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### TECHNICAL REPORT

September 1, 1995, through November 30, 1995

# Project Title: DEVELOPMENT OF REGENERABLE COPPER-BASED SORBENTS FOR HOT GAS CLEANUP

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### **ABSTRACT**

The overall objective of this study is to determine the effectiveness of the copper-chromite sorbent (developed in previous ICCI-funded projects) for longer duration application under optimum conditions in the temperature range of 550°-650°C to minimize sorbent reduction and degradation during the cyclic process.

To achieve this objective, several formulations of copper chromite sorbents are prepared. These sorbent formulations are screened for their desulfurization and regeneration capability at predetermined temperatures and gas residence times. The durability of the best sorbent formulation identified in the screening tests is evaluated in "long-term" durability tests conducted at the optimum operating conditions. This includes testing the sorbent in pellet and granular forms in packed- and fluidized-bed reactors.

During this quarter, twenty one copper chromite-based sorbent formulations were prepared. Two sorbent formulations that have acceptable crush strength, designated as CuCr-10 and CuCr-21, were tested over 5 and 6 cycles respectively. The results indicate that both sorbents are reactive toward H2S at 650 °C and that the reactivity of the sorbents are relatively constant over the first 5 to 6 cycles. The H2S prebreakthrough concentrations were generally about 20 to 30 ppm, making them suitable for IGCC application.

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#### 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°C) 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 relies heavily on the development of regenerable sorbent materials which can efficiently reduce H2S from several thousand ppm 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.

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

A novel copper chromite sorbent has been developed under an earlier ICCI-funded project for much higher temperature application (750°-850°C). Although excellent desulfurization efficiency has been achieved with this sorbent at these extreme conditions, the results indicate that the sorbent will undergo reduction during sulfidation stage, reducing the sorbent capacity for high desulfurization efficiency. The results of the previous study also indicated that the rate of reduction of the copper chromite sorbent is significantly lower below 650°C, suggesting that to avoid loss of desulfurization efficiency, the hot gas cleanup application with this sorbent should be limited to 650°C.

This study focuses on the evaluation of the regenerable novel copper-chromite sorbents for hot gas cleanup application at 550° to 650°C in long duration cyclic tests to provide the data necessary for direct comparison with zinc titanate sorbents.

Several formulations of copper chromite sorbent are produced in granules (i.e. diameter = 0.02 to 0.08 cm) as well as pellet form (i.e., diameter = 0.1 to 0.5 cm). These sorbent formulations are tested in a packed-bed as well as a fluidized-bed reactor in the sulfidation temperature range of 550°C to 650°C. Parametric studies are conducted that include the effect of regeneration temperature, sorbent composition, and gas residence time. The best sorbent formulation and operating conditions identified in the parametric tests are used to determine the sorbent durability in long-term tests

During this quarter, twenty one copper chromite-based sorbent formulations were prepared. Two sorbent formulations that have acceptable crush strength, labeled as CuCr-10 and CuCr-21, were tested over 5 and 6 cycles respectively. The H2S breakthrough curves for these sorbents are shown in Figures 7 and 8 respectively. The results indicate that both sorbents are reactive toward H2S at 650°C and that the reactivity of the sorbents

are relatively constant over the first 5 to 6 cycles. The H2S prebreakthrough concentrations were generally about 20 to 30 ppm, making them suitable for IGCC application.

The experimental data from this study will be used to estimate the extent of desulfurization in large commercial equipment. The analyses will provide the information necessary for reactor scale-up and operating conditions to achieve the desired level of desulfurization. The results of long-term durability tests will also provide the data for estimating the "fresh sorbent makeup rate" in the desulfurization process. The data will be used to determine the most effective sorbent and estimate the cost of the hot gas cleanup process.

### 1 OBJECTIVES

The overall objective of this study is to determine the effectiveness of the copperchromite-based sorbents for longer duration application under optimum conditions in the temperature range of 550°-650°C to minimize sorbent reduction and degradation during the cyclic process.

The specific objectives of this work are to:

- 1. Prepare and characterize large quantities of copper-chromite sorbents.
- 2. Determine the "best" sorbent formulation.
- 3. Determine the optimum sulfidation and regeneration temperature.
- 4. Determine the overall durability of the "best" formulation at the optimum operating conditions in long duration tests.
- 5. Develop a mathematical model to predict the sorbent performance and the rate of fresh sorbent makeup in hot gas cleanup process.

#### 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 H2S (from several thousand ppm 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 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. (1-5) 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 500°C to 750°C. While the sulfidation kinetics of iron oxide are very good, (3) 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. 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 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.

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 rate 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, ZnFe<sub>2</sub>O<sub>4</sub>, developed by DOE/METC has reached pilot-stage (testing) for desulfurization of low-Btu gases. The H<sub>2</sub>S removal efficiency of ZnFe<sub>2</sub>O<sub>4</sub> is similar to ZnO because zinc ferrite is converted into a mixture of ZnO and Fe<sub>3</sub>O<sub>4</sub> when exposed to the reducing gas. Similarly, the rate of zinc loss (via zinc vaporization) is the same in both ZnFe<sub>2</sub>O<sub>4</sub> and ZnO, hence, 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 H<sub>2</sub>S 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. (6-8,11-13,20-37)

Desirable characteristics of a hot gas cleanup sorbent include:

- Stable pore structure
- 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<sub>3</sub>, Zn<sub>2</sub>TiO<sub>4</sub>, and Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub><sup>(6-8,24)</sup> 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 zinc titanate 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. <sup>(24,31)</sup>

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 determination of overall cost of hot gas cleanup process. It has been shown that straight line extrapolation of the data obtained in the "life-cycle" tests with zinc titanate will lead to an estimated fresh sorbent make-up rate of up to 20 times the initial bed inventory. (32) The results suggest that development of other types of sorbents, especially non zinc-based, should be pursued to insure the viability of the hot gas desulfurization process.

Copper-based sorbents do not suffer from metal volatility problems, hence, they could be used at elevated temperature without loss of reactivity and capacity 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 H2S and H<sub>2</sub> (or CO) the following reactions take place:

$$2CuO + H_2 = Cu_2O + H_2O$$
 (Partial Reduction) (1a)

$$Cu_2O + H2S = Cu_2S + H_2O$$
 (Sulfidation) (1b)

or

$$2CuO + 2H_2 = 2Cu + 2H_2O$$
 (Complete Reduction) (2a)

$$2Cu + H2S = Cu2S + H2$$
 (Sulfidation) (2b)

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

$$2CuO + H2S + H_2 = Cu_2S + 2H_2O$$
 (3)

In view of the large H<sub>2</sub>/H2S ratio and the ease of reduction in Reaction (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 in reducing atmosphere.

Copper-based sorbents have been studied in earlier ICCI-funded programs. (33-37) The joint IGT/MIT team systematically examined and ranked several novel binary oxides of copper in terms of their sulfidation equilibria, reduction stability, sulfidation reactivity, and regenerability at temperatures in the range of 750° to 850°C. 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 with chromium and cerium were the most promising sorbents for such high temperature hot gas cleanup applications.

Further testing of the copper chromite and copper cerium sorbents in the temperature range of 750° to 850°C indicated that these sorbents have the tendency to reduce in the fuel gas environment. The sorbents (especially copper chromite) exhibited excellent desulfurization efficiency similar to that of copper oxide during the early stages of sulfidation. The performance of the sorbents significantly improved by lowering the sulfidation temperature from 850° to 750°C. Because copper chromite showed better desulfurization efficiency and regenerability compared to copper-cerium, this sorbent was selected for further evaluation. The result of a 25-cycle test performed on the copper chromite sorbent at 750°C is shown in Figure 1 indicating that although the sorbent exhibits excellent desulfurization efficiency (H2S<sub>exit</sub><10 ppm) at up to 50% conversion the reactivity of the sorbent gradually decreased in the cyclic process.

The reduction in the reactivity of copper chromite at 750°C is similar to that of zinc titanate at 550°C. However, unlike the zinc titanate sorbent, the loss of reactivity of copper chromite should not be attributed to metal vaporization. Despite the considerably higher temperature application, 750°C compared to 550°C, copper-chromite does not suffer from metal volatilization problems. In this case, the loss of reactivity is probably due to agglomeration of metallic copper produced by reduction, that results in loss of surface area, and slower sulfidation reaction rates. The sorbent reduction is significantly lower at lower temperature as shown in Figure 2 indicating that reaction time required for complete reduction of copper chromite is 10 times higher at 650°C compared to 750°C. A plot of sorbent weight as fraction of initial weight in the TGA experiment (shown in Figure 3) indicates that while the sorbent is essentially completely reduced at 850°C, only a small fraction of the sorbent is reduced at 650°C. The extent of reduction is expected to be much lower at 550°C.

Based on the results of the extensive testing conducted in the previous ICCI-funded programs, copper chromite is the best sorbent candidate for further development for hot gas cleanup application in the temperature range of 550° to 650°C. However, additional work is needed to determine the effectiveness of the sorbent in this temperature over a large number of cycles. The sorbent formulation may also be modified by using other "binders" and "enhancers" to improve physical and chemical durability of the sorbent such as attrition resistance and reduction stability in the long duration cyclic operation.

This study focuses on the evaluation of the sorbents performance in the temperature range of 550° to 650°C. The study also addresses the physical durability of the sorbent in terms of attrition resistance and overall stability of the sorbent by exposing the sorbent to long-duration cyclic tests.

#### EXPERIMENTAL PROCEDURE

This project is divided into the following four tasks:

- Task 1. Sorbent Synthesis and Characterization
- Task 2. Parametric Studies
- Task 3. "Long-Term" Durability Studies
- Task 4. Data Analyses and Reactor Modeling

The experiments proposed in this program will be conducted in a state-of-the-art high pressure thermogravimetric analyzer (HPTGA) and the high-pressure/high-temperature reactor (HPTR) unit as well as the ambient pressure batch packed-/fluidized-bed unit. The schematic diagrams of the reactor systems to be used in this project are shown in Figures 4 through 6.

#### Task 1. Sorbent Synthesis and Characterization

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

The copper chromite based sorbents are prepared in the form of bulk mixed oxides with good interdispersion and high surface area. Attrition resistant extruded oxide (1-5 mm) are produced from the copper chromite powders having high surface area and reasonably high compressive crush strength. An inorganic binder material such as bentonite or other types of clay may be added to the powder to enhance the physical strength of the sorbent. Additionally, granules of the copper chromite sorbents in the range of -20 +60 mesh size (i.e. dp = 0.02-0.08 cm) with high pore volume (>0.5 cm³/g) and high crush strength are also produced for testing in this project

The starting material will have the same sorbent composition identified in the previous ICCI-funded project. However, because the goal of this project is directed toward fluidized-bed application at somewhat lower temperature application (i.e. 550° to 650°C), the sorbent formulation may be modified to suit the desired range of application. The modification of the sorbent formulation may include changing the proportion of active,

support, and binder material, addition of other "modifiers" or "enhancers", as well as sorbent preparation procedure.

During this quarter, a total of 21 different formulation of copper chromite based sorbents were prepared. These formulations included both bulk and supported sorbents, using different preparation techniques. Because the sorbent durability is directly related to its initial crush strength, only two sorbents, namely CuCr-10 and CuCr-21, having acceptable crush strength were selected for testing in Task 2.

### Task 2. Parametric Studies

The objective of this task is to identify the "best" sorbent formulation and optimum operating conditions for "long term" durability studies.

These tests will be conducted in the ambient pressure as well as high pressure using thermogravimetric analyzer and fixed-/fluidized-bed reactors. Most of the tests in the program are conducted at ambient pressure because of the lower cost and ease of operation. The high pressure experiment are designed to provide the necessary information regarding the applicability of the low pressure data for high pressure application.

#### **HPTGA Studies**

The effects of operating temperature and pressure on the reduction, sulfidation and regeneration of the copper chromite sorbents are determined in the high pressure thermogravimetric analyzer (HPTGA) unit. This state-of-the-art HPTGA unit is capable of operation at 1000°C and 100 bar in corrosive atmosphere. This is possible because the design of the unit is based on balanced pressure concept. All the hot wetted parts of the unit are made of quartz to eliminate reaction with corrosive and reactive gases. This is especially important when conducting gas/solid reaction tests involving very low concentrations (i.e., <1%) of reactant gases.

These tests are designed to provide information regarding the relative magnitude of the reduction and sulfidation reaction rates in the temperature range of 550° to 650°C during sulfidation as well as the extent of sulfate formation during regeneration in the desired temperature range. The effect of reaction pressure is determined by conducting tests at ambient as well as elevated pressure (i.e. 20 atm) to ensure the applicability of the data to actual process conditions.

The schematic diagram of the HPTGA unit is shown in Figure 4. In a typical HPTGA test, the wire-mesh basket containing the sample is initially in the upper section of the reactor in which a downward flow of an inert gas at ambient temperature is maintained. During this time the desired condition is established in the lower, heated section of the reactor in the presence of flowing inert gases. The reactor gas is then changed to a gas

mixture with the desired composition when the reactor temperature has reached the designed value. The test is initiated by lowering the sample into the heated zone while its weight is continually monitored and recorded as the sorbent reacts with the gas. The test is terminated when the sample weight reaches a constant value (no weight loss or gain).

Because the gas flow rates in the reactor are sufficiently high to essentially eliminate changes in the gas composition, the reactions occur under a constant and known environment. Under these conditions the weight loss-versus-time characteristics can be used to determine the reaction rates under constant conditions.

In the sulfidation/regeneration cyclic tests, the sample is first exposed to the reducing gas containing hydrogen sulfide followed by the regeneration gas mixture. The sequence of reactions is:

$$2CuO + H_2 = Cu_2O + H_2O$$
 (Partial Reduction) (1a)

$$Cu_2O + H2S = Cu_2S + H_2O$$
 (Sulfidation) (1b)

or

$$2CuO + 2H_2 = 2Cu + 2H_2O$$
 (Complete Reduction) (2a)

$$2Cu + H2S = Cu2S + H2$$
 (Sulfidation) (2b)

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

$$2CuO + H2S + H_2 = Cu_2S + 2H_2O$$
 (3)

If the reduction reactions occur faster than sulfidation reaction, as in reactions 1a and 2a, the sample will initially lose weight as it is being reduced. However, the sample weight is expected to increase to the original weight during sulfidation because solid feed material (2CuO) and the product of sulfidation (Cu<sub>2</sub>S) have the same molecular weight. The minimum weight of the sample during these tests is an effective indicator of the relative rate of the sulfidation and reduction reactions. The sample weight is not expected to change during regeneration reaction:

$$Cu_2S + 2O_2 = 2CuO + SO_2$$
 (4)

because the solids in the feed and product have the same weight. Therefore, an increase in the sample weight is generally an indication of sulfate formation.

#### Fixed-Bed Tests With Granules

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 are determined in the fixed-bed reactor. The optimum operating conditions for sulfidation and regeneration determined in the HPTGA tests are used in this series of tests. Based on the data generated and the expertise gained in the previous studies, it is believed that 5 to 10 cycles is needed for each set of condition (i.e., composition, temperature, and pressure) to assess the physical/chemical stability of the sorbent. The sorbents in this series of tests consist of granules with an average diameter in the range of 0.04 to 0.08 cm (i.e. -20+60 mesh). The small size of the particles allows operation with small quantity of sample without "channeling" that occur when pellets are used in a small bed.

The schematic diagram of the fixed bed/fluidized bed unit is shown in Figure 5. 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 fluidized-bed pressure.

In a typical test, a known quantity of the sorbent is loaded into the reactor and the reactor is heated to the desired temperature using the desired gas mixture (without H2S). The gas is switched to a mixture containing H<sub>2</sub> and the H2S concentration in the reactor effluent is determined by an on-line dedicated gas chromatograph. The test is terminated when the H2S concentration reaches a predetermined value (i.e., 200-500 ppmv). The gas is switched to an inert mixture and the temperature is changed to the regeneration temperature (if different) and switched to the desired regeneration gas mixture. The SO<sub>2</sub> concentration in the reactor effluent is determined by the on-line gas chromatograph. The test is terminated when SO<sub>2</sub> concentration drops to a very low level (less than 50 ppm).

In addition to the tests involving granules, a series of up to 10 cycles are conducted at the optimum operating condition using pellets with diameter in the range of 1 to 5 mm, having the "best" sorbent formulation as determined in the fixed-bed tests with the granules. These tests will provide the additional information regarding the physical durability of the larger pellet in long term testing.

A series of up to 10 cycles of sulfidation/regeneration tests are conducted at elevated pressure (20 bar) in the HPTR unit (shown in Figure 6) using the pellets. A schematic diagram of the high-pressure high-temperature reactor (HPTR) is given in Figure 6. The unit is suitable for fixed-bed and fluidized-bed mode of operation and is designed for operation at a maximum temperature of 1000°C at a pressure of 30 bar. The reactor is capable of handling corrosive gas mixtures including hydrogen sulfide (H2S) and sulfur dioxide (SO<sub>2</sub>). The unit has an outer shell constructed of stainless steel to withstand the static pressure, while ceramic materials are used for the wetted internal section of the

reactor to prevent corrosion of the unit during exposure to corrosive gases such as SO<sub>2</sub> and H2S. A ceramic tube directs the corrosive gas mixture to the quartz reactor. All of the hot wetted parts are made of quartz materials. Dry nitrogen is purged between the outer shell and the ceramic tube to prevent corrosion and to balance pressure. The reactor is heated by a four-zone electrical furnace.

The two copper chromite-based sorbents, CuCr-10 and CuCr-21, were tested over 5 to 6 cycles in the fix bed reactor at 650 °C at a space velocity of 2000 hr<sup>-1</sup> using a simulated coal gas containing 5000 ppm of H2S. The results of these tests are presented in the section "RESULTS AND DISCUSSION".

#### Fluidized-Bed Tests

This series of tests is conducted at ambient pressure as well as high pressure with the granules in fluidized bed mode of operation. Up to 10 cycles of sulfidation regeneration are performed in the fluidized-bed mode to determine the suitability of the "best" formulation for fluidized-bed applications at the optimum operating conditions. The results of these tests are compared with those of zinc titanate sorbent under similar operating conditions that is currently being tested in pilot-plant scale reactors.

### Task 3. "Long-Term" Durability Studies

The objective of this task is to determine the suitability of the sorbent for long term application in hot gas cleanup process.

The "best" sorbent formulation will be subjected to cyclic sulfidation/regeneration process at "optimum" operating conditions over at least 20 cycles. The tests in this task are designed to provide the necessary information for estimating the rate of fresh sorbent make-up as described in Task 4 below.

## Task 4. Data Analyses and Reactor Modeling

The objective of this task is to provide guidelines for estimating the of "fresh sorbent makeup rate" in the hot gas desulfurization process.

The experimental data to be obtained in Task 3 will be used to estimate the extent of desulfurization in larger commercial equipment. The analyses will provide the necessary information regarding the requirement for reactor size and operating conditions to achieve a desired level of desulfurization in such a unit. The results of long-term durability tests will also provide the necessary information to estimate the "fresh sorbent makeup rate" in the desulfurization process to determine the cost of the hot gas cleanup process.

### 10 RESULTS AND DISCUSSION

During this quarter, twenty one copper chromite based sorbent formulations were prepared. Two sorbent formulations that have acceptable crush strength, designated as CuCr-10 and CuCr-21, were tested over 5 and 6 cycles respectively. The  $H_2S$  breakthrough curves for these sorbents are shown in Figures 7 and 8, respectively. The results indicate that both sorbents are reactive toward  $H_2S$  at 650 °C and that the reactivities of the sorbents are relatively constant over the first 5 to 6 cycles tested. The  $H_2S$  prebreakthrough concentrations were generally about 20 to 30 ppm, making them suitable for IGCC application.

#### CONCLUSIONS AND RECOMMENDATIONS

Based on the results of sulfidation/regeneration cyclic tests, it appears that both CuCr-10 and CuCr-21 are suitable for IGCC application.

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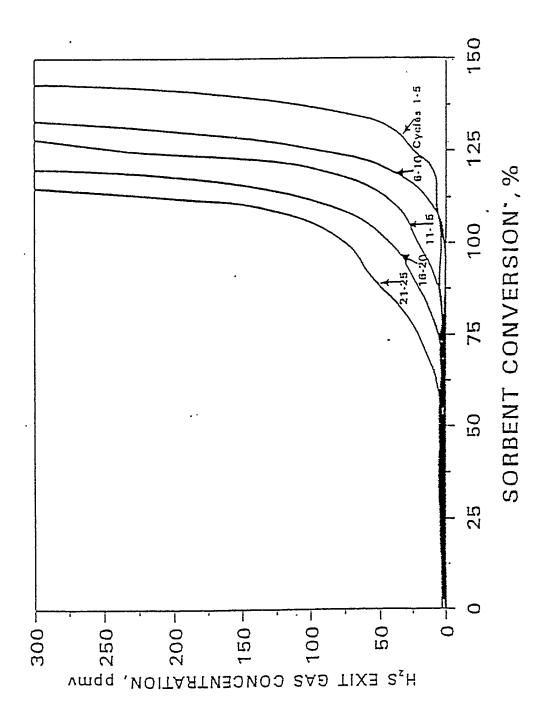


Figure 1. AVERAGE H<sub>2</sub>S BREAKTHROUGH PROFILES FOR COPPER CHROMITE

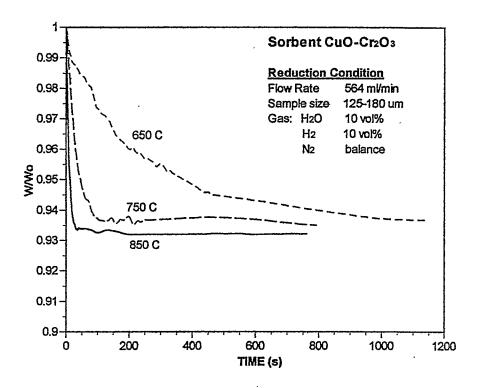


Figure 2. REDUCTION OF COPPER CHROMITE SORBENT AT VARIOUS TEMPERATURES

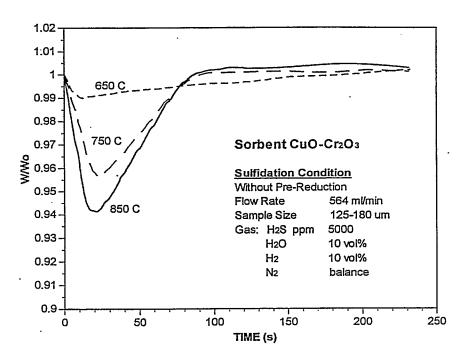


Figure 3. SULFIDATION OF COPPER CHROMITE SORBENT AT VARIOUS TEMPERATURES

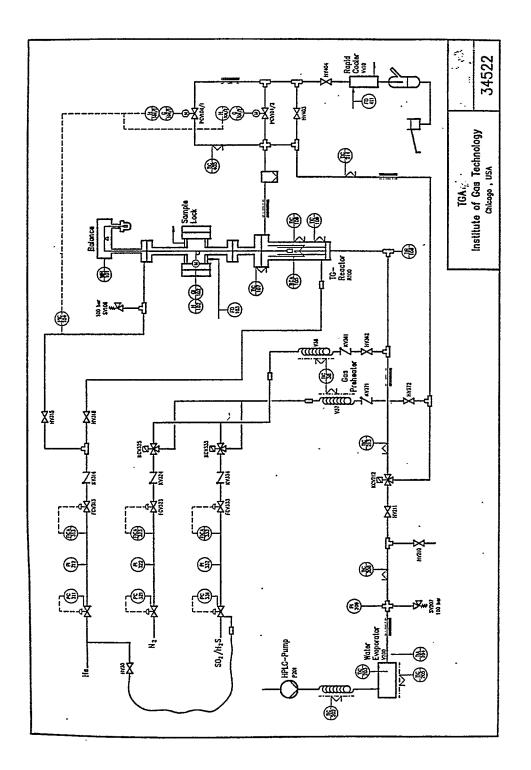


Figure 4. SCHEMATIC DIAGRAM OF THE PRESSURIZED TGA UNIT

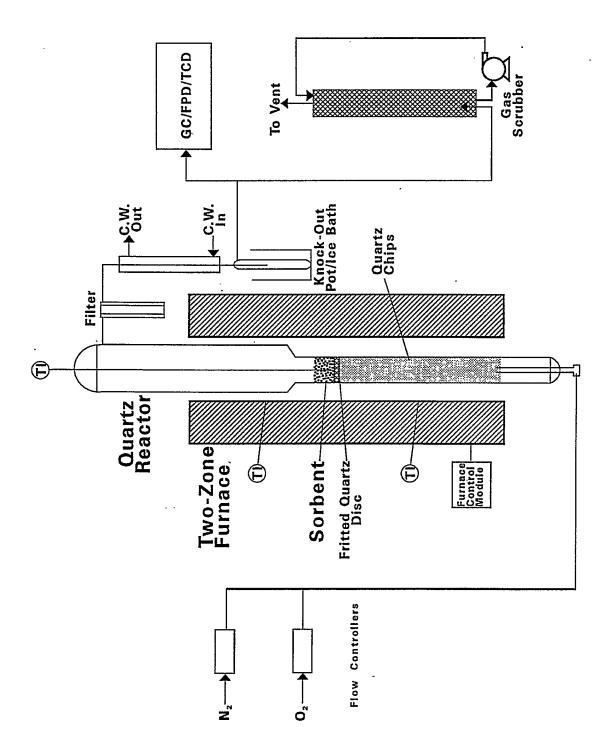


Figure 5. SCHEMATIC DIAGRAM OF THE PACKED/FLUIDIZED-BED REACTOR SYSTEM

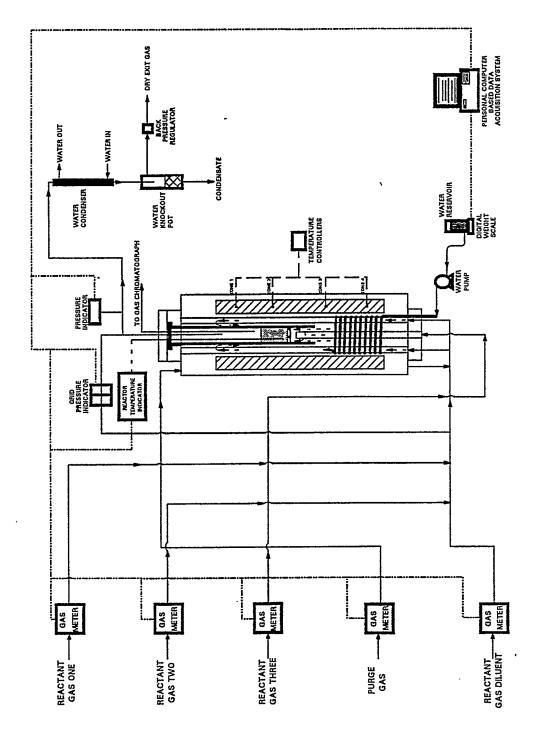


Figure 6. SCHEMATIC DIAGRAM OF THE HIGH PRESSURE/HIGH TEMPERATURE REACTOR (HPTR)

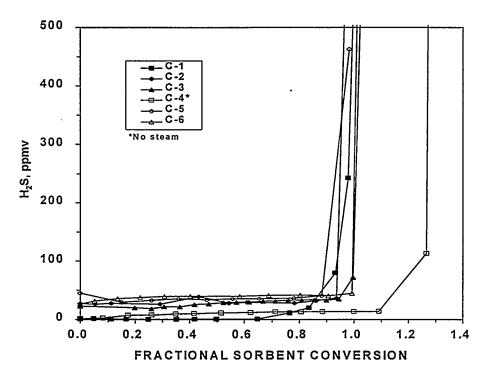


Figure 7. H<sub>2</sub>S BREAKTHROUGH CURVES FOR CuCr-10 SORBENT

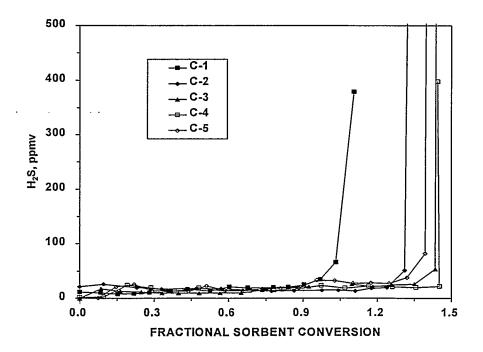


Figure 8. H<sub>2</sub>S BREAKTHROUGH CURVES FOR CuCr-21 SORBENT

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