in physical and chemical properties that have occurred as a result of cyclic testing. Characterization results of the tested sorbents shall be compared to those of the fresh sorbents. The sorbents' performance measurements shall include, but not be limited to, the ppm level of hydrogen sulfide in the cleaned gas, sorbent utilization, and sorbent capacity.

A test plan will be prepared and submitted to GE-CRD/DOE for approval before initiating the tests. The test plan will include detailed experimental procedure, operating conditions during absorption and regeneration including temperature, pressure, superficial gas velocity, sorbent particle size, bed height, simulated gas composition, steam content, and any additional information needed to completely define the test plan. The test plan will also define the number of cycles with each sorbent, number of sorbents to be tested, and the experimental data that will be collected during the experiments.

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Figure 1. H₂S EQUILIBRIUM CONCENTRATION IN FUEL GAS WITH VARIOUS OXIDES (U-GAS)



Figure 2. H₂S EQUILIBRIUM CONCENTRATION IN FUEL GAS WITH VARIOUS OXIDES (TEXACO)



FIGURE 3. PHASE STABILITY DIAGRAMS FOR CU-S-O (TOP) AND MO-S-O (BOTTOM) SYSTEMS



Figure 4. H₂S BREAKTHROUGH CURVES FOR CuCr-1



Figure 5. H₂S BREAKTHROUGH CURVES FOR CuCr-2



Figure 6. H₂S BREAKTHROUGH CURVES FOR UCI-4169 ZINC TITANATE



Figure 7. EFFECT OF TEMPERATURE ON EFFECTIVE CONVERSION



Figure 8. EFFECT OF TEMPERATURE ON MAXIMUM SPACE VELOCITY



Figure 9. EFFECT OF TEMPERATURE ON MAXIMUM EFFECTIVE SULFUR CAPACITY



Figure 10. CONVERSIONS FOR SORBENT IGTSS-1 AT 350°C



Figure 11. H₂S BREAKTHROUGH CURVES FOR SORBENT IGTSS-1 AT 350°C



Figure 12. CONVERSIONS FOR SORBENT IGTSS-11 AT 450°C



Figure 13. H₂S BREAKTHROUGH CURVES FOR SORBENT IGTSS-11 AT $450^{\rm o}{\rm C}$



Figure 14. H2S BREAKTHROUGH CURVES FOR IGTSS-6 SORBENT AT 350°C



Figure 15. FRACTIONAL CONVERSION OF IGTSS-6 SORBENT IN SUCCES-SIVE CYCLES AT 350°C



Figure 16. CONVERSIONS FOR SORBENTS WITH HIGHER THEORETICAL SULFUR CAPACITIES



Figure 17. EFFECT OF FRESH SORBENT ACTIVATION METHOD ON SUL-FIDATION PERFORMANCE OF IGTSS-122 SORBENT AT 450°C.



Figure 18. COMPARISON OF SULFIDATION PERFORMANCE OF SEVERAL ZINC-BASED SORBENTS AT 450^oC IN TGA UNIT



Figure 19. H₂S BREAKTHROUGH CURVES FOR THE BASELINE UCI-4169 SORBENT



Figure 20. H2S BREAKTHROUGH CURVES FOR THE IGTSS-122 SORBENT



Figure 21. H2S BREAKTHROUGH CURVES FOR THE IGTSS-314B SORBENT



Figure 22. H2S BREAKTHROUGH CURVES FOR THE IGTSS-325A SORBENT



Figure 23. COMPARISON OF SULFIDATION PERFORMANCE OF IGTSS-057 SORBENT AT 450°C AND 350°C



Figure 24. H2S BREAKTHROUGH CURVES FOR THE IGTSS-057 SORBENT



Figure 25. H2S BREAKTHROUGH CURVES FOR THE IGTSS-179 SORBENT



Figure 26. AIR JET ATTRITION APPARATUS



Figure 27. COMPARISON OF AJI RESULTS OF FCC CATALYST AT DIFFER-ENT FACILITIES



Figure 28. COMPARISON OF AJI RESULTS OF DIFFERENT MATERIALS AT IGT AND AKZO



Figure 29. COMPARISON OF AJI RESULTS OF DIFFERENT SORBENTS



Figure 30. SCHEMATIC DIAGRAM OF THE HIGH-PRESSURE/HIGH-TEMPERATURE REACTOR (HPTR) UNIT



Figure 31. H₂S BREAKTHROUGH CURVES FOR THE UCI-4169 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR



Figure 32. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-314B SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR



Figure 33. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-325A SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR



Figure 34. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-057 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR



Figure 35. H₂S BREAKTHROUGH CURVES FOR THE IGTSS-179 SORBENT IN HIGH PRESSURE BENCH-SCALE FLUIDIZED BED REACTOR