DE-AC21-94MC31089--03

#3

ADVANCED SORBENT DEVELOPMENT

Topical Report

Prepared by

Javad Abbasian

Institute of Gas Technology
1700 South Mt. Prospect Rd.
Des Plaines, Illinois 60018

for

National Energy Technology Laboratory
P. O. Box 880
3610 Collins Ferry Rd.
Morgantown, West Virginia 26507-0880
CONTRACT No. DE-AC21-94MC31089

IGT Project No. 65094

January 2000

DISCLAIMER

DISCLAIMER

Executive Summary

This report is submitted to the United States Department of Energy in partial fulfillment of the contractual requirements for the project titled, 'Advanced Sorbent Development', under agreement number DE-AC21-94MC31089.

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 (H_2S) from coal-derived fuel gases in a fluidized-bed reactor.

The goal was to develop sorbents that are capable of reducing the H2S 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.

This topical report focuses on the investigation directed toward preparation of zinc-based sorbents using the sol-gel approach that has been shown to require only a moderate temperature for calcination, while resulting in significantly more attrition-resistant sorbents. The sorbents prepared in this part of the investigation and the results from their evaluation in packed-bed and fluidized-bed reactors are described in this report.

Eleven (11) sorbent formulations were prepared using a sol-gel approach. The nominal zinc oxide content of the sorbents prepared during the reporting period ranged from 10 to 40%. The calcination temperature ranged from 450 to 725°C. Granules from each of the above sorbents were then produced in the desired size range of 425-600 μm and 45-180 μm for testing in the packed-bed and fluidized-bed reactors, respectively. The granular sorbents were then evaluated for their H2S removal efficiency and effective sulfur capacity (i.e., H2S concentration prior to breakthrough and the total amount of sulfur loaded at breakthrough time). Sulfidation tests was carried out in the temperature range of 350 to 550°C and a gas space velocity of 2000 hr-1 for packed-bed and 5000 hr-1 for fluid-bed tests. Reacted sorbent regeneration was investigated in the temperature range of 480 to 650°C. Fresh as well as reacted samples from selected sorbents were subjected to chemical analysis and physical characterization, including BET surface area, porosity and pore size distribution, particle density, and XRD analysis. Four selected sorbent formulations (i.e., IGTSS-353, -354, -357, and -359) were also evaluated for their attrition resistance properties in accordance with the ASTM D5757-95 method. Their performance was compared against those of selected sorbents previously developed in this program and that of a leading candidate zinc titanate sorbent (i.e., EX-SO3) for the Piñon Pine Demonstration Project.

The results of ASTM D5757-95 attrition tests indicate that the new sol-gel derived zinc-based sorbents achieved attrition losses that are about 1/2 that of the FCC material, 1/10 those of the conventional bulk zinc-based sorbents, and 1/3 of the leading EX-SO3 sorbent.

A modified Sol-Gel technique has been used to produce ZnO-based sorbents with unique properties that are unattainable by conventional sorbent preparation methods. This method

eliminates the need for excessively high thermal treatment temperatures to impart the required physical strength and has made possible the achievement of the challenging combination of high reactivity (desirable pore size distribution and high surface area), high attrition resistance, and regenerability at lower temperature.

The results of the sulfidation/regeneration tests conducted with these new sorbents indicate that the new class of zinc-based sorbents produced by a modified sol-gel technique are capable of reducing the H_2S content of the coal gas to about 1-2 ppmv level in the lower temperature range for IGCC applications. The effective sulfur capacity of the sorbent ranged from about 6 to 8% in the temperature range of 350 to 550°C. The results also indicate that the effective sulfur capacity of the sorbent is maintained during the cyclic process. Complete regeneration of the sorbents was achieved in the temperature range of 538 to 593°C.

Based on the results obtained in this program, the IGTSS-354 sorbent was selected for further investigation. A small batch of the IGTSS-354 sorbent is being prepared by a commercial sorbent manufacturer for evaluation in the high-pressure bench-scale fluidized-bed reactor to demonstrate the suitability of this sorbent for coal gas desulfurization in the transport reactor at Piñon Pine.

Table of Contents

List of Tables

List of Figures

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 (H_2S) from coal-derived fuel gases in a fluidized-bed reactor.

The goal was to develop sorbents that are capable of reducing the H2S 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.

INTRODUCTION

Zinc-based sorbents have emerged as the leading candidates for the removal of H2S from coal-derived fuel gases at high temperatures and pressures in integrated gasification combined cycle (IGCC) processes. These sorbents have resulted from numerous investigations, mainly at temperatures in the range of 500 to 650°C. Significant advances have been made; however, for desulfurization in fluid-bed and/or transport reactors, there are still some concerns regarding their ability to resist attrition due to the mechanical forces as well as the chemical transformations they undergo in such applications. These sorbents have generally been prepared in bulk form using conventional techniques, such as solid oxide mixing or co-precipitation followed by extrusion, granulation, or spray drying, with physical strength imparted to them through high temperature treatment, commonly referred to as calcination or induration. Due to sintering effects, the desirable sorbent characteristics, such as surface area and porosity, are diminished with increasing calcination temperature, adversely affecting the reactivity of the sorbent. Because the reactivity of a sorbent undergoes an Arrhenius-type decrease with decreasing temperature, this trade-off between sorbent mechanical strength and physico-chemical properties represents more of a concern in the moderate temperature range of 343 to 538 °C that is currently of industrial interest.

Over 100 zinc-based sorbents have been prepared and evaluated in this program in an effort to develop attrition-resistant sorbents that are sufficiently reactive in the moderate temperature range. Figures 1-3 report the results obtained with 2 selected zinc-based sorbents, as well as those obtained with a commercial zinc titanate sorbent manufactured by United Catalyst, Inc. (UCI-4169). Although these sorbents exhibited acceptable reactivities towards H2S, their attrition resistance properties were not sufficiently high to meet stringent criteria that have been set for the transport reactor in the Piñon Pine Clean Coal Demonstration Project. Attrition jet indexes (AJI), as determined by the ASTM D 5757-95 method, were determined to be in the range of 75 to 85% for these zinc-based sorbents.

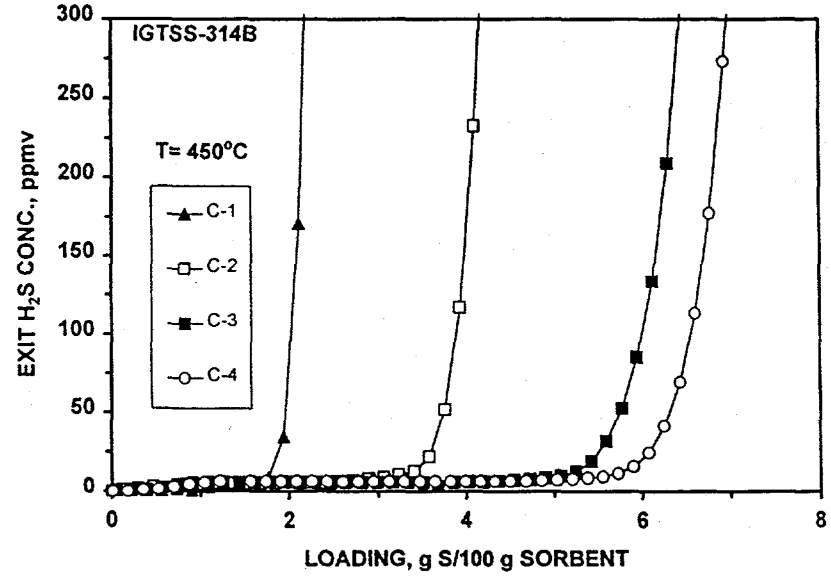
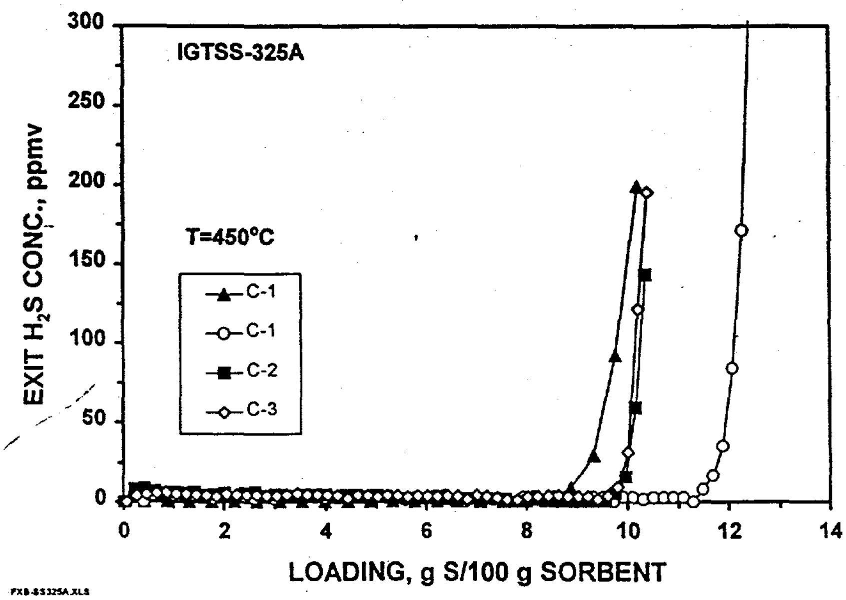


Figure 1. H_2S Breakthrough Curves for the IGTSS-314B Sorbent



FXB-SS325A.XLS
G-F094-176(S2-S4)(2)

Figure 2. H_2S Breakthrough Curves for the IGTSS-325A Sorbent

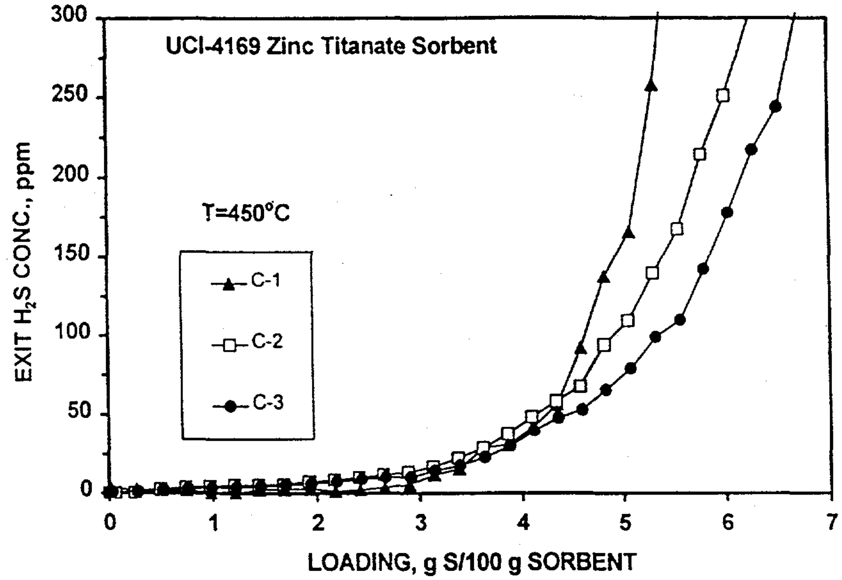


Figure 3. H_2S Breakthrough Curves for the UCI-4169 Zinc Titanate Sorbent

Research at IGT and elsewhere addressed the problem by investigating alternative support materials for zinc oxide. The rationale for this approach is that the addition of titania (TiO_2) to form zinc titanate may not be the best option to pursue because it was used in the past to reduce the vapor pressure of zinc, thereby improving its stability at elevated temperatures. The compounding of ZnO, however, is inevitably accompanied by reduction in chemical reactivity. In addition, alternative sorbents, based on the oxides of iron, copper, and manganese, have also been pursued at IGT to determine the best material for striking an acceptable balance between chemical reactivity and attrition resistance. Some success has been achieved with copper and manganese, but not with iron.

Manganese-based sorbents combine the advantages of high sulfur capacity and high reactivity in the moderate temperature range, without any need for sorbent pre-conditioning or activation. One leading manganese-based sorbent developed in this study (i.e., IGTSS-057) was found to achieve an effective sulfur capacity of over 20 g S/100 g sorbent at 450°C. However, a temperature of at least 750°C is required for oxidative regeneration of manganese-based sorbents. This may not be readily acceptable by the current desulfurization application at Piñon Pine, which requires ignition temperatures of about 550°C during regeneration.

A new class of copper-based sorbents was found to possess the best combination of chemical reactivity, attrition resistance, and regenerability. One of these sorbents (i.e., IGTSS-179) was shown to have excellent H_2S removal efficiency and an effective sulfur capacity approximating 7 grams of sulfur per 100 grams of sorbent at 450°C, as shown in Figure 4. This sorbent formulation was also found to have an attrition loss that is over 7 times lower than that of UCI-4169 sorbent. However, sustaining good and uniform fluidization with 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, resulting in sluggishness, which ultimately led to defluidization of the bed. The fluidization behavior of the sorbent has been shown to improve with increasing gas velocities. Therefore, good fluidization behavior is expected to be achievable at much higher velocities in the transport reactor with this sorbent. Unfortunately, because of the limitations imposed by the operating conditions specified in the DOE/FETC Test Protocol for evaluation of candidate sorbents for transport reactor applications (i.e., bubbling fluidized-bed batch systems), the suitability of this class of sorbents for the transport reactor applications cannot be demonstrated.

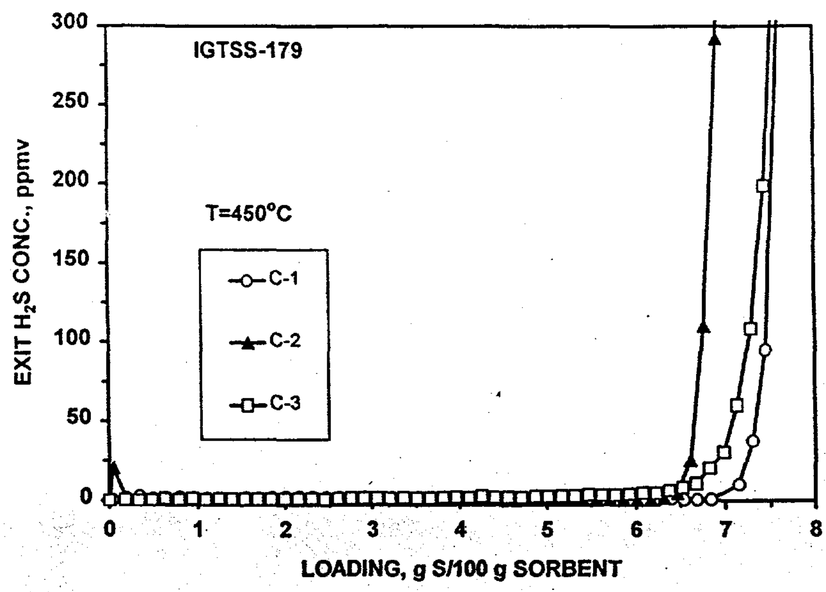


Figure 4. H2S Breakthrough Curves for the IGTSS-179 Sorbent

Given the desirable properties offered by zinc oxide, however, further investigation of zinc-based sorbents as potentially suitable desulfurizing agents in the moderate temperature range is warranted. Moreover, zinc oxide has a demonstrated capability of being sufficiently reactive at "low" temperatures; for example, zinc oxide is used in a commercial application as a once-through sorbent for desulfurizing natural gas at temperatures below 316°C. For these reasons, secondary efforts have been geared towards employing <u>alternative sorbent preparation techniques</u> that have been shown to produce mechanically strong, porous solids with median pore diameters in the range of interest. Review of the literature identified sol-gel processing as a promising method. **This report focuses on the results of the work performed in the development and evaluation of zinc-based sorbents produced by sol-gel techniques.**

Sol-gel processing is defined broadly as the preparation of ceramic materials by preparation of a sol, gelation of the sol, and removal of the solvent. The sol is a colloidal suspension of solid particles in a liquid and may be produced from inorganic or organic precursors. For example, common precursors for aluminum oxide include inorganic salts such as $Al(NO_3)_3$ and organic compounds such as $Al(OC_4H_9)_3$. The latter is an example of an alkoxide, the class of precursors widely used in sol-gel research because they react readily with water (i.e., hydrolysis reaction). Gels have a huge interfacial area, typically 300-1000 m^2/g, and this enormous area serves as a driving force to bring about sintering at exceptionally low temperatures, compared to ordinary ceramic materials. Therefore, a considerable amount of the extraordinary properties (high surface areas and small pore sizes) of unfired gels are retained following calcination, offering the possibility of using the gel as a substrate for chemical reactions. These properties, characteristic of inorganic gels as a result of low-temperature processing, are unattainable by conventional sorbent preparation techniques and should be exploited in hot gas desulfurization applications. One important consideration is to maintain the necessary properties after heat treatment, and in fact, the uniqueness of sol-gel derived materials diminishes as the heat treatment is increased.

Therefore, the main focus of this part of this on-going investigation has been to explore the possibility of preparing zinc-based sorbents using the sol-gel approach that has been shown to require only a moderate temperature for calcination, while resulting in significantly more attrition-resistant sorbents. The sorbents prepared in this part of the investigation and the results from their evaluation in packed-bed and fluidized-bed reactors are described in this report.

SORBENT PREPARATION AND EVALUATION

Eleven (11) sorbent formulations were prepared using a sol-gel approach, where a stable sol is first prepared from a titania precursor (alkoxide and/or powder). The required amount of a zinc precursor (zinc nitrate) is then added to bring the zinc oxide content to the desired level. The resulting solution is then well mixed to disperse the reactive oxide, thickened, dried, and finally calcined at the desired temperature for a predetermined period. The nominal zinc oxide content of the sorbents prepared during the reporting period ranged from 10 to 40%. The calcination temperature ranged from 450 to 725°C. The designations for the sorbents prepared and their nominal ZnO content are summarized in Table 1.

Table 1. Zinc-Based Sorbents Prepared using Sol-Gel Approach

Sorbent Designation	ZnO Content, wt% (nominal)
IGTSS-349	10
IGTSS-350	40
IGTSS-351	20
IGTSS-353	30
IGTSS-354	30
IGTSS-355	30
IGTSS-356	30
IGTSS-357*	30
IGTSS-358*	30
IGTSS-359	30
IGTSS-360	40

* Sorbent does not contain any titania

Granules from each of the above sorbents were then produced in the desired size range of 425-600 μm and 45-180 μm for testing in the packed-bed and fluidized-bed reactors, respectively.

The granular sorbents were then evaluated for their H2S removal efficiency and effective sulfur capacity (i.e., H2S concentration prior to breakthrough and the total amount of sulfur loaded at breakthrough time). Sulfidation tests was carried out in the temperature range of 350 to 550°C and a gas space velocity of 2000 hr-1 for packed-bed and 5000 hr-1 for fluid-bed tests. Two sulfidation gas compositions have been used: The first one consisted of 10% H2O, 10% H2, 20% CO, 10% CO2, 2% H2S, and 48% N2 and the second one consisted of 10% H2O, 40% H2, 2% H2S, and 48% N2. Reacted sorbent regeneration was investigated in the temperature range of 480 to 650°C (900 to 1200°F) using a gas mixture containing 2-7% O2, 0-10% H2O, and balance N2. Fresh as well as reacted samples from selected sorbents were subjected to chemical analysis and physical characterization, including BET surface area, porosity and pore size distribution, particle density, and XRD analysis. Four selected sorbent formulations (i.e., IGTSS-353, -354, -357, and -359) were also evaluated for their attrition resistance properties in accordance with the ASTM D5757-95 method. Their performance was compared against those of selected sorbents previously developed in this program and that of a leading candidate zinc titanate sorbent (i.e., EX-SO3) for the Piñon Pine Demonstration Project. The results of extensive evaluation of the sorbents prepared by sol-gel techniques are presented and discussed below.

RESULTS AND DISCUSSION

Sorbent Characterization.

The results of physical characterization of two selected sol-gel-derived sorbents (i.e., IGTSS-353 and –354) as well as those of selected sorbents previously prepared by conventional techniques are summarized in Table 2. Comparison of the sorbents presented in Table 2 indicates that although all these sorbents have similar densities and porosities, the mercury pore surface areas of the sol-gel derived sorbents are one to two orders of magnitude higher than those prepared by other techniques. The high surface areas of the sol-gel-derived sorbents should be attributed to significantly smaller pore diameters in these sorbents. This desirable combination of high porosity, high surface area, and small pore diameters resulted in higher reactivity and much higher attrition resistance, as will be discussed later.

Table 2. Physical Characteristics of Selected Sorbents

Sorbent Designation	Main Reactive Metal	Bulk Density (g/cm^3)	Hg Particle Density ρ_b, (g/cm^3)	Skeletal Density, ρ_a (g/cm^3)	Porosity (%)	Total Hg Pore Surface Area (m^2/g)
IGTSS-353(sol-gel)	Zn	1.55	2.43	3.66	33.6	39.23
IGTSS-354(sol-gel)	Zn	1.55	2.13	4.12	48.1	56.92
IGTSS-314B	Zn	1.35	2.27	4.48	49.4	3.34
IGTSS-325A	Zn	1.32	1.93	4.55	57.5	2.59
UCI-4169	Zn	1.37	1.38	3.14	56.1	0.72
IGTSS-057	Mn	1.75	1.62	4.69	65.6	9.21
IGTSS-179	Cu	2.05	3.06	4.17	26.7	5.23

Comparison of Attrition Resistance

Figure 5 reports the results from attrition tests carried out on the IGTSS-353 and IGTSS-354 sorbents. These results are also compared against those obtained previously with the commercial UCI-4169 zinc titanate sorbent and two selected bulk zinc-based sorbents developed earlier in this program. Also shown in Figure 5 are the results from the baseline FCC material. The results reported in Figure 5 are in terms of the attrition jet index (AJI), as defined by the ASTM D5757-95 procedure, which corresponds to the 5-hour loss. As shown in this figure, the new sol-gel derived zinc-based sorbents achieved attrition losses that are about half that of the FCC material and about 1/10 those of the conventional bulk zinc-based sorbents.

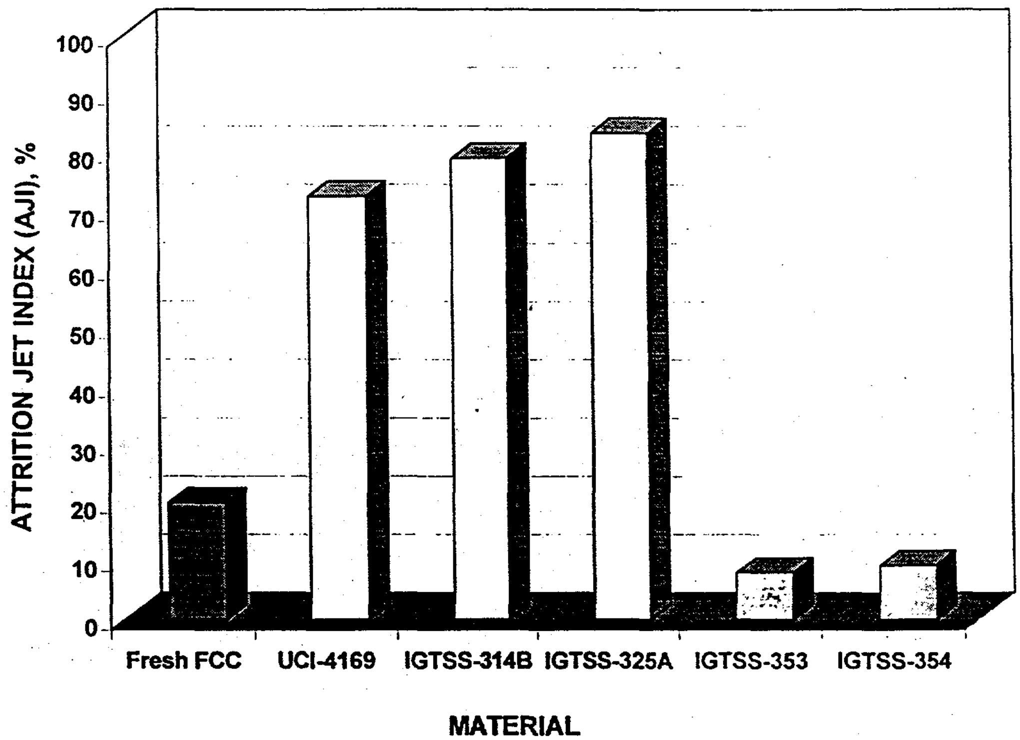


Figure 5. Attrition Resistance of New and Conventional ZnO-Based Sorbents (5-hr Loss)

Figure 6 reports the attrition losses obtained with the IGTSS-353 and IGTSS-354 sorbents during the second hour only of the 5-hour attrition test. This modified procedure of the ASTM D5757-95 method has been reported to provide adequate assessment of the relative attrition resistance of sorbent materials for the purpose of screening effective sorbents for the Piñon Pine application. Also shown in Figure 6 are the results obtained with other leading regenerable sorbents developed at IGT (i.e., IGTSS-179 and IGTSS-345B) and the results reported for EX-SO3 zinc titanate sorbent. This latter is currently the leading sorbent being considered for the Piñon Pine Clean Coal Demonstration Project. As shown, Both IGTSS-353 and IGTSS-354 exhibit significantly lower attrition losses that are 3 to 4 times better than the leading EX-SO3 sorbent.

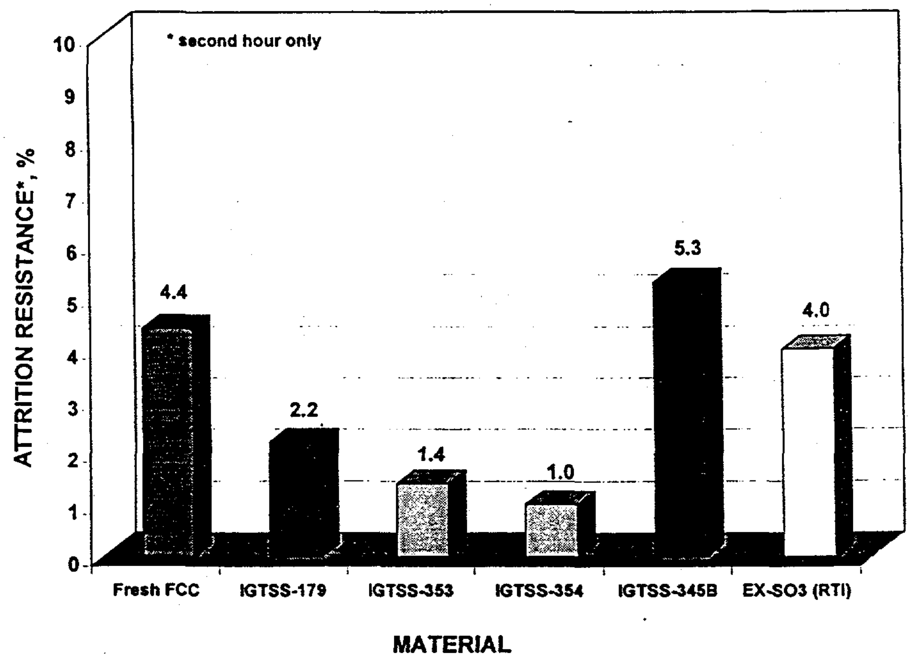


Figure 6. Attrition Resistance of Selected Sorbents (2nd hr Only)

Figure 7 compares the performance of IGTSS-353 and IGTSS-354 sorbents with those of other selected copper-based (IGTSS-179), manganese-based (IGTSS-057), zinc-based (UCI-4169), and mixed-oxide (IGTSS-345B) sorbents in the attrition unit. Attrition resistance in this figure is reported in accordance with DOE/FETC's definition of (5^{th} hr – 1^{st} hr)/4, i.e., the average per hour loss due to attrition with the first hour loss not taken into consideration. As shown, IGTSS-353 and IGTSS-354 demonstrated significantly lower attrition losses among all the sorbents.

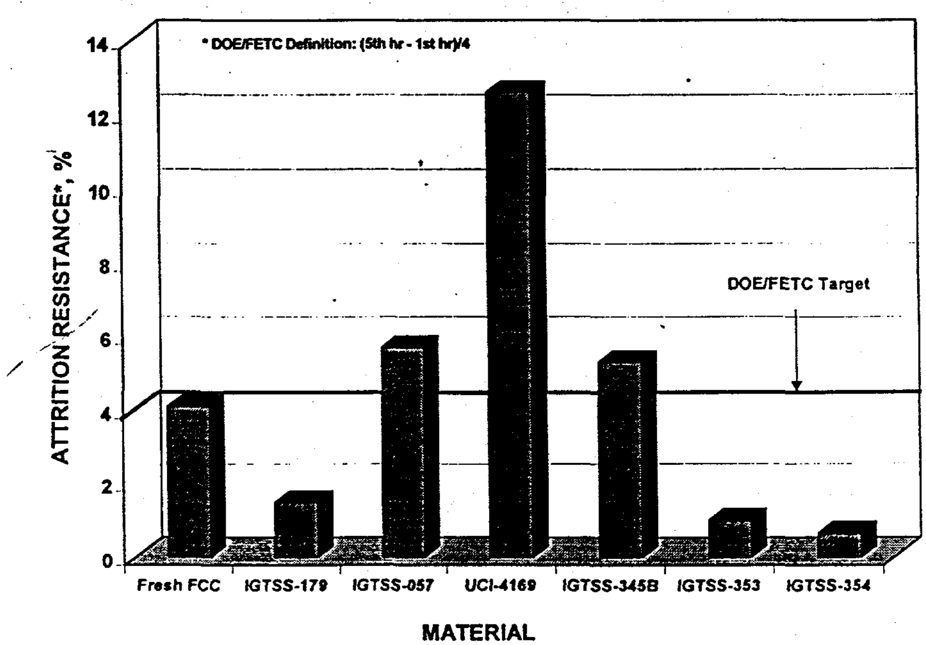


Figure 7. Attrition Resistance of Selected Sorbents

Evaluation of Chemical Reactivity, Regenerability, and Durability

All eleven (11) sol-gel-derived sorbents prepared in this program (see Table 1) were evaluated for their reactivity towards H_2S in the packed-bed reactor. The extent of evaluation of each sorbent (i.e., number of cycles, parametric studies, etc.) depended on the performance of the sorbent. The most promising sorbents were also evaluated in the fluidized-bed reactor. The ranges of operating conditions used during sorbent evaluation are presented in Table 3. The results of evaluation of the sorbents are discussed below.

Table 3. Ranges of Operating Parameters

Operating Parameters	Ranges of Operating Parameters
Sorbent Size, μm	425-600 (Packed-Bed)
	45-180 (Fluid-Bed)
Sulfidation Temperature, °C	350-550
Sulfidation Space Velocity, hr^{-1}	2000-5000
Sulfidation Gas Composition, Vol%	
CO_2	0-10
CO	0-20
H_2	10-40
H_2O	10-11
H_2S	1-2
N_2	Balance
Regeneration Temperature, °C	480-650
Regeneration Space Velocity, hr^{-1}	2000-5000
Regeneration Gas Composition, Vol%	
O_2	2-9
H_2O	0-10
N_2	balance

IGTSS-349

The results obtained from packed-bed testing of the first sol-gel-derived sorbent prepared in this program (i.e., IGTSS-349) is shown in Figure 8. This sorbent has a nominal ZnO content of about 10 wt%, which corresponds to a theoretical sulfur capacity of 3.95%. As shown in Figure 8, this sorbent achieved near complete conversion of ZnO in the packed-bed, which is indicative of very high sulfidation reactivity. This sorbent was regenerated at 650°C using a dry O_2-N_2 mixture; however, because of the heat generated by the exothermic regeneration reaction and the exposure of this sorbent to temperatures higher than 750°C, the effectiveness of this sorbent in subsequent sulfidation tests was reduced by about 50%. Given its low ZnO content, no further evaluation was performed with this sorbent and the efforts were directed towards preparation of higher capacity sorbents.

IGTSS-350

Following the encouraging results obtained with the low-capacity IGTSS-349 sorbent, IGTSS-350 was prepared containing 40% ZnO. However, this sorbent exhibited very low reactivity during the first cycle and no further testing was performed on this sorbent. Initially, the unexpected low reactivity observed with this sorbent was attributed to its high ZnO content. Consequently, efforts were directed towards determination of the optimum ZnO content for sol-gel-derived sorbents.

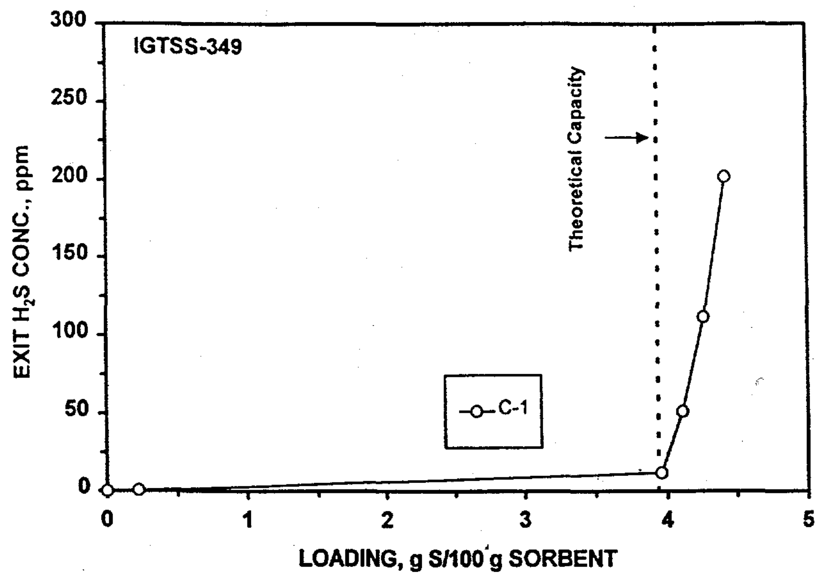


Figure 8. Sulfidation Performance of IGTSS-349 Sorbent

IGTSS-351

This sorbent which contains about 20% ZnO also exhibited very high reactivity, achieving complete conversion at 450°C during the first sulfidation. However, the reactivity of this sorbent declined by about 25% following regeneration at 650°C. This result further confirmed that regeneration of this sorbent at an initial temperature of 650°C (peak temperature above 750°C) will have an adverse effect on the effectiveness of the sorbent. Based on the results obtained with this sorbent, it was decided to increase the ZnO content of the sorbents to 30% while limiting the regeneration temperature to 600°C.

IGTSS-353

The results of six (6) cycles of sulfidation/regeneration performed with this sorbent, which contains 30% ZnO, are presented in Figure 9. This sorbent was regenerated at 593°C (1100°F) using a O_2-N_2 gas mixture, achieving a peak temperature below 650°C during regeneration. As shown in Figure 9, this sorbent exhibited excellent reactivity towards H_2S, achieving a sulfur loading of 6-7% over the six cycles completed without any loss of reactivity.

A second series of tests consisting of four cycles was conducted with this sorbent to investigate the effect of regeneration condition on the performance of the sorbent. The parameters investigated included the effect of temperature (538 versus 593°C) as well as the effect of addition of steam (10%) to the regeneration gas. Figure 10 shows that the regeneration temperature in the range of 538-593°C does not affect the performance of the sorbent. The SO_2 released during these regeneration tests are presented in Figure 11, indicating that the theoretical (i.e., based on stoichiometry) concentration of SO_2 can be achieved in this temperature range.

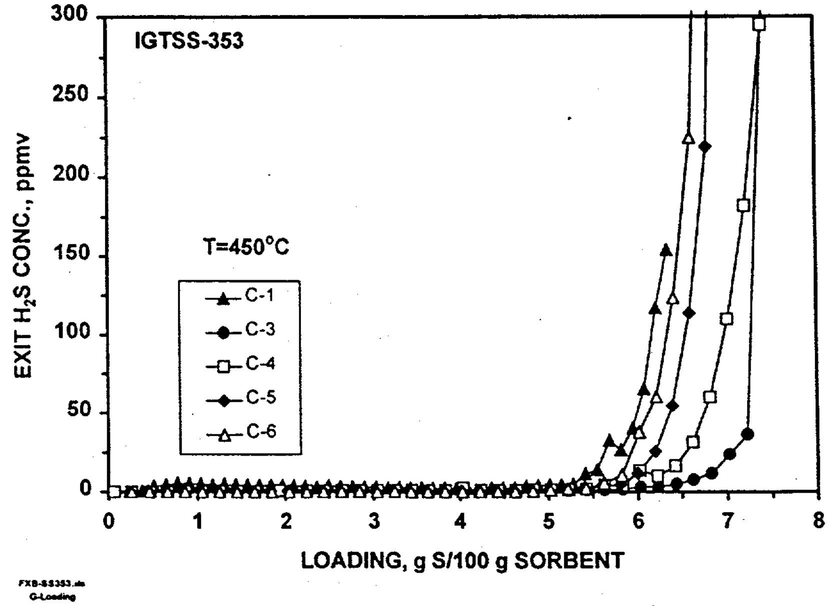


Figure 9. Performance of IGTSS-353 Sorbent

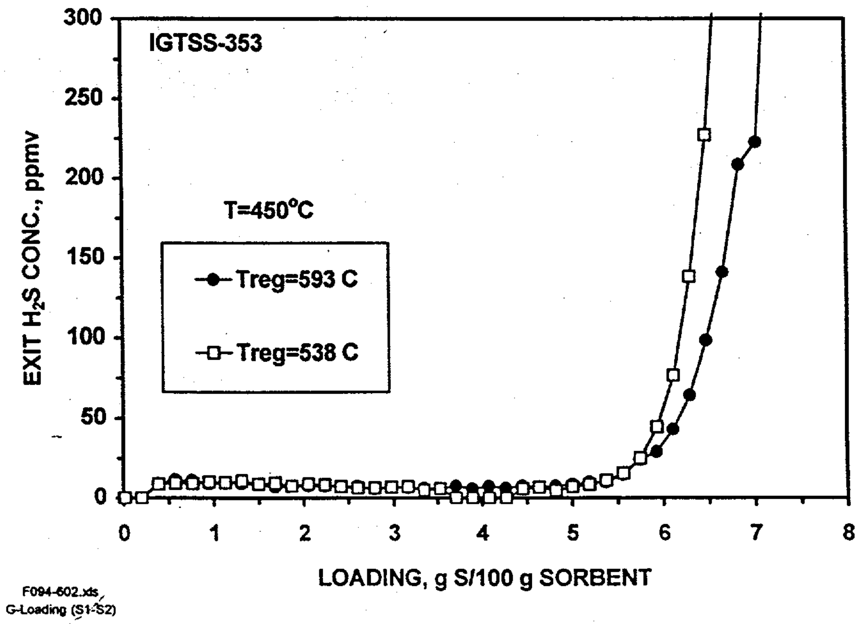


Figure 10. Performance of IGTSS-353 Following Different Regeneration Temperatures

IGTSS-354

To improve the tolerance of the sorbent for exposure to high temperature, the IGTSS-354 was prepared by modifying the IGTSS-353 formulation through addition of a non-titania material to the sorbent. The results of ten (10) cycles completed with this sorbent at 450°C are presented in Figure 12, indicating that the effective sulfur capacity of this sorbent was maintained in the cyclic process. The lower effective capacity in cycle 9 is the result of incomplete regeneration in the preceding cycle, which was carried out at 538°C with a dry O_2-N_2 gas mixture. Although the effective sulfur capacity improved in the subsequent cycle (i.e., S-10), which followed a regeneration at 593°C, because of possible sulfate formation during regeneration at the lower temperature, the effective sulfur capacity was not fully restored.

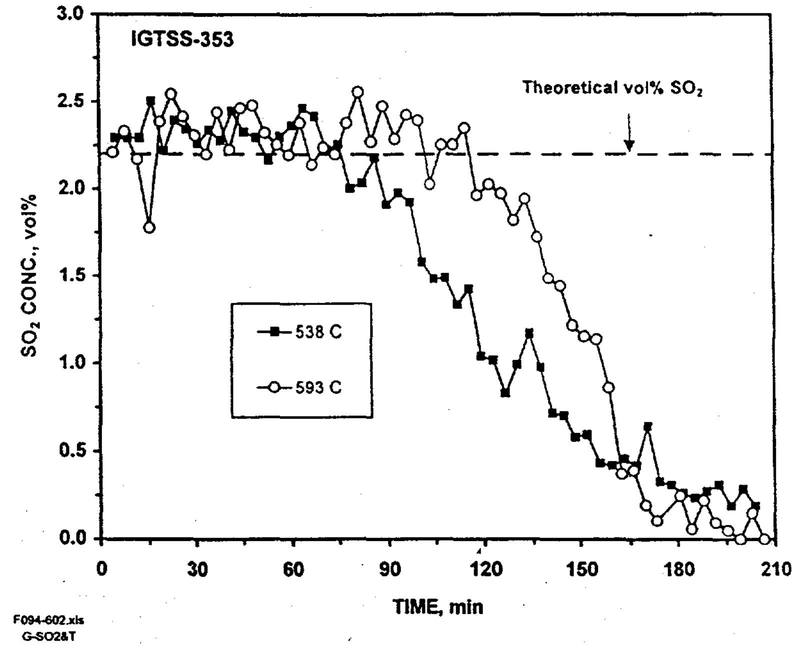


Figure 11. Regeneration of IGTSS-353 at Different Temperatures

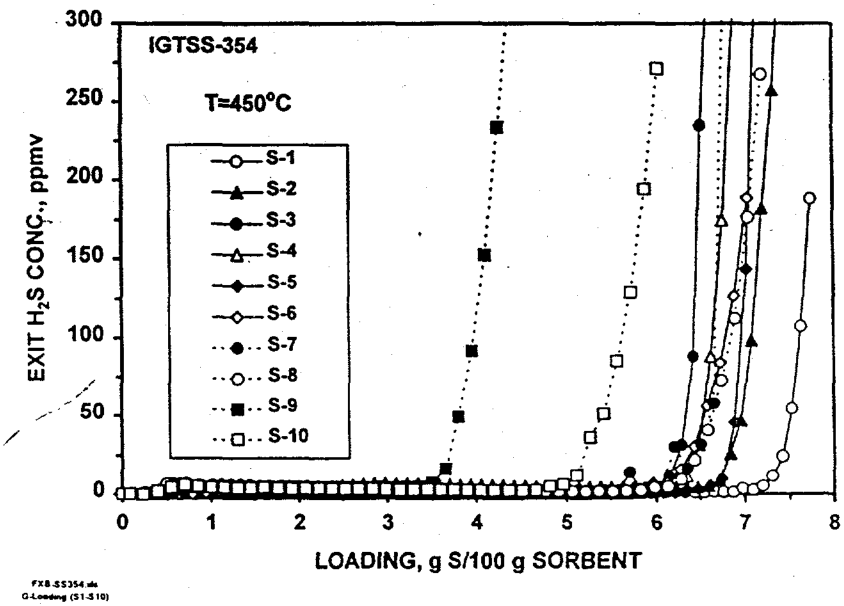


Figure 12. Performance of IGTSS-354 Sorbent

The H_2S and SO_2 concentrations in the reactor effluent during a typical sulfidation/regeneration cycle are presented in Figure 13. The feed gas during the sulfidation test contained 2% H_2S. The results indicate excellent sulfur balance achieved in these tests, confirming the observed sulfur loading during sulfidation. The results of chemical analysis indicated a sulfur loading of 9% (sulfide S) at the reactor entrance after sulfidation and 0.2% (sulfate S) after regeneration, which are also consistent with the experimental results, which indicate an average sulfur loading of about 7% and complete regeneration.

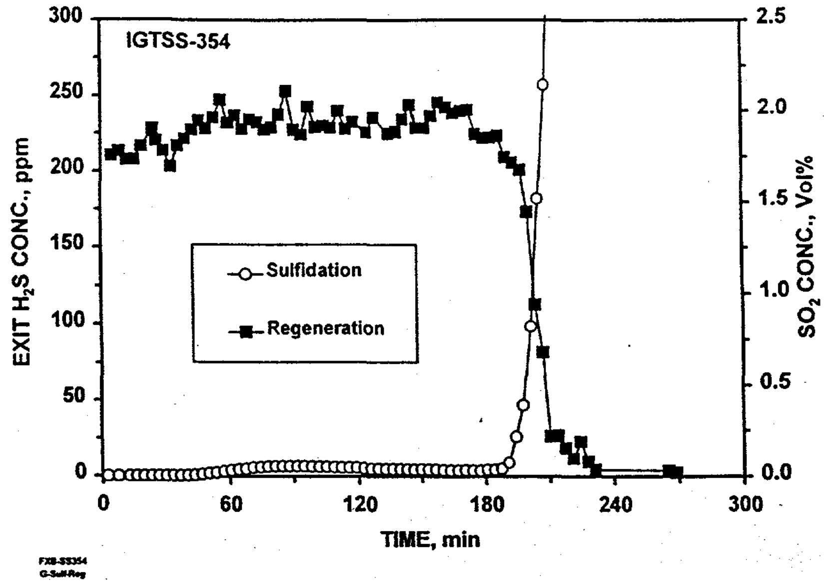


Figure 13. Sulfur Balance in a Typical Sulfidation/Regeneration Cycle

The effects of temperature and steam content of the regeneration gas on the regenerability of the IGTSS-354 sorbent are shown in Figures 14 and 15. The results indicate that the sorbent can be fully regenerated at 593°C with or without steam; however, to fully regenerate the sorbent at 538°C, the presence of steam in the regeneration gas is required.

To ensure reproducibility of the sorbent preparation procedure, a second batch of the IGTSS-354 sorbent was prepared and evaluated over two cycles. The results of these tests are presented in Figure 16, which are similar to those obtained with the first batch of IGTSS-354 sorbent presented earlier in Figure 12.

The performance of the IGTSS-354 sorbent in the fluidized-bed reactor was also determined over four cycles. The results of these tests are shown in Figure 17, indicating that the sorbent achieved an effective sulfur loading of about 6% at 450°C in the fluidized-bed reactor, where the gas residence time was less than one second.

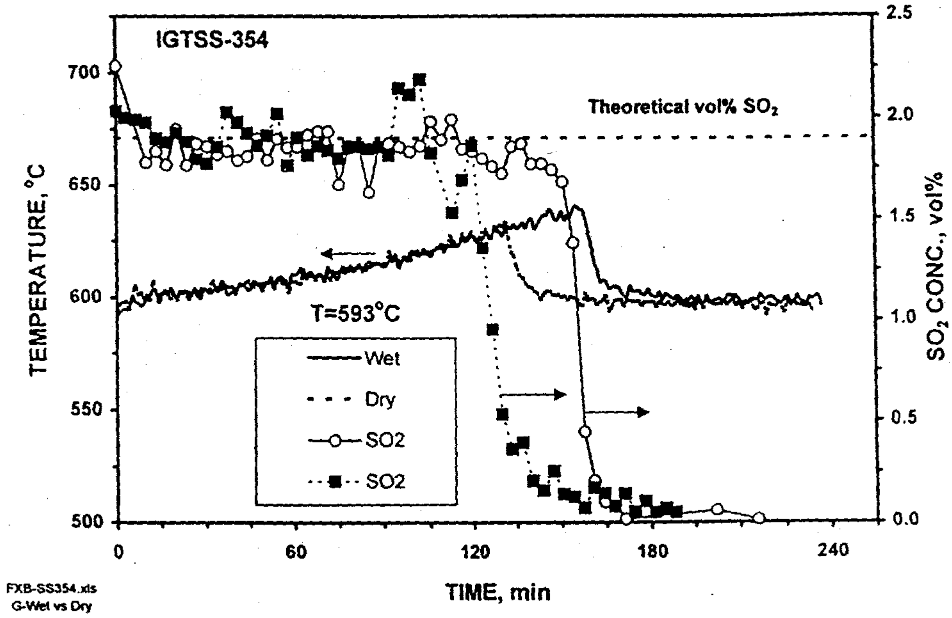


Figure 14. Effect of Steam on Regenerability of IGTSS-354 Sorbent

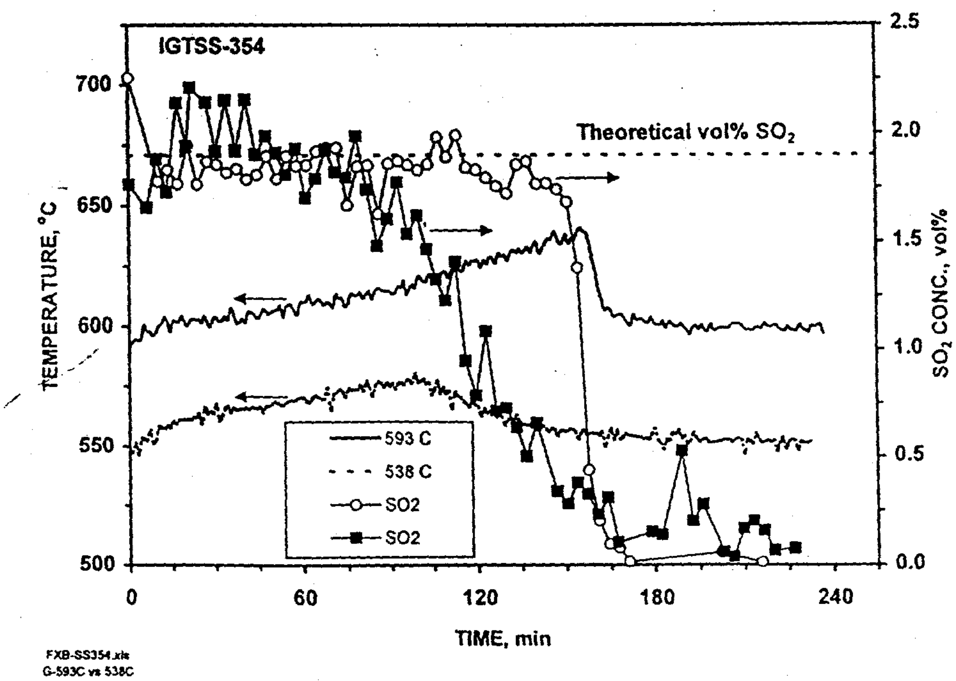


Figure 15. Effect of Temperature on Regenerability of IGTSS-354 Sorbent

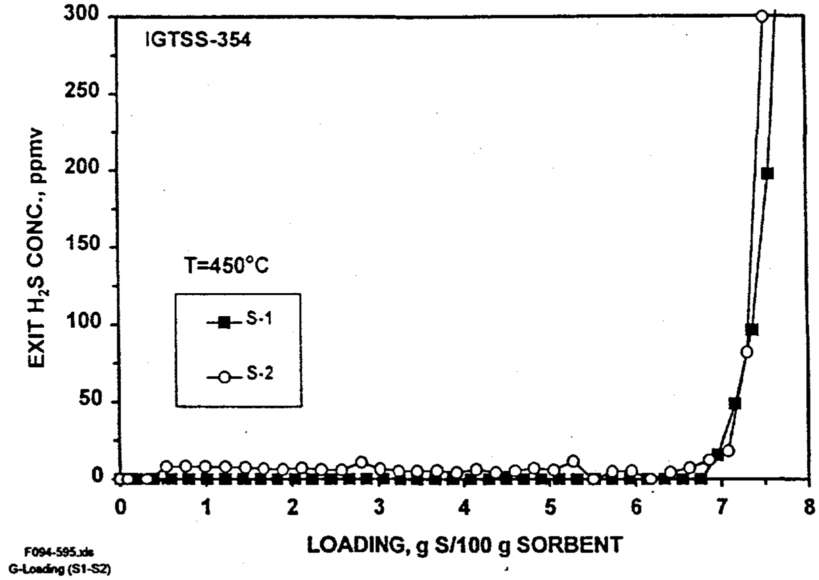


Figure 16. Performance of IGTSS-354 Sorbent (2nd Batch)

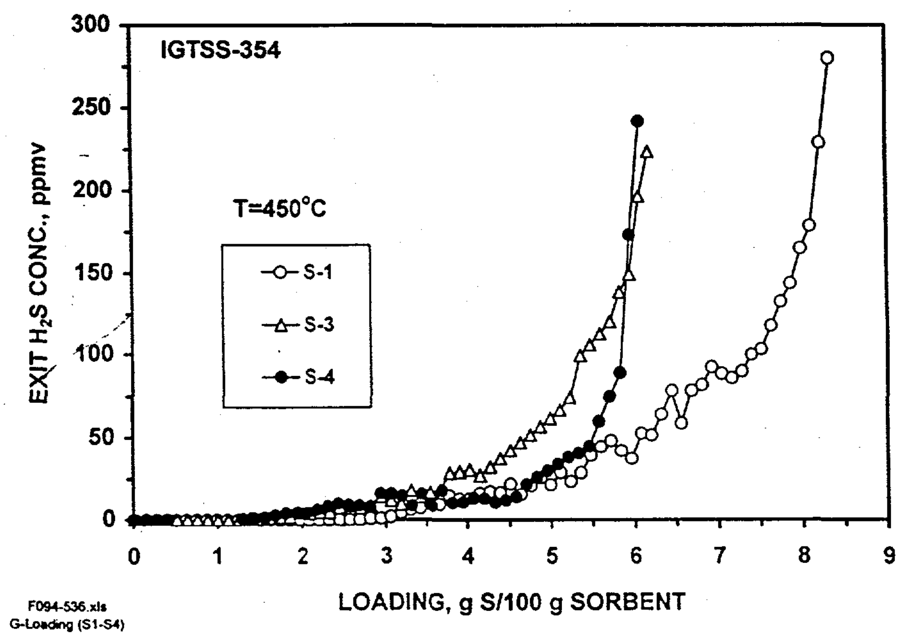


Figure 17. Performance of IGTSS-354 Sorbent in Fluidized-Bed Reactor

IGTSS-355

The effect of exposure to high temperature on the performance of these sol-gel-derived sorbents was investigated by preparing the IGTSS-355 sorbent, which is similar to the IGTSS-353 sorbent, except that it was exposed to a calcination temperature of 750°C during sorbent preparation. Evaluation of sulfidation reactivity of this sorbent in the packed-bed reactor resulted in an effective sulfur capacity of less than 2%, confirming the detrimental effect of exposure to temperatures above 750°C. Analysis of the physical properties of this sorbent indicated that its mercury surface area is about 2 orders of magnitude lower than that of the IGTSS-353 sorbent.

IGTSS-356

The effect of calcination temperature on the sorbent performance was further investigated by preparing the IGTSS-356 sorbent, which is also similar to the IGTSS-353, except that this sorbent was calcined at 650°C, which is the highest temperature expected during sorbent regeneration. The effective sulfur capacity of this sorbent was determined in the packed-bed at 450°C and was found to be similar to that of IGTSS-353. The results obtained with IGTSS-355 and IGTSS-356 indicate that the sorbent can maintain its high effective sulfur capacity as long as the sorbent is exposed to temperatures below 650°C.

IGTSS-357

This sorbent which contains about 30% ZnO and a non-titania support, was prepared to investigate the suitability of alternative support materials. The performance of this sorbent over four cycles at 450°C is presented in Figure 18. These results indicate that although the effective sulfur capacity of this sorbent during the first cycle is comparable to that of the IGTSS-353 sorbent, the effective sulfur capacity decreases in subsequent cycles to about 4%. This decline in the performance of the sorbent is probably due to changes in the physical and chemical properties of the sorbent in the cyclic process.

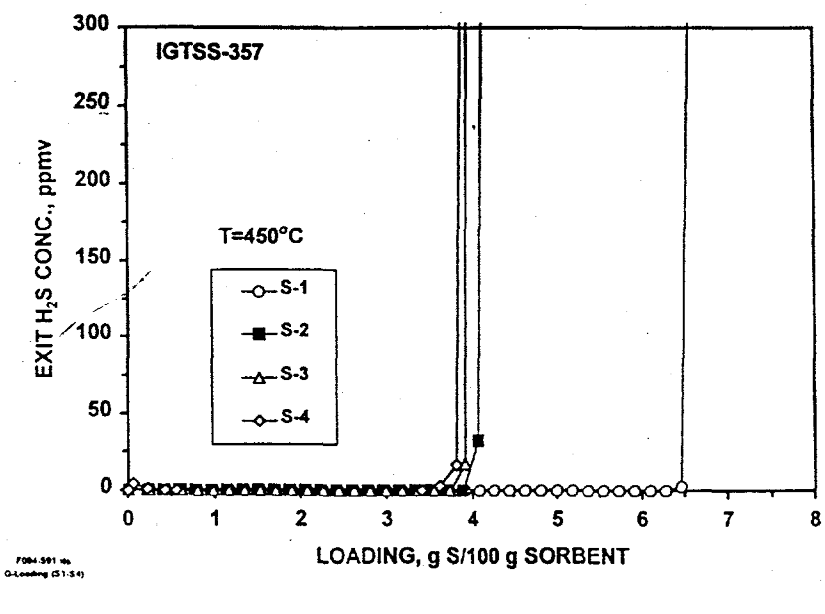


Figure 18. Performance of IGTSS-357 Sorbent

IGTSS-358

This sorbent also contained 30% ZnO and another non-titania support. However, evaluation of this sorbent in the packed-bed reactor resulted in immediate breakthrough, indicating the reactivity of this sorbent towards H_2S is very low.

IGTSS-359

Given the excellent results obtained with the IGTSS-354 sorbent, the preparation procedure was simplified to reduce the number of steps to lower the sorbent preparation costs. These efforts resulted in the IGTSS-359 sorbent, which was shown to have similar attrition resistance and effective sulfur capacity compared to the IGTSS-354 sorbent. The performance of the IGTSS-359 sorbent in the temperature range of 350 to 550°C is shown in Figure 19, indicating that the sorbent can maintain its high sulfur capacity even at 350°C. The SO_2 concentration and the reactor temperature during regeneration are presented in Figure 20, indicating improved regenerability for IGTSS-359 (sharper SO_2 concentration profile) compared to the IGTSS-354 sorbent.

IGTSS-360

Given the unexpectedly low effective sulfur capacity observed with IGTSS-350 and the adverse effect of exposure to high temperature on the performance of the sorbents, it was postulated that the low reactivity of IGTSS-350 might have been due to exposure to high temperature during the preparation step. Consequently, IGTSS-360 was prepared containing 40% ZnO, while the calcination temperature was closely controlled below 650°C. The results of three sulfidation cycles carried out at 450°C with this sorbent formulation are presented in Figure 21, indicating that the effective sulfur capacity of this sorbent is generally higher than those of IGTSS-353 and IGTSS-354, which should be attributed to the higher ZnO content of the IGTSS-360 sorbent.

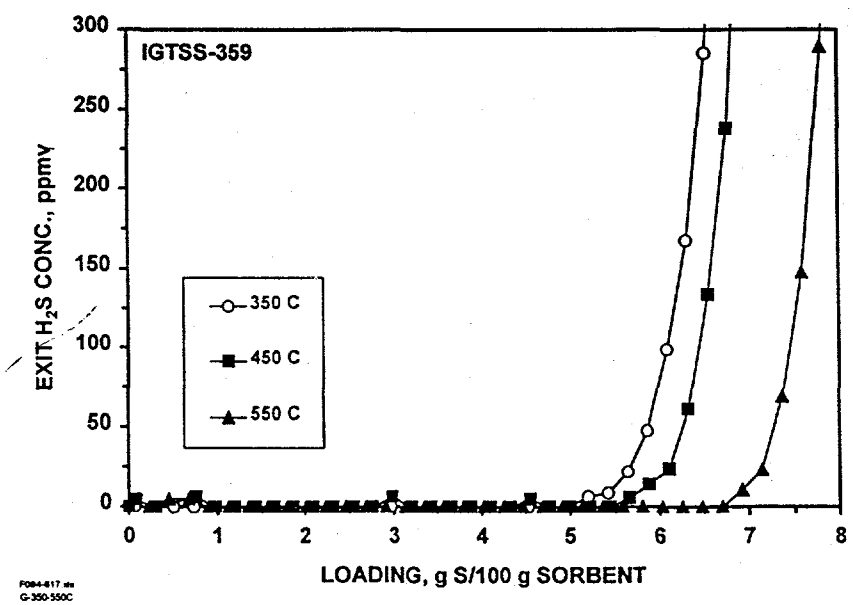


Figure 19. Performance of IGTSS-359 Sorbent

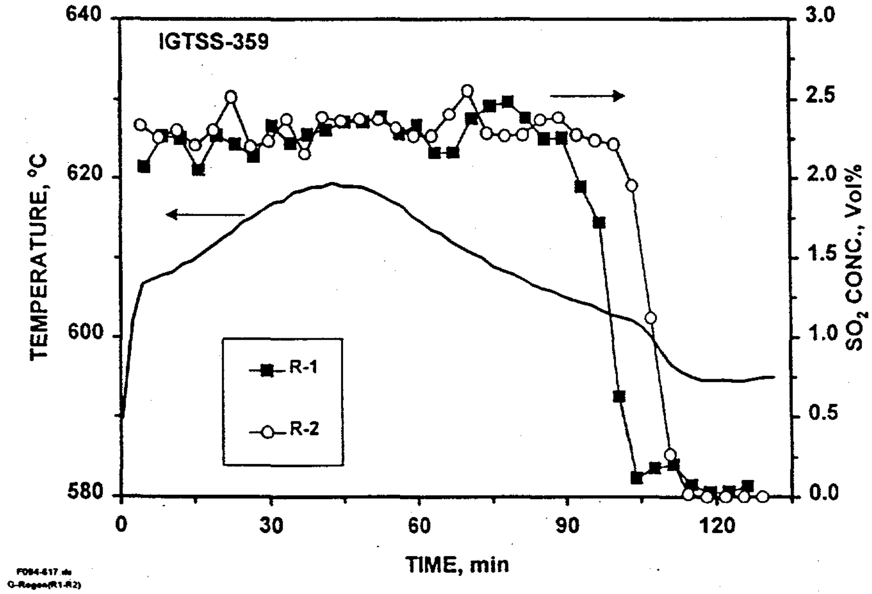


Figure 20. Temperature and SO2 Profiles during Regeneration of IGTSS-359

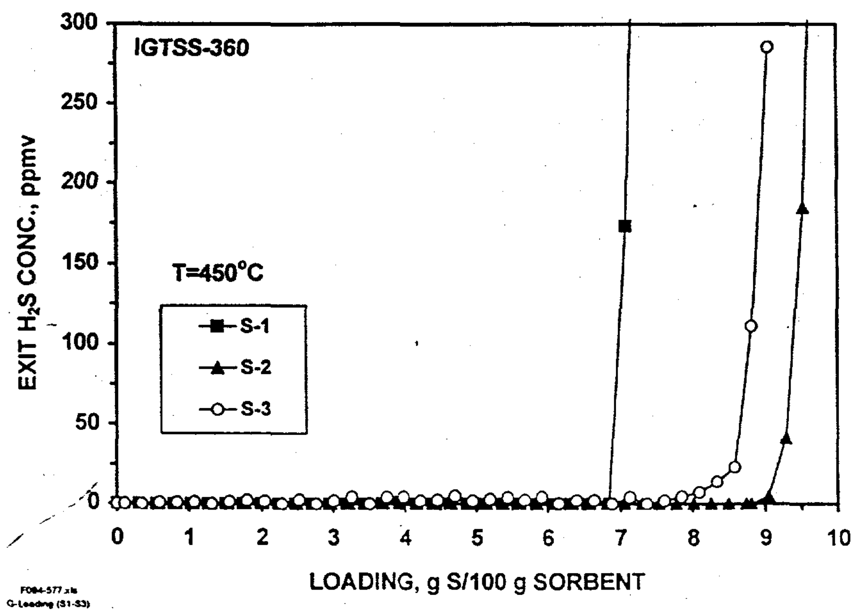


Figure 21. Performance of IGTSS-360 Sorbent

CONCLUSIONS

A modified Sol-Gel technique has been used to produce ZnO-based sorbents with unique properties that are unattainable by conventional sorbent preparation methods. This method eliminates the need for excessively high thermal treatment temperatures to impart the required physical strength and has made possible the achievement of the challenging combination of high reactivity (desirable pore size distribution and high surface area), high attrition resistance, and regenerability at lower temperature.

Based on the results obtained in this program, the IGTSS-353, IGTSS-354, and IGTSS-360 are capable of reducing the H2S content of the coal gas to desirable levels in the temperature range of 350 to 550°C for IGCC applications. A small batch of the IGTSS-354 sorbent is being prepared by a commercial sorbent manufacturer for evaluation in the high-pressure bench-scale fluidized-bed reactor to demonstrate the suitability of this sorbent for coal gas desulfurization in the transport reactor at Piñon Pine The goal was to develop sorbents that are capable of reducing the H2S 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.