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Project Title: **COPPER-BASED SORBENTS FOR HOT GAS
DESULFURIZATION SYSTEMS**

ICCI Project Number: 96-1/2.2A-3
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ABSTRACT

The overall objective of this study was to produce highly reactive and attrition resistant copper-based sorbents for removal of hydrogen sulfide from coal gas and to evaluate the effectiveness of the superior sorbent formulations in multi-cycle tests under process conditions closely simulating those of the Clean Coal Technology IGCC Demonstration Programs.

To achieve this objective, several formulations of copper-based sorbent pellets and granules were prepared. These sorbent formulations were evaluated for their attrition resistance and crush strength as well as their desulfurization and regeneration capabilities.

During this study, a method was established for the preparation of copper chromite powders that are easily amenable to pelletization. Copper chromite sorbents in the form of spherical pellets, cylindrical tablets, and granules were prepared. Based on packed-bed reactor testing and crush strength evaluation, these sorbents were found to be suitable for moving-bed (pellets and tablets) and fluidized-bed (granules) desulfurization applications at 600°C. However, these copper chromite sorbents required an activation step to enhance their reactivity at 600°C and were found to have unacceptably low reactivities for fuel gas desulfurization at temperatures below 500°C.

A new class of attrition-resistant copper-based sorbents in the form of pellets and granules was prepared for lower temperature application. This new class of copper-based sorbents was evaluated at 350° to 450°C and was found to have a far superior performance in this lower temperature application, achieving an average effective sulfur capacity of 9.3 g S/100 g sorbent at 450°C and about 6.3 g S/100 g sorbent at 350°C, with a pre-breakthrough H₂S concentration in the cleaned fuel gas of below 1 ppmv.

EXECUTIVE SUMMARY

Integrated Gasification Combined-Cycle (IGCC) Power Plants and Integrated Gasification Fuel Cell (IGFC) Power Generation Technologies are among the leading contenders for coal conversion. Coal gas desulfurization to sufficiently low levels at elevated temperatures (i.e., $T > 350^\circ$) is now recognized as crucial to efficient and economic coal utilization in advanced IGCC and IGFC power generation processes. The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials which 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 additional desired features of the sorbents.

The zinc-based sorbents, such as zinc titanate, have been shown to suffer from zinc volatilization at elevated temperatures (i.e., $T > 550^\circ C$), leading to sorbent deterioration, increasing sorbent replacement costs, and the overall cost of hot gas cleanup. Copper-based sorbents, because of the high melting point of the metal, do not suffer from this problem.

A novel copper-chromite sorbent has been developed in a recent ICCI-funded project for hot coal gas desulfurization in a fluidized-bed. The results obtained in this previous study indicated that the copper-chromite sorbent produced in granular form (i.e., CuCr-29), had a much higher attrition resistance compared to a commercial granular zinc titanate sorbent (i.e., UCI-4169), as well as excellent desulfurization efficiency. Furthermore, unlike most zinc titanate sorbents, the reactivity of IGT's CuCr-29 copper-chromite sorbent gradually and consistently improved during the 20 cycles tested.

This study focused on the production of highly reactive and attrition resistant copper-based sorbents and on the evaluation of the effectiveness of the superior sorbent formulations in multi-cycle tests, under process conditions closely simulating those of the Clean Coal Technology IGCC Demonstration Programs.

In this program, a number of formulations of attrition resistant copper-based sorbent pellets ($dp = 2 - 5$ mm) as well as granules ($dp = 0.1 - 0.3$ mm) were produced. Initially, the starting materials and sorbent composition were comparable to those identified in the previous ICCI-funded project. However, because the goal of this project was also directed toward moving-bed technology, the sorbent composition was modified to suit the desired applications. Such modifications included additives (to enhance and/or maintain porosity) and thermal treatment history (i.e., induration temperature and time). In addition, to minimize attrition losses and achieve optimum packing efficiency, a special pelletization technique was used to produce durable and highly reactive spherical sorbent pellets.

A method was established for the preparation of copper-based powders that are easily amenable to pelletization. Copper-based sorbents in the form of cylindrical tablets,

spherical pellets, and granules were prepared. The average particle diameters of the spherical pellets and the granules were 0.35 cm and 0.02 cm, respectively. The crush strengths of the pellet formulations were determined in accordance with ASTM procedures and were found to exceed the requirement for moving-bed applications.

A selected number of copper chromite sorbents were subjected to multi-cycle testing in the ambient pressure packed-bed unit to demonstrate their durability and regenerability. These tests were conducted at a space velocity of 2000 hr⁻¹ in the sulfidation temperature range of 600° to 650°C and at a regeneration temperature of 750°C. The results obtained indicate that all selected formulations of copper chromite sorbents are sufficiently reactive toward H₂S at 600°C. The pre-breakthrough H₂S concentration in the cleaned gas was less than 5 ppmv with the granular formulations, and below 10 ppmv with the pellets, qualifying the granular formulations for fluidized-bed and the pellet formulations for moving-bed desulfurization of fuel gases at elevated temperatures. However, these copper chromite sorbent formulations were found to require an activation step to enhance their reactivities toward H₂S.

The suitability of two copper chromite sorbents (i.e., CuCr-29 and CuCr-41G) was also assessed for application in the lower temperature range of 350° to 450°C. These copper chromite sorbents, which have been developed for the temperature range of 550° to 650°C, were found to have unacceptably low reactivities for fuel gas desulfurization at lower temperatures, even following activation.

A new class of attrition-resistant copper-based sorbents in the form of pellets and granules was prepared and evaluated in a packed-bed reactor. One of these formulations (i.e., IGTSS-145) was sulfided repeatedly at 600°C and regenerated at 725°C, and was found to perform remarkably well without requiring activation, unlike the copper chromite sorbents. This new class of copper-based sorbents was also evaluated at 350° to 450°C and several formulations were found to have a far superior performance in this lower temperature application. The best sorbent formulation (i.e., IGTSS-179) had an average effective sulfur capacity of 9.3 g S/100 g sorbent at 450°C and about 6.3 g S/100 g sorbent at 350°C, with a pre-breakthrough H₂S concentration in the cleaned fuel gas of below 1 ppmv.

The reproducibility of the sorbent preparation technique developed at IGT was confirmed by making two different batches of the IGTSS-179 sorbent followed by testing at 450°C. The results obtained also served to corroborate the fact that the IGTSS-179 copper based sorbent does not require an activation step to enhance its reactivity toward H₂S at 450° or 350°C.

Multi-cycle testing of two formulations of the new class of copper-based sorbents determined the effectiveness of one sorbent formulation (i.e., IGTSS-145) for desulfurization applications at 450°C and the effectiveness of another sorbent formulation (i.e., IGTSS-179) for those applications at 350° to 450°C.

OBJECTIVES

The overall objective of this study was to produce highly reactive and attrition resistant copper-based sorbents for removal of hydrogen sulfide from coal gas and to evaluate the effectiveness of the superior sorbent formulations in multi-cycle testing under process conditions closely simulating those of the leading Clean Coal Technology IGCC Demonstration Programs.

The specific objectives of this study were to:

1. Synthesize a number of formulations of copper-based sorbents.
2. Identify several formulations with acceptable attrition resistance properties.
3. Determine the superior sorbent formulations, based on chemical reactivity, regenerability, as well as all other relevant physical and chemical properties.
4. Determine the optimum operating conditions for sulfidation and regeneration.
5. Determine the overall durability of the superior formulations in multi-cycle testing at optimum process conditions.

INTRODUCTION AND BACKGROUND

Integrated Gasification Combined-Cycle (IGCC) Power Plants and Integrated Gasification Fuel Cell (IGFC) Power Generation Technologies are among the leading contenders for coal conversion. Coal gas desulfurization to sufficiently low levels at elevated temperatures is now recognized as crucial to efficient and economic coal utilization in advanced IGCC and IGFC power generation processes. The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials which 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 additional desired features of the sorbents.

The zinc-based sorbents, such as zinc titanate, have been shown to suffer from zinc volatilization at elevated temperatures, leading to sorbent deterioration, increasing sorbent replacement costs and the overall cost of hot gas cleanup processes. Copper-based sorbents, because of the high melting point of the metal, do not suffer from this problem.

A novel copper-chromite sorbent was developed in a recent ICCI-funded project for hot coal gas desulfurization in a fluidized-bed reactor. The results obtained in this previous study indicated that the copper-chromite sorbent produced in granular form (i.e., CuCr-29) had much higher attrition resistance compared to a commercial granular zinc titanate

sorbent (i.e., UCI-4169), as well as excellent desulfurization efficiency. Furthermore, unlike most zinc titanate sorbents, the reactivity of IGT's CuCr-29 copper-chromite sorbent gradually and consistently improved during the 20 cycles tested.

The sorbent preparation techniques developed at IGT in the course of earlier ICCI-funded projects have been directly applied to produce highly reactive sorbents. Furthermore, to minimize attrition losses and achieve optimum packing efficiency, a special pelletization technique has been used to produce spherical, durable, and highly reactive sorbent pellets and granules for moving-bed and fluidized-bed applications, respectively.

The research and development for high-temperature desulfurization of fuel gases has been sponsored primarily by the Morgantown Energy Technology Center (METC) of the United States Department of Energy (U.S. DOE). Over the last two decades, a number of studies have been reported on high-temperature H₂S removal, primarily using various transition metal oxides as regenerable sorbents.⁽¹⁻³⁾

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.⁽²⁻⁵⁾ The thermodynamic equilibrium for sulfidation of ZnO is quite favorable, yielding desulfurization down to a few ppm H₂S. The sulfidation kinetics of ZnO, however, are much slower⁽⁶⁾ compared to those 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.

In recent years, it has been shown that certain mixed oxides have superior properties compared to single oxides for hot gas cleanup.^(4,5,7-9) A compound of zinc and iron oxides, zinc ferrite (ZnFe₂O₄) developed by DOE/METC has reached pilot-stage testing for desulfurization of low-Btu gases.^(10,11) The H₂S removal efficiency of ZnFe₂O₄ is similar to ZnO because zinc ferrite is converted into a mixture of ZnO and Fe₃O₄ when exposed to the reducing fuel gas. Similarly, the rate of zinc loss (via zinc vaporization) is the same in both ZnFe₂O₄ and ZnO, limiting the application of zinc ferrite to temperatures below 550°C. Long-term "life cycle" testing of zinc ferrite at 550°C has indicated that the sorbent reactivity toward H₂S gradually decreases in the cyclic process requiring "fresh sorbent makeup" to maintain the desired level of desulfurization efficiency in the process.

Because of the apparent limitations of the zinc ferrite sorbent, many investigators have been conducting research to develop a superior mixed metal oxide sorbent.^(4,5,12-26)

Desirable characteristics of a hot gas cleanup sorbent include:

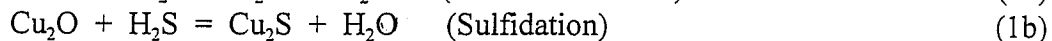
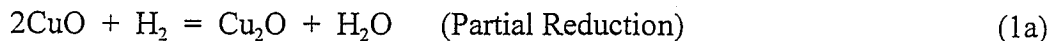
- Stable pore structure and high surface area
- Good reactivity toward H₂S
- Improved sulfidation equilibrium
- Improved regenerability

- High sorbent capacity
- Improved sulfur capture capability at higher temperature.

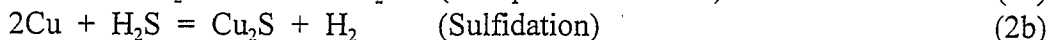
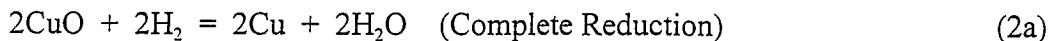
Work on zinc titanates such as ZnTiO_3 , Zn_2TiO_4 , and $\text{Zn}_2\text{Ti}_3\text{O}_8$,^(4,5,15) has shown that titanium oxide is a better alternative to iron oxide additives in terms of the higher stability of the titanates over the ferrite compounds of zinc, and their similar sulfidation equilibria. However, long term “life cycle” testing of a zinc titanate sorbent in the temperature range of 550° to 750°C has indicated that this sorbent also suffers from zinc losses leading to sorbent degradation and loss of reactivity in the cyclic process, as shown in Figures 1 and 2.⁽²⁰⁾

The loss of reactivity can generally be used to estimate the fresh sorbent “make up” rate, that is believed to be one of the key factors in determining the overall cost of hot gas cleanup processes. Mojtahedi and Abbasian⁽²¹⁾ have shown that straight line extrapolation of the data obtained in “life-cycle” tests with zinc titanate will lead to an estimated annual fresh sorbent makeup rate of up to 20 times the initial bed inventory. The results suggest that development of other types of sorbents, especially non zinc-based, should be pursued to insure the viability of hot gas desulfurization processes.

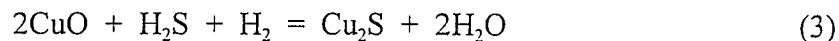
Copper-based sorbents do not suffer from metal volatility problems, hence, they could be used at elevated temperature without loss of reactivity associated with metal vaporization. Bulk copper oxide, however, suffers from thermodynamic limitations and has not been considered as a practical sorbent. In contact with a reducing gas containing H_2S and H_2 (or CO) the following reactions take place:



or



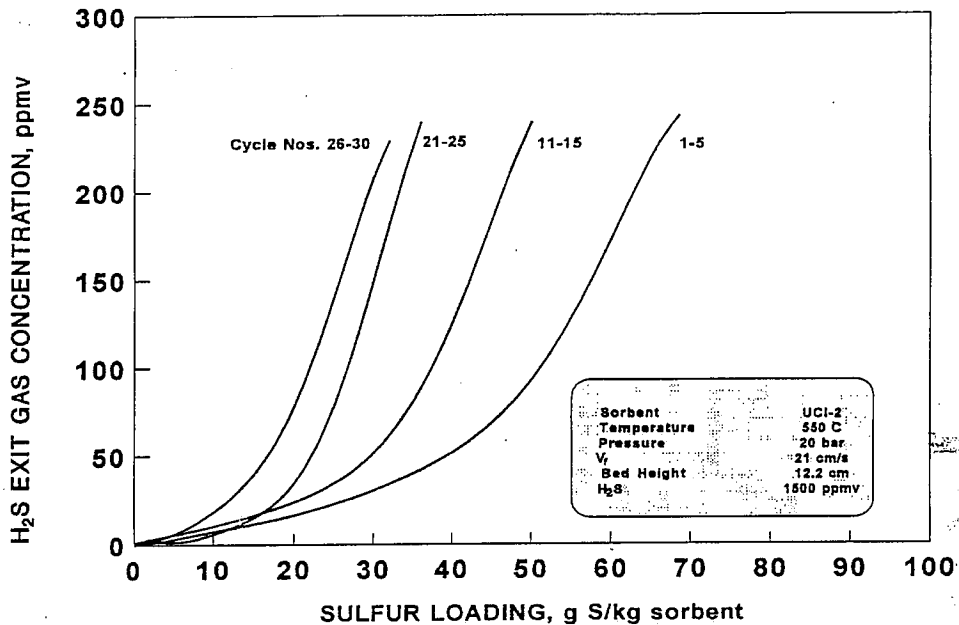
Combining the reduction and sulfidation reactions will result in the overall sulfidation reaction:



In view of the large $\text{H}_2/\text{H}_2\text{S}$ ratio and the ease of reduction in Reactions (1a and 2a), sulfidation will be governed by the equilibrium of Reaction (2b) which usually results in an insufficient level of desulfurization. Moreover, agglomeration of the metallic copper produced by reduction would result in a material of low surface area and poor kinetics. However, the sorbent performance can be improved by combining copper oxide with other oxides to improve the sorbent stability against reduction in fuel gas atmospheres.

The principal investigator of this program has studied copper-based sorbents in earlier ICCI-funded programs.⁽²²⁻²⁹⁾ In one such program, the sorbents studied included oxides of

chromium, cerium, aluminum, magnesium, manganese, titanium, iron, and silicon. The results of this study indicated that mixed binary oxides of copper and chromium were the most promising sorbents for high temperature hot gas cleanup applications.⁽²³⁻²⁸⁾ Further testing of the copper-chromite sorbent indicated that although the sorbent is reduced in the fuel gas environment, excellent desulfurization efficiency, similar to that of copper oxide, can be obtained during the early stages of sulfidation.



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Figure 1. H₂S BREAKTHROUGH CONCENTRATION IN FLUIDIZED-BED WITH A ZINC TITANATE SORBENT

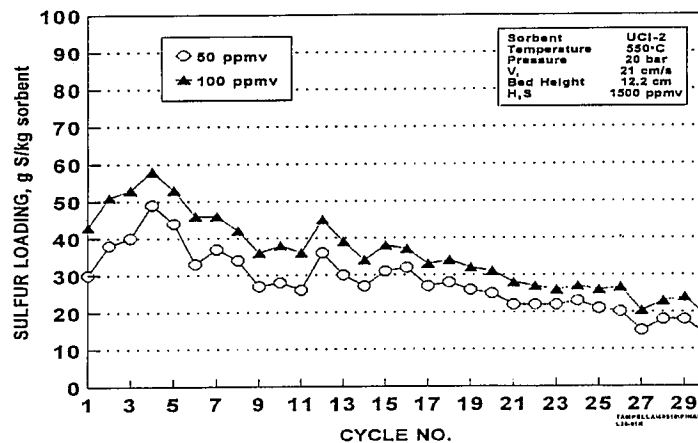


Figure 2. SULFUR LOADING OF A ZINC TITANATE SORBENT IN SUCCESSIVE CYCLES

In a recent ICCI-funded project, IGT developed a novel copper-chromite sorbent (i.e., CuCr-29), in granular form, for hot coal gas desulfurization in a fluidized-bed reactor. Figure 3 shows the results of attrition tests conducted in a sonic attrition unit with the CuCr-29 sorbent, a commercial granular zinc titanate sorbent (i.e., UCI-4169), as well as a dolomite and a limestone. These results indicate that the attrition resistance of the CuCr-29 is far superior to that of the UCI-4169 which has successfully been tested in a pilot scale fluidized-bed desulfurization unit.⁽³¹⁾

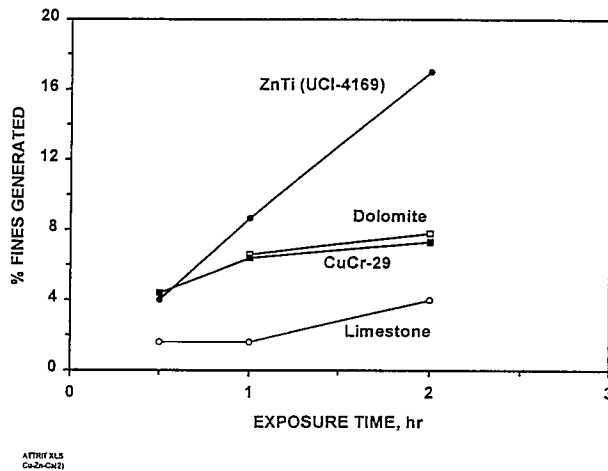


Figure 3. ATTRITION RESISTANCE OF VARIOUS SORBENTS

A fortuitous feature of the CuCr-29 sorbent is its capability to achieve extremely low levels of H_2S in the cleaned fuel gas even at high temperatures, since this sorbent is stabilized against complete reduction to elemental copper. The effect of temperature on sorbent desulfurization performance in the range of 550° to 650°C is shown in Figure 4. This figure clearly indicates that a sulfidation temperature of 600°C achieved superior desulfurization efficiency (< 1 ppm H_2S) and the highest effective sulfur capacity.

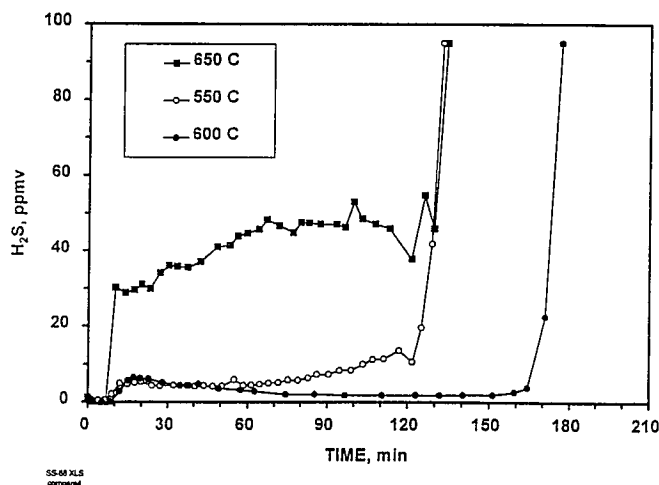


FIGURE 4. EFFECT OF TEMPERATURE ON DESULFURIZATION PERFORMANCE OF CuCr-29 SORBENT

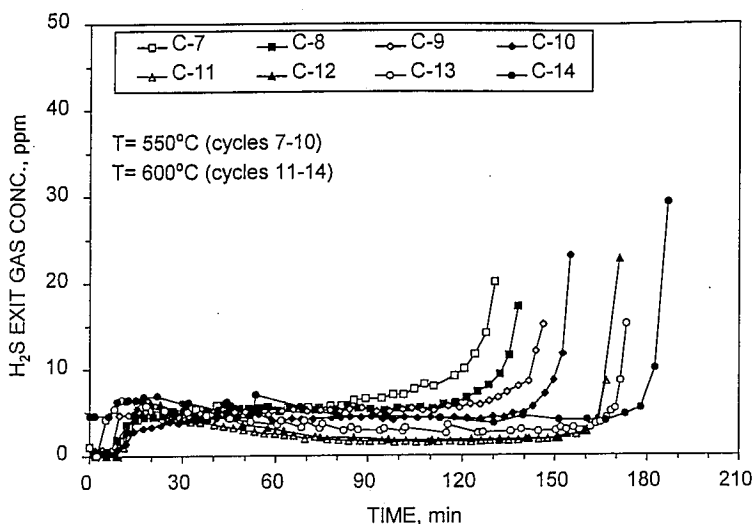


FIGURE 5. EFFECT OF MULTI-CYCLE TESTING ON DESULFURIZATION PERFORMANCE OF CuCr-29 SORBENT

The desulfurization reactor can have a fixed-, a moving-, or a fluidized-bed design. The fixed-bed design has been shown to reduce the H_2S content of the cleaned gas to very low levels; however, its operation is not continuous and requires large-scale high temperature valves. Interest has shifted to moving- and fluidized-bed systems due mainly to the sorbent decrepitation problem experienced with fixed-beds. Moving-beds offer several advantages over fixed-bed systems such as improved process control and the ability to maintain more favorable sulfur concentration and regeneration temperatures.

Moving-bed systems, shown in Figure 6, have been under development mainly at General Electric. The Hot Gas Cleanup (HGCU) Process has been developed to remove sulfur, particulates, and halogens from high-temperature fuel gas streams using regenerable mixed metal oxide sorbents suitable for moving-bed applications.⁽³²⁾ The ultimate goal is to incorporate this technology into advanced IGCC power generation systems, such as the Tampa Electric Clean Coal Demonstration Program. The HGCU system has been designed to process approximately 8000 lb/hr of low heating value fuel gas produced by the GE fixed-bed gasifier. The raw fuel gas is provided to the HGCU system at about 300 psig and 550°C.

In the moving-bed configuration, the sulfided sorbent is removed, continuously or in a batch manner, from the bottom of the sulfidation vessel and fed to a second vessel for regeneration. The sulfided sorbent is continuously replaced with fresh regenerated sorbent. Consequently, both the crush strength of the sorbent and its sorption capacity after repeated cycling are of critical importance. The desired characteristics of a sorbent suitable for moving-bed fuel gas desulfurization systems are:⁽³³⁾

- A high theoretical sulfur capacity and a high reactivity for both sulfidation and regeneration;
- High crush strength and resistance to attrition or physical disintegration; and
- Suitable pellet size and shape to promote good bulk flowability.

Therefore, one of the major challenges in the development of moving-bed systems remains the development of attrition resistant and sufficiently reactive regenerable sorbents in the temperature range of current practical interest, i.e., 350° to 650°C.

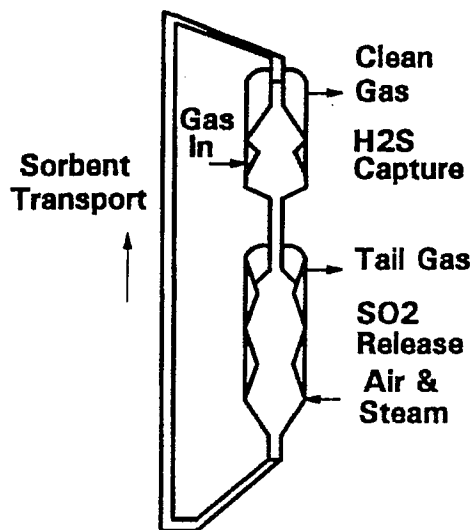


FIGURE 6. SCHEMATIC DIAGRAM OF A MOVING-BED HOT GAS CLEANUP SYSTEM

GE's HGCU system has utilized several mixed metal oxide sorbents including zinc ferrite, zinc titanate, and Z-Sorb. As stated earlier, one major problem associated with all zinc-based sorbents is sulfate formation which is found to occur whenever SO_2 is present in the regeneration gas. Sulfation leads to volume expansion and swelling of sorbent pellets eventually causing them to spall and crack. For example: a 5 to 6-mm diameter sulfided pellet has been reported to expand to 9 mm after regeneration when sulfate was formed.⁽³⁴⁾ Certainly, in a moving-bed operation some of the pellets will be saturated with sulfur and the regeneration gas will contain some SO_2 . Therefore, sulfate formation is unavoidable along with accompanying spalling and cracking. Sorbent spalling is unacceptable because it results in larger pressure drops across the reactor causing lost efficiency and increased operating and maintenance costs.

Siriwardane et al.⁽³⁵⁾ showed that the degree of spalling can be reduced by adding molybdenum to zinc titanate sorbents. It is interesting to note that sorbent spalling was observed in all tests except where the sorbent sulfur loading was less than 3% (i.e., 3

gS/100 g sorbent), which is well below the minimum sulfur capacity requirement for moving-bed applications (i.e., 6 to 7 lbs sulfur per ft³ bed).⁽³⁶⁾

One problem faced by many of the pellet-based sorbent systems is that the pellets are typically formed through extrusion processes which provide essentially cylindrical-shaped pellets. Spherical pellets are more desirable because they offer better handling and packing characteristics. The spherical shape also eliminates the edges which are the site of degradation due to stresses during use as well as handling of typical cylindrical sorbent pellets.

The sorbent preparation techniques developed at IGT in the course of earlier ICCI-funded projects have been directly applied to produce highly reactive and attrition resistant sorbent pellets for moving-bed applications. Furthermore, to minimize attrition losses and achieve optimum packing efficiency, the applicability of a special pelletization technique that was developed by one of the co-investigators,⁽³⁷⁾ has been extended to the production of durable and highly reactive spherical copper-based sorbent pellets.

This research program focused on the production of highly reactive and attrition resistant copper-based sorbents and on the evaluation of the effectiveness of the superior sorbent formulations in multi-cycle tests, under process condition closely simulating those of the leading Clean Coal Technology IGCC Demonstration Programs.

EXPERIMENTAL PROCEDURES

This project was divided into the following three tasks:

Task 1. Sorbent Synthesis and Characterization

Task 2. Evaluation of Sorbent Reactivity and Regenerability

Task 3. Multi-Cycle Durability Studies

The experiments in this program were conducted in the ambient pressure batch packed-bed reactor. The schematic diagram of this reactor system is shown in Figure 7.

Task 1. Sorbent Synthesis and Characterization

The objective of this task was to prepare copper-based sorbents with the desired characteristics for testing in Task 2 and Task 3.

In this program, a number of formulations of attrition resistant copper-based sorbent pellets ($d_p = 2 - 5$ mm) as well as granules ($d_p = 0.1 - 0.3$ mm) were produced. The starting materials and sorbent composition were generally comparable to those identified in a recent ICCI-funded project.⁽²⁹⁾ However, the sorbent composition was modified to suit the desired application. Such modifications included additives (to enhance and/or

maintain porosity) and thermal treatment history (i.e., induration temperature and time). An inorganic binder material, such as bentonite or other types of clay, was also added to the powder to enhance the physical strength of the sorbents and also to render the starting powder more amenable to pelletization. Small quantities of each formulation were prepared for initial screening based on crush strength and attrition resistance.

Initially, emphasis was placed on developing a method for the preparation of copper-chromite powders that were easily amenable to pelletization. Copper-chromite sorbents with sufficient mechanical strength, in the form of spherical pellets as well as tablets, were prepared. An Instron Universal Testing Instrument (Model 1011) was used to perform mechanical tests on copper-chromite pellets. In a typical test, a pellet was loaded onto a loading frame and a moving crosshead applied a load to the pellet at a commanded speed, in accordance with ASTM procedures. A calibrated transducer in the moving crosshead then measured the applied load at breakage. This load is known as the crush strength and is given in force divided by contact length (i.e., lbs/mm of pellet diameter).

A total of fourteen (14) formulations of copper-based sorbents were prepared which included ten (10) formulations of copper-chromite. The results from crush strength tests conducted on these sorbent pellets indicated that several formulations had crush strengths exceeding the requirement for moving-bed applications. For example, one such pellet formulation (i.e., CuCr-37) had an average crush strength exceeding 15 lbs/mm, which is more than twice the requirement specified by the Department of Energy for moving-bed sorbents.

Two copper-chromite sorbent formulations in the form of spherical pellets (i.e., CuCr-41P and CuCr-42P), with significantly different porosities were prepared to determine the effect of porosity on the crush strength as well as the reactivity of the sorbent toward H_2S . The average particle diameter of the spherical pellets in both moving bed formulations was about 0.3 cm. The CuCr-42P pellet formulation was more porous and had a lower crush strength than the CuCr-41P formulation. All copper-chromite sorbent formulations prepared in this program required an activation step to enhance their reactivities toward H_2S , as discussed later in this report.

A new class of copper-based sorbent formulations, with significantly different compositions than copper-chromite sorbents, was prepared for lower temperature application. These new sorbents, by virtue of their make-up, did not require an activation step to enhance their reactivities toward H_2S even at lower temperatures, as discussed in more detail below.

Task 2. Evaluation of Sorbent Reactivity and Regenerability

The objective of this task was to identify the superior sorbent formulations and optimum operating conditions for "long-term" durability studies.

The effectiveness of the sorbents at the optimum operating conditions in terms of desulfurization and regeneration efficiencies as well as their physical/chemical stability in the successive sulfidation/regeneration cyclic tests were determined in the packed-bed reactor. The approximate values and ranges of operating parameters for evaluation of the selected sorbents in the packed-bed reactor system are presented in Table 1. The compositions of the simulated fuel gases used are shown in Table 2, and were chosen to simulate the Texaco and KRW coal gases in the Tampa Electric moving-bed and Sierra Pacific (Pinon Pine) IGCC demonstration projects. Tampa Electric and Sierra Pacific are two of six (6) major Clean Coal Demonstration Programs in the U.S. and are designed to use GE's moving-bed and KRW's transport reactor technologies for hot gas desulfurization, respectively.

The schematic diagram of the packed-/fluidized-bed reactor unit used in this task is shown in Figure 7. The unit essentially consists of a quartz reactor which is externally heated by two electric furnaces, equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, and monitoring the reactor pressure. The reactor system is configured for flowing gas downwards for both sulfidation and regeneration. An upward flow direction is used for fluidized-bed application. A coarse porous quartz frit near the middle of the 2.5-cm ID by 0.8-m tall reactor is used to support the sorbent bed. A thermocouple sheathed with a 3-mm closed-end alumina tube is used to measure temperature. Temperature is recorded as a function of time using a computerized data acquisition system. Teflon^R tubing is used to convey SO₂/H₂S-containing exit gas at temperatures lower than 200°C.

Table 1. OPERATING CONDITIONS FOR SORBENT EVALUATION

<u>Parameter</u>	<u>Condition</u>
Sorbent Formulations	up to 4
Mode of Operation	Fixed Bed
Temperature	538° to 650°C
Pressure	1 atm
Space Velocity	1000 to 4000 hr ⁻¹ (25°C, 1 atm)

Table 2. SIMULATED FUEL GAS COMPOSITION FOR SORBENT EVALUATION

<u>Component</u>	<u>TEXACO</u>	<u>KRW</u>
	<u>Vol. %</u>	<u>Vol. %</u>
H ₂	30	15
CO	45	21
CO ₂	10	6
H ₂ O	12	9
N ₂	2	49
H ₂ S	1	0.1

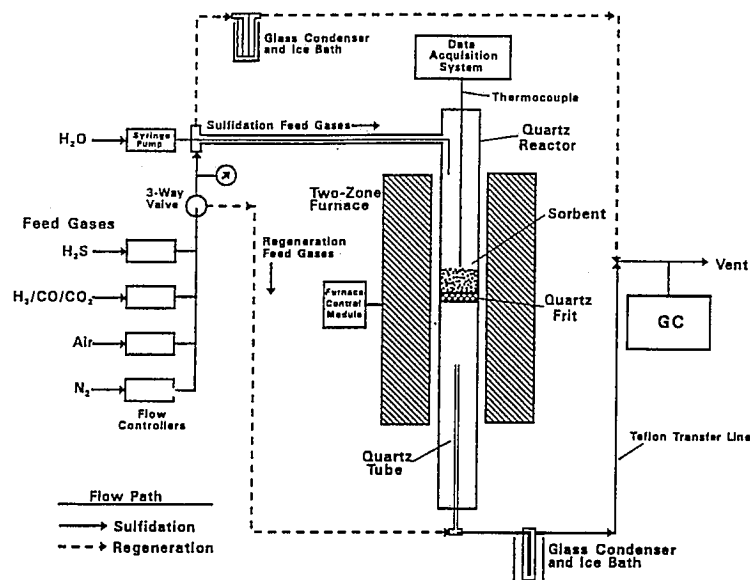


Figure 7. SCHEMATIC DIAGRAM OF THE AMBIENT PRESSURE PACKED-FLUIDIZED-BED REACTOR SYSTEM

In a typical test, a known quantity of each sorbent is loaded into the packed-bed reactor and the reactor is brought to the desired temperature and exposed to a gas mixture containing the desired level of H_2S . The reactor exit gas is analyzed by a gas chromatograph equipped with appropriate detectors for determination of the H_2S content. Sulfidation of the sorbent is carried out by feeding the H_2S -containing gas until the H_2S concentration in the reactor exit gas reaches approximately 500 ppmv. Following sulfidation, the reactor is switched to the regeneration mode by stopping the flow of sulfidation gas to the reactor and bringing the reactor to the desired reaction temperature with continuous passage of nitrogen flowing through the reactor. Once the desired temperature is attained, the flow of regeneration gas is begun. A slipstream of the gas from the reactor is diverted to the gas chromatograph for measurement of H_2S and SO_2 concentrations. Prior to each test, the gas chromatograph is calibrated using calibration standard gas samples.

A series of tests was conducted to determine the effect of the activation procedure on the effective sulfur capacity as well as on the reactivity of the sorbents toward H_2S . As indicated earlier, all copper-chromite sorbent formulations prepared in this program were found to require an activation step to enhance their reactivities toward H_2S . Following the activation step, a selected number of copper-chromite sorbent formulations that had acceptable attrition resistance properties were subjected to a series of sulfidation/regeneration cycles in the ambient pressure packed-bed unit to demonstrate their durability and regenerability. These tests were conducted at a space velocity of 2000 hr^{-1} at a sulfidation temperature of 600°C . The results of these tests are presented and discussed in the section "RESULTS AND DISCUSSION."

Another series of tests was conducted to evaluate the sulfidation performance of the IGTSS-145 copper-based sorbent at 600°C, as well as its regenerability at 725°C. As mentioned earlier, the composition of this sorbent differs significantly from that of copper-chromite sorbents. One remarkable feature of this formulation is that it did not require an activation step to enhance its reactivity toward H₂S, unlike the copper-chromite sorbents developed earlier (i.e., CuCr-29, CuCr-41G, etc.). Based on the encouraging results obtained with this formulation at 600°C and the fact that current emphasis is shifting toward development of lower temperature desulfurization sorbents a modified version of this sorbent formulation (i.e., IGTSS-179) was prepared and its sulfidation performance in the temperature range of 350° to 450°C was evaluated. The suitability of the two copper chromite sorbents (i.e., CuCr-29 and CuCr-41G) was also assessed at these lower temperatures. These tests were conducted in the ambient pressure packed-bed unit at a space velocity of 2000 hr⁻¹. Regeneration was carried out using a 6% O₂-N₂ gas mixture. The results of these tests are presented and discussed in the section "RESULTS AND DISCUSSION."

Task 3. Multi-Cycle Durability Studies

The objective of this task was to determine the suitability of the superior sorbent pellets and/or granules for long-term application in hot gas cleanup processes.

The tests in this task were carried out in the ambient pressure packed-bed reactor. The schematic diagram of this unit is shown in Figure 7. Based on the data generated and the expertise gained in previous ICCI-funded projects, it is believed that about 5 to 10 cycles are required for each set of conditions (i.e., composition, temperature, and pressure) to assess the physical/chemical stability of each sorbent. Therefore, in this task, seven (7) superior sorbent formulations selected in Task 2 were subjected to multi-cycle testing of sulfidation/regeneration.

The copper-chromite sorbent formulations prepared early in this program (i.e., CuCr-36 and CuCr-37) were subjected to a series of nine (9) sulfidation/regeneration cycles in the packed-bed reactor using a simulated coal gas for sulfidation and oxygen-deficient air for regeneration. Sulfidation tests with both formulations were carried out at 650°C during the first four cycles, and at 600°C in all subsequent cycles. The sorbent formulations CuCr-41G, CuCr-41P, and CuCr-42P were each subjected to five (5) cycles of sulfidation/regeneration at 600°C. Two of the new class of copper-based sorbents (i.e., IGTSS-145 and IGTSS-179) were subjected to multi-cycle testing in the packed-bed reactor to evaluate their effectiveness at 350° to 450°C. The results of these tests are presented and discussed in the section "RESULTS AND DISCUSSION."

RESULTS AND DISCUSSION

The crush strengths of a selected number of copper-chromite sorbents prepared were determined in accordance with ASTM procedures. The results indicate that two of the

sorbent formulations in the form of cylindrical tablets as well as spherical pellets (designated as CuCr-36 and CuCr-37, respectively) had average crush strengths exceeding 15 lbs/mm, which is more than twice the requirement specified by the Department of Energy for moving-bed sorbents.

Two series of tests, each consisting of nine cycles, were conducted with the CuCr-36 and CuCr-37 sorbent pellets in the ambient pressure packed-bed unit to demonstrate their durability and regenerability. These tests were conducted at a space velocity of 2000 hr^{-1} in the sulfidation temperature range of 600° to 650°C . The H_2S breakthrough curves for the two series of tests are presented in Figures 8-10. The results indicate that similar to the CuCr-29 copper chromite granules, the sorbent sulfur capacity improved with each cycle, particularly during the first few sorbent "activation" cycles. However, as expected, because of the larger size and lower packing density of the pellets, the effective sorbent capacity of the pellets is lower than that of the granules.

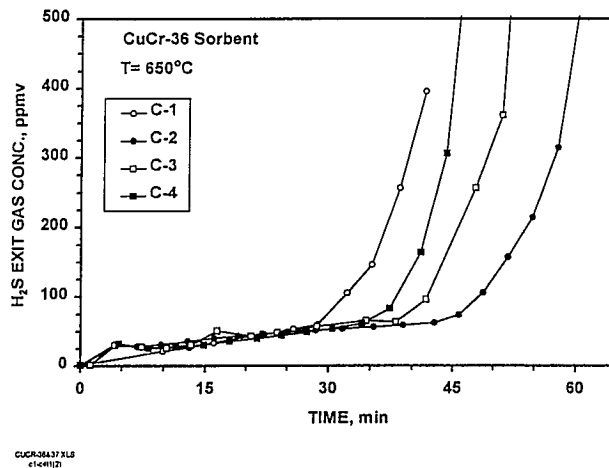


Figure 8. RESULTS FROM FIRST FOUR ACTIVATION CYCLES AT 650°C FOR CuCr-36 SORBENT PELLETS

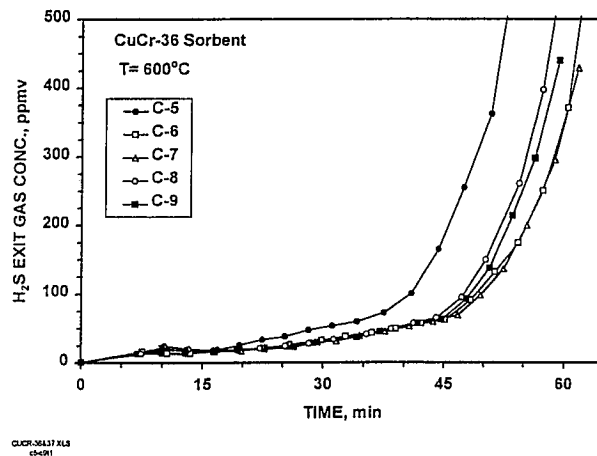


Figure 9. RESULTS FROM CYCLES 5-9 DURING MULTI-CYCLE TESTING OF CuCr-36 SORBENT PELLETS AT 600°C

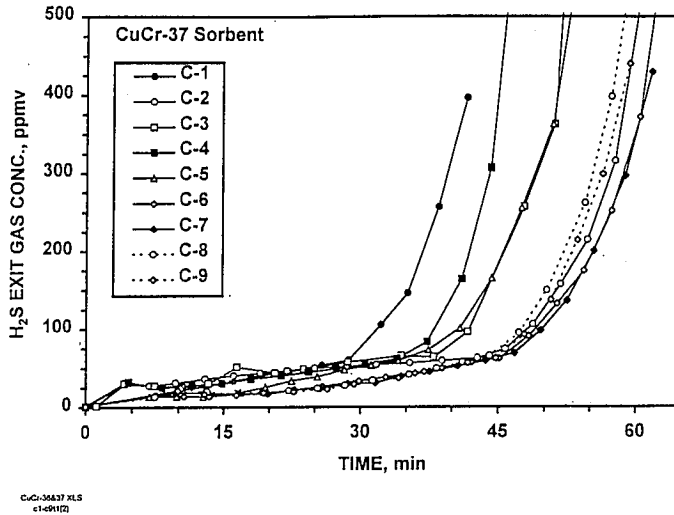


Figure 10. BREAKTHROUGH CURVES FOR CuCr-37 SORBENT PELLETS DURING SULFIDATION AT 600°C

The H₂S breakthrough curves for the granular CuCr-41G sorbent formulation, before and after activation, are shown in Figure 11, indicating that the reactivity of this sorbent strongly depends on the preceding activation step. As shown in Figure 11, the effective sulfur capacity of the CuCr-41G sorbent after activation increased by 500%. Following activation, the granular CuCr-41G sorbent formulation was subjected to a series of five (5) sulfidation/regeneration cycles. The results obtained, shown in Figure 12, indicate that this sorbent is highly reactive toward H₂S, reaching a breakthrough time of over two hours with a pre-breakthrough H₂S concentration in the cleaned gas of below 5 ppmv.

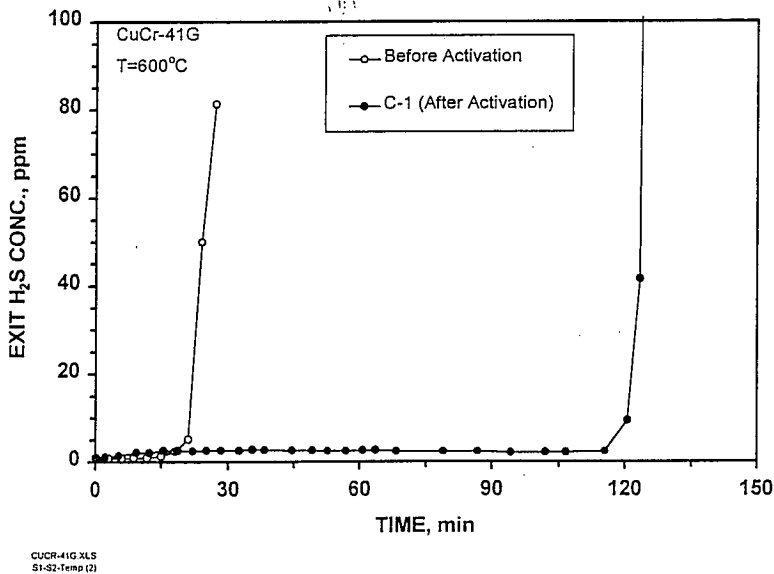


Figure 11. EFFECT OF ACTIVATION PROCEDURE ON ENHANCEMENT OF GRANULAR CuCr-41G SORBENT REACTIVITY

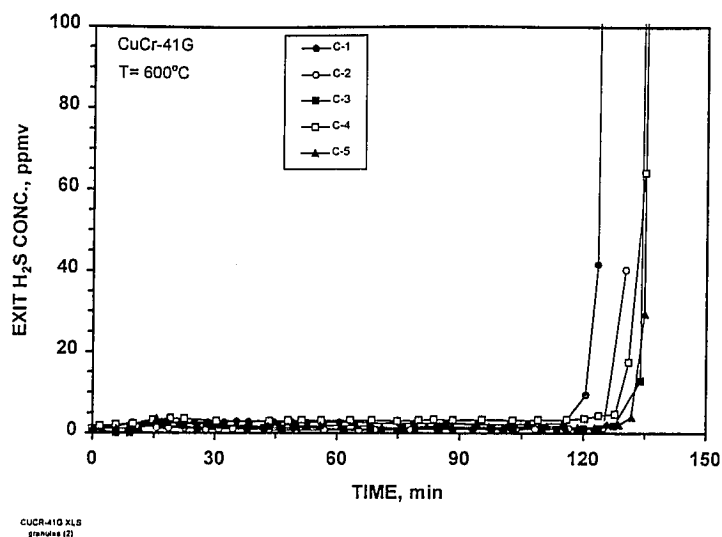


Figure 12. BREAKTHROUGH CURVES FOR THE GRANULAR CuCr-41G SORBENT DURING SULFIDATION AT 600°C

The H₂S breakthrough concentration for the CuCr-41P sorbent formulation is shown in Figure 13. The results indicate that the reactivity of the CuCr-41P pellet formulation toward H₂S at 600°C is sufficiently high, although, as expected the effective capacity of the pellet formulation is lower than that of the granules. The pre-breakthrough H₂S concentration in the cleaned gas in the pellet tests was below 10 ppmv, qualifying this pellet formulation for hot fuel gas desulfurization based on moving-bed technology.

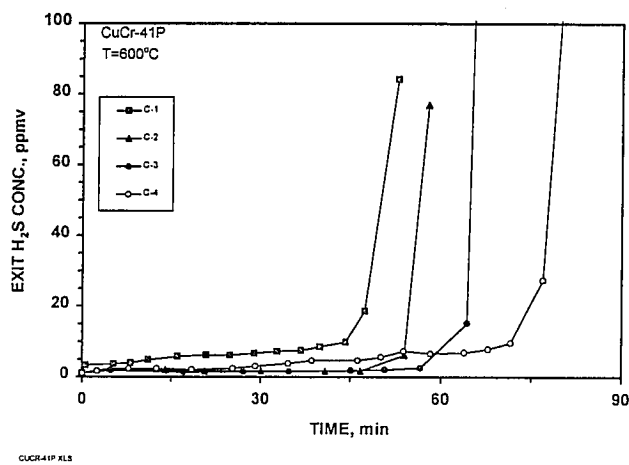


Figure 13. BREAKTHROUGH CURVES FOR THE CuCr-41P PELLETS DURING SULFIDATION AT 600°C

Figure 14 shows the pre-breakthrough H₂S concentration for the CuCr-42P sorbent formulation. The results indicate that this pellet formulation, which is more porous than the CuCr-41P formulation, has a higher reactivity, and a higher effective sulfur capacity

compared to the CuCr-41P sorbent formulation. However, the higher porosity resulted in lower crush strength, which may be inadequate for long-term application.

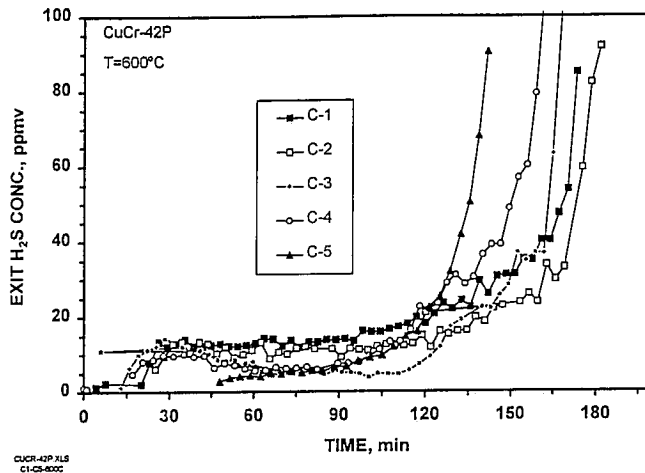


Figure 14. BREAKTHROUGH CURVES FOR THE CuCr-42P PELLETS DURING SULFIDATION AT 600°C

The H₂S breakthrough curves for the IGTSS-145 formulation are shown in Figure 15 for sulfidation cycles 1 through 5 at 600°C. One remarkable feature of this formulation is that, although it is highly attrition resistant, it did not require an activation step to enhance its reactivity toward H₂S, unlike the copper-chromite sorbents (i.e., CuCr-29 and CuCr-41G). As shown in Figure 15, the pre-breakthrough times for the five sulfidation tests conducted ranged from 3 to about 4 hours. Although the pre-breakthrough time during sulfidation appears to be slowly decreasing in the cyclic process, the performance of this formulation is significantly better than those obtained with CuCr-29 and CuCr-41G copper chromite sorbents both from a sulfur removal efficiency as well as sorbent utilization viewpoints. In addition, IGTSS-145 copper-based sorbent was found to be readily regenerable at 725°C with a 6% O₂-N₂ gas mixture, as shown in Figure 16.

Following the favorable results obtained with the IGTSS-145 copper-based sorbent at 600°C, and given the current strong industrial interest in the development of regenerable sorbents for lower temperature applications (i.e., 350° to 538°C), a modified version of IGTSS-145 (i.e., IGTSS-179) was prepared for testing in this lower temperature range. The results from five (5) sulfidation tests conducted using the IGTSS-179 sorbent are reported in Figure 17, indicating that this sorbent did not require an activation step to enhance its reactivity at 450°C. As shown in Figure 17, the average pre-breakthrough time for this sorbent at 450°C was about 2.5 hours. Even at 350°C the results shown in Figure 17 indicate that this sorbent is highly reactive toward H₂S, reaching a breakthrough time of over 100 minutes during cycle 4, and 2.5 hours during cycle 5, with a pre-breakthrough H₂S concentration in the cleaned fuel gas of below 1 ppmv.

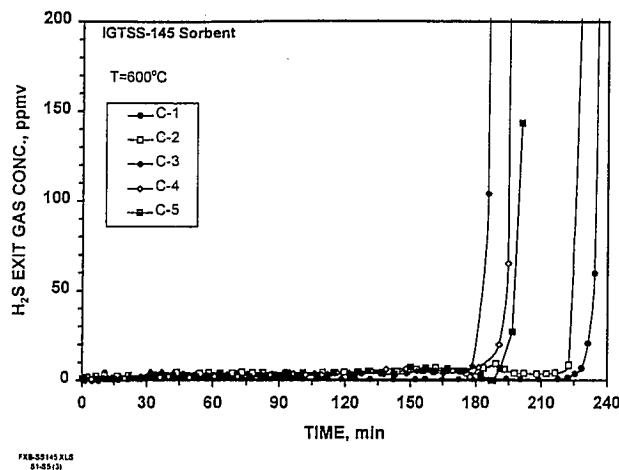


Figure 15. BREAKTHROUGH CURVES FOR THE IGTSS-145 SORBENT DURING SULFIDATION AT 600°C

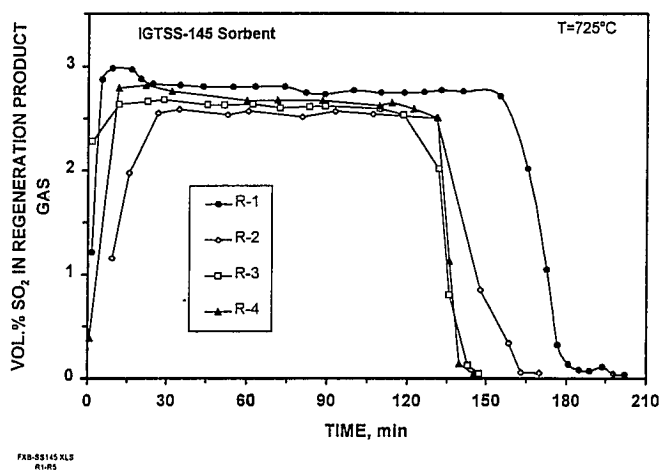


Figure 16. SO₂ CONTENT OF THE REACTOR EFFLUENT DURING REGENERATION OF THE IGTSS-145 SORBENT AT 725°C

The results obtained with the CuCr-29 copper-chromite sorbent at 350° and 450°C are reported in Figure 18 for cycles 1 and 3. Cycle 2 served as an activation step. As shown in Figure 18, the results indicate that the reactivity of the CuCr-29 sorbent, even following activation, is considerably lower than the reactivity of the IGTSS-179 sorbent.

The performance of the CuCr-41G sorbent at 350°C is reported in Figure 19 for cycles 4 and 5. Despite being activated and its lower strength (because of its higher porosity) compared to the IGTSS-179 sorbent, the effective sulfur capacity of the CuCr-41G sorbent was about 35% that of the IGTSS-179 sorbent at 350°C.

Given the excellent results obtained with the IGTSS-179 copper-based sorbent at lower temperatures, a second batch of this formulation was prepared and tested mainly to confirm the reproducibility of the sorbent preparation technique developed in this

program. The results from the first cycle using IGTSS-179 sorbent from two different batches are shown in Figure 20, clearly indicating the reproducibility of the sorbent preparation technique.

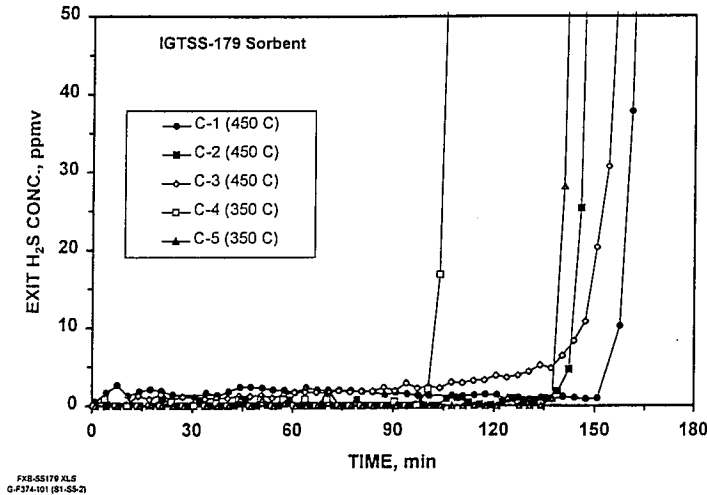


Figure 17. BREAKTHROUGH CURVES FOR THE IGTSS-179 SORBENT DURING SULFIDATION AT 350° AND 450°C

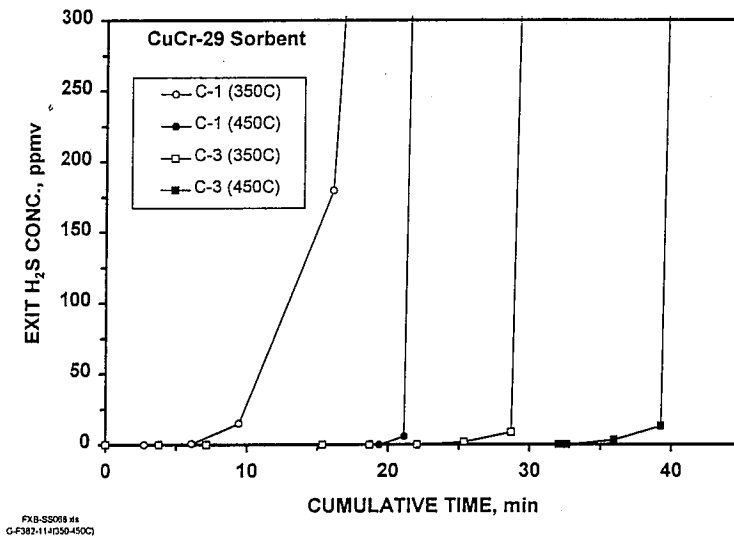


Figure 18. BREAKTHROUGH CURVES FOR THE CuCr-29 SORBENT DURING SULFIDATION AT 350° AND 450°C

Three series of multi-cycle testing involving sorbents IGTSS-145 and IGTSS-179 were then carried out to evaluate their performance in the lower temperature range. In the first series five (5) sulfidation/regeneration cycles were carried out using IGTSS-145 sorbent. The results from these packed-bed tests at 450°C are presented in Figure 21, clearly indicating the suitability of the IGTSS-145 sorbent for fuel gas desulfurization at this

temperature. As seen in Figure 21, no noticeable deterioration in sorbent desulfurization performance is observed during the five (5) cycles completed. The average pre-breakthrough time of 234 minutes for the five (5) cycles shown in Figure 21 corresponds to an average effective sulfur capacity of 9.3 g S/100 g sorbent at 450°C.

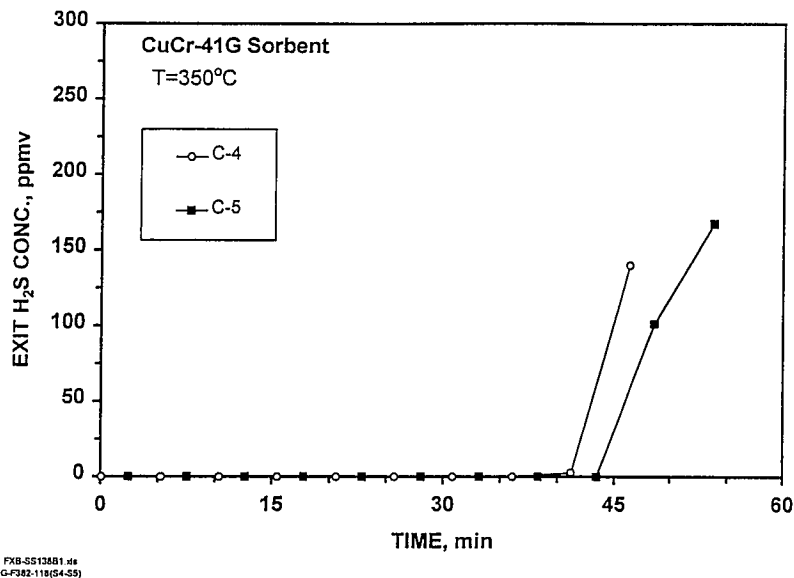


Figure 19. BREAKTHROUGH CURVES FOR THE CuCr-41G SORBENT DURING SULFIDATION AT 350°C (AFTER ACTIVATION)

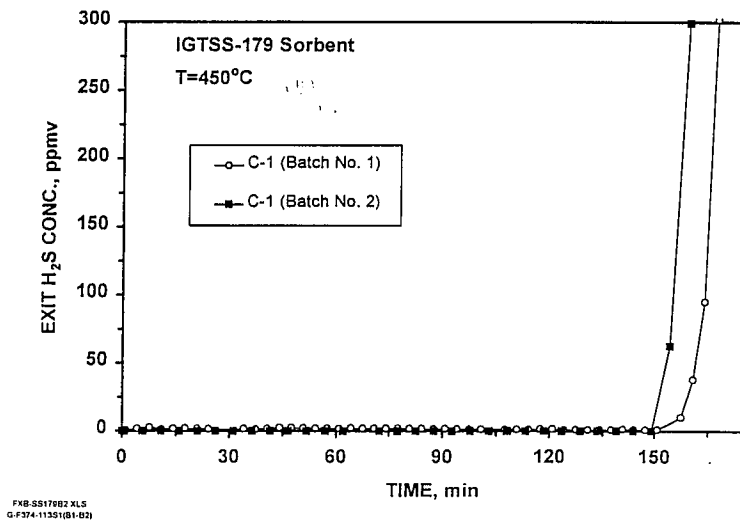


Figure 20. REPRODUCIBILITY OF THE IGTSS-179 SORBENT

The performance of the IGTS-145 sorbent was also evaluated at the lower temperature of 350°C. The results from a series of five (5) sulfidation/regeneration cycles completed on a fresh batch of the IGTS-145 sorbent are shown in Figure 22. As indicated in this figure, the performance of this sorbent appears to decline with cycling.

The performance of the IGTSS-179 sorbent was also evaluated at 350°C in a series of five (5) sulfidation/regeneration cycles. The results from the five sulfidation tests and the four intervening regeneration tests conducted are presented in Figure 23 and Figure 24, respectively. As shown in Figure 23, the sulfidation performance of the IGTSS-179 sorbent was quite consistent during the five cycles conducted at 350°C, achieving an average pre-breakthrough time of 148 minutes which corresponds to an average effective sulfur capacity of 6.3 g S/100 g sorbent. In addition, Figure 24 shows that the IGTSS-179 sorbent is readily regenerable at the lower regeneration temperature of 650°C.

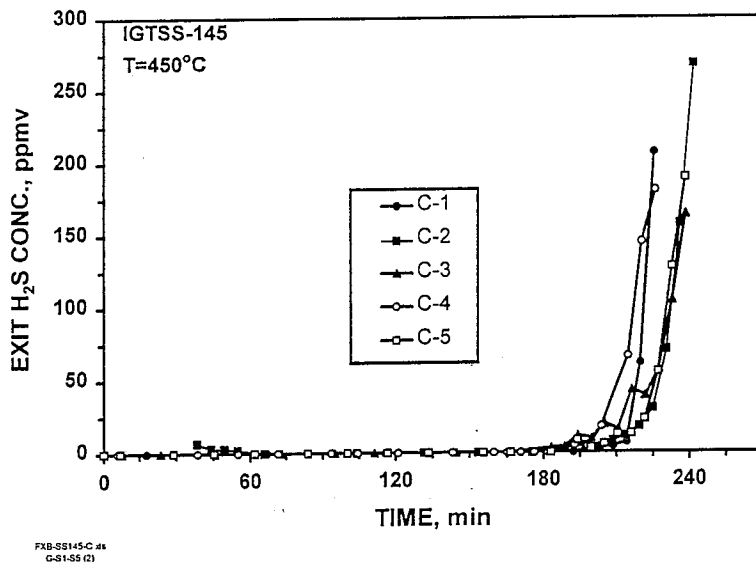


Figure 21. BREAKTHROUGH CURVES FOR THE IGTSS-145 SORBENT DURING SULFIDATION AT 450°C

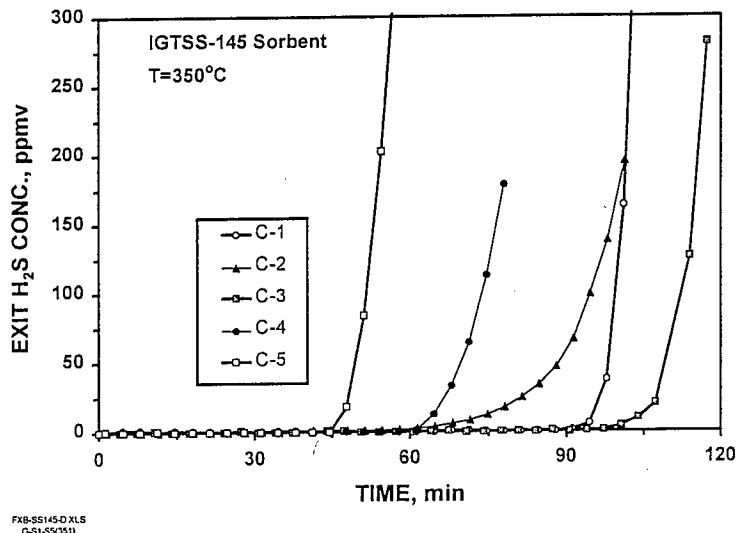


Figure 22. BREAKTHROUGH CURVES FOR THE IGTSS-145 SORBENT DURING SULFIDATION AT 350°C

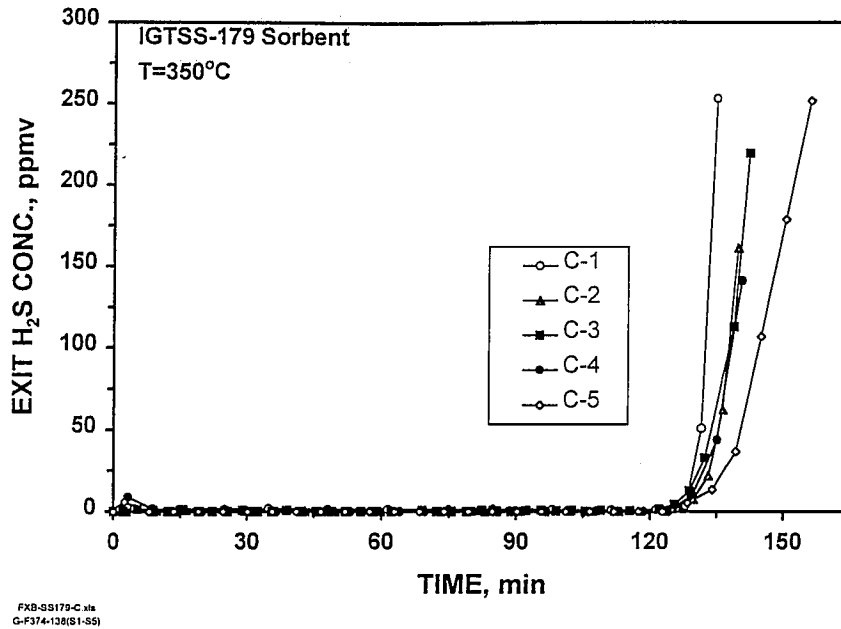


Figure 23. BREAKTHROUGH CURVES FOR THE IGTS-179 SORBENT DURING SULFIDATION AT 350°C

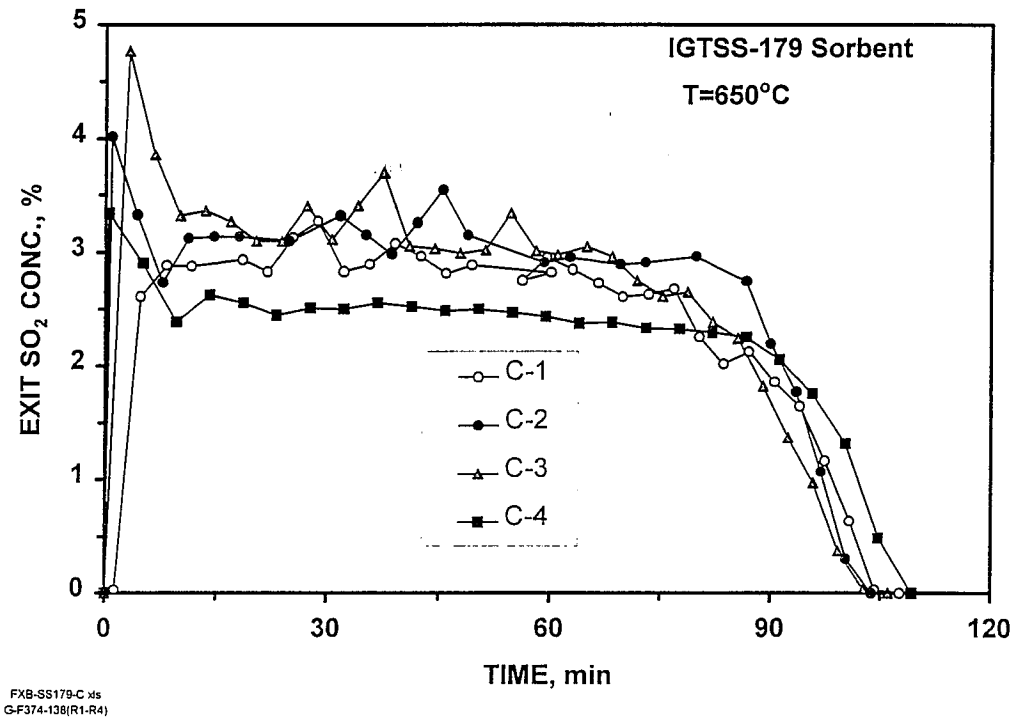


Figure 24. SO₂ CONTENT OF THE REACTOR EFFLUENT DURING REGENERATION OF THE IGTS-179 SORBENT AT 650°C

CONCLUSIONS AND RECOMMENDATIONS

The results obtained in this program indicate that the CuCr-36 and CuCr-37 copper-chromite sorbent pellets have high crush strengths as well as excellent reactivity toward H₂S in the temperature range of 600° to 650°C. The pre-breakthrough H₂S concentration in the cleaned gas is < 50 ppmv, qualifying these formulations for hot fuel gas desulfurization based on moving-bed technology.

Two formulations of a new class of copper-based sorbents (i.e., IGTSS-145 and IGTSS-179) performed remarkably well at 600°C, requiring no activation step despite their high attrition resistance.

The IGTSS-145 sorbent is also shown to be very effective for fuel gas desulfurization at 450°C, while the IGTSS-179 sorbent was found to have superior performance at the lower temperature of 350°C, achieving an average effective sulfur capacity of 6.3 g S/100 g sorbent at this temperature, with pre-breakthrough H₂S levels in the cleaned fuel gas of below 1 ppmv.

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