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

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ABSTRACT

The overall objective of this study was 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, a large number of different formulations of copper chromite based sorbents were prepared in the form of granules (i.e., dp = 0.02-0.08 cm) and pellets (i.e., dp = 1-5 mm). Three (3) formulations of attrition resistant granules of the copper chromite sorbent (i.e., CuCr-10, CuCr-21, and CuCr-29) as well as one (1) copper chromite sorbent in pellet form (i.e., CuCr-36) were selected for cyclic desulfurization tests. The desulfurization and regeneration capabilities of the selected formulations as well as the effects of operating parameters were determined, to identify the “best” sorbent formulation and the optimum operating conditions. The durability of the “best” sorbent formulation was determined in “long-term” multicycle tests conducted at the optimum operating conditions. The attrition resistance of the selected formulations were determined and compared with those of other sorbents, including a limestone, a dolomite, and a commercial zinc titanate sorbent.

The results obtained in this study indicate that, the CuCr-29 sorbent has excellent attrition resistance and desulfurization performance, which are far superior to the commercial zinc titanate sorbents. The optimum desulfurization temperature in terms of sorbent efficiency and utilization appears to be about 600°C. Sorbent regeneration at 750°C ensured complete conversion of the copper sulfide to oxide without sulfate formation or reactivity deterioration in subsequent cycles. The sulfidation reactivity and sulfur capacity of the CuCr-29 sorbent consistently improved during the first 25 cycles. The CuCr-36 sorbent pellets also exhibited excellent desulfurization performance making this formulation a good candidate for moving-bed application.
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°C-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 focused on the evaluation of the regenerable novel copper-chromite sorbents for hot gas cleanup application at 550°C to 650°C in long duration cyclic tests to provide the data necessary for direct comparison with zinc titanate sorbents.

A large number of copper chromite sorbent formulations were 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 were first screened to select the formulation with acceptable crush strength. Three (3) formulations of attrition resistant granules of the copper chromite sorbent (i.e., CuCr-10, CuCr-21, and CuCr-29) as well as one (1) copper chromite sorbent in pellet form (i.e., CuCr-36) were selected for cyclic desulfurization tests. The selected formulations were tested in the packed-bed reactor in the sulfidation temperature range of 550°C to 650°C. The parametric studies included the effect of sulfidation temperature and sorbent pre-reduction on the desulfurization performance of the sorbents. The attrition resistance of the selected formulations were determined and compared with those of other sorbents, including a limestone, a dolomite, and a commercial zinc titanate sorbent. The best sorbent formulation and operating conditions identified in the
parametric tests were used to determine the sorbent durability in long-term tests in the high pressure fluidized bed reactor (HPTR) unit.

The results obtained in this project, indicate that the CuCr-29 sorbent has excellent attrition resistance, which is far superior to that of the commercial UCI-4169 zinc titanate sorbent. Furthermore, the CuCr-29 sorbent has superior desulfurization performance, achieving less than 5 ppm H₂S concentration in the cleaned fuel gas. The optimum desulfurization temperature in terms of sorbent efficiency (terminal H₂S levels in the cleaned fuel gas) and utilization (sulfur capacity at breakthrough or effective capacity) appears to be about 600°C. Pre-reduction did not appear to affect the performance of the CuCr-29 sorbent. Sorbent regeneration at 750°C ensured complete conversion of the copper sulfide to oxide without sulfate formation or reactivity deterioration in subsequent cycles. The sulfidation reactivity and sulfur capacity of the CuCr-29 sorbent consistently improved during the first 25 cycles. The CuCr-36 sorbent pellets also exhibited excellent desulfurization performance making this formulation a good candidate for moving-bed application.
OBJECTIVES

The overall objective of this study was to determine the effectiveness of the copper-chromite-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 were 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. Predict the sorbent performance and to estimate the rate of fresh sorbent makeup in hot gas cleanup processes.

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.

Research and development efforts for high-temperature desulfurization of fuel gases have 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. 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, 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. 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. The H₂S removal efficiency of ZnFe₂O₄ is similar to ZnO because zinc ferrite is converted into a mixture of ZnO and Fe₂O₃ when exposed to the reducing gas. Similarly, the rate of zinc loss (via zinc vaporization) is the same in both ZnFe₂O₄ 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 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.

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$_3$, Zn$_2$TiO$_4$, and Zn$_2$Ti$_3$O$_8$ $^{(4,18,19)}$ 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$^\circ$ to 750$^\circ$C has indicated that this sorbent also suffers from zinc losses leading to sorbent degradation and loss of reactivity in the cyclic process.$^{(18)}$

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 processes. 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.$^{(19)}$ 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 H$_2$S and H$_2$ (or CO) the following reactions take place:

\begin{align}
2\text{CuO} + \text{H}_2 &= \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad \text{(Partial Reduction)} \\
\text{Cu}_2\text{O} + \text{H}_2\text{S} &= \text{Cu}_2\text{S} + \text{H}_2\text{O} \quad \text{(Sulfidation)}
\end{align}

or

\begin{align}
2\text{CuO} + 2\text{H}_2 &= 2\text{Cu} + 2\text{H}_2\text{O} \quad \text{(Complete Reduction)} \\
2\text{Cu} + \text{H}_2\text{S} &= \text{Cu}_2\text{S} + \text{H}_2 \quad \text{(Sulfidation)}
\end{align}

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

\[2\text{CuO} + \text{H}_2\text{S} + \text{H}_2 = \text{Cu}_2\text{S} + 2\text{H}_2\text{O}\] \hspace{1cm} (3)

In view of the large H$_2$/H$_2$S 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 atmospheres.
Copper-based sorbents have been studied by the principal investigator of this project in earlier ICCI-funded programs.\textsuperscript{(21-25)} 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\textdegree{} to 850\textdegree{}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\textdegree{} to 850\textdegree{}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\textdegree{} to 750\textdegree{}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\textdegree{}C is shown in Figure 1, indicating that although the sorbent exhibits excellent desulfurization efficiency (H\textsubscript{2}S\textsubscript{exit}<10 ppm) at up to 50\% conversion, the reactivity of the sorbent gradually decreased in the cyclic process. It must be noted that sorbent conversion in Figure 1 was calculated based on copper oxide conversion to Cu\textsubscript{2}S upon sulfidation. The fact that conversion exceeded unity in certain sulfidation tests is indicative of the formation of other copper sulfide species having a Cu to S molar ratio of less than 2.

The reduction in the reactivity of copper chromite at 750\textdegree{}C is similar to that of zinc titanate at 550\textdegree{}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\textdegree{}C compared to 550\textdegree{}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\textdegree{}C compared to 750\textdegree{}C. A plot of sorbent weight as fraction of initial weight in the TGA experiments (shown in Figure 3) indicates that while the sorbent is essentially completely reduced at 850\textdegree{}C (during sulfidation), only a small fraction of the sorbent is reduced at 650\textdegree{}C. The extent of reduction is expected to be much lower at 550\textdegree{}C.

Based on the results of extensive testing conducted in the previous ICCI-funded programs,\textsuperscript{(21-25)} copper chromite was identified as the best sorbent candidate for further development for hot gas cleanup application in the temperature range of 550\textdegree{} to 650\textdegree{}C. However, additional work was needed to determine the effectiveness of the sorbent in this temperature over a large number of cycles. In order to improve physical and chemical durability of the sorbent such as attrition resistance and reduction stability in the long
duration cyclic operation, it was necessary to modify the sorbent formulation by using other "binders" and "enhancers" to produce a sorbent with the desired characteristics.

This study focused on the evaluation of the performance of a number of sorbent formulations in the temperature range of 550° to 650°C. The study also addressed the physical durability of the sorbents in terms of attrition resistance and overall stability by subjecting the sorbents to long-duration cyclic tests.

EXPERIMENTAL PROCEDURE

This project was 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 were conducted in the state-of-the-art high pressure thermogravimetric analyzer (HPTGA), 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 used in this project are shown in Figures 4 through 6.

Task 1. Sorbent Synthesis and Characterization

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

A total of thirty six (36) different formulations of copper chromite based sorbents were prepared in the form of bulk mixed oxides with good interdispersion and high surface area. Three (3) formulations of attrition resistant granules (-20 +60 mesh size) of the copper chromite sorbents (i.e., dp = 0.02-0.08 cm) as well as one (1) copper chromite sorbent in pellet form (i.e., dp = 1-5 mm) were 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 were added (when necessary) to the powder to enhance the physical strength of the sorbents. In addition to the four selected sorbents, two additional copper chromite sorbents (i.e., CuCr-34 and CuCr-35) were also prepared to assess the effect of preparation technique on sorbent resistance to attrition.
Measurement of Attrition Resistance

An attrition test unit was used to measure the relative resistance of several sorbents to attrition. The schematic diagram of the unit is shown in Figure 7. To compare the attrition resistance of the sorbents produced in this project with those of other sorbents, the attrition resistance of a limestone, a dolomite, and a commercial zinc titanate sorbent were also determined at the same operating conditions. The zinc titanate sorbent, designated as ZnTi (UCI-4169), has been extensively tested in IGT's bench scale high-pressure/high-temperature reactor (HPTR) as well as Enviropower's pilot-scale desulfurization units and has been shown to have acceptable attrition resistance for fluidized-bed operation.

In a typical attrition test, the air flow is set to generate sonic velocity, thus creating a strong shearing effect and turbulence to provide measurable attrition between the particles. After a specified period of time the test is terminated and the change in the particle size distribution is determined.

Task 2. Parametric Studies

The objective of this task was to identify the “best” sorbent formulation and optimum operating conditions for “Long Term” durability studies.

Packed-Bed Tests

These tests were conducted in the ambient pressure packed-/fluidized-bed reactors using selected sorbent formulations with acceptable crush strength. The effects of sulfidation temperature and sorbent pre-reduction on the desulfurization performance of the sorbents were investigated to identify the optimum operating conditions and the best sorbent formulation.

The schematic diagram of the packed-/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 reactor 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 \( \text{H}_2\text{S} \)). The gas is switched to a mixture containing \( \text{H}_2 \) and the \( \text{H}_2\text{S} \) concentration in the reactor effluent is determined by an on-line dedicated gas chromatograph. The test is terminated when the \( \text{H}_2\text{S} \) 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 \( \text{SO}_2 \) concentration in the reactor effluent is determined by the on-line gas chromatograph. The test is terminated when \( \text{SO}_2 \) concentration drops to a very low level (less than 50 ppm).
Three (3) formulations of attrition resistant granules of the copper chromite sorbents (i.e., CuCr-10, CuCr-21, and CuCr-29) were selected for testing in this task. The particle diameter of these sorbents were in the range of -20 +60 mesh size (i.e., dp = 0.02-0.08 cm). In addition to the granules, one (1) copper chromite sorbent (i.e., CuCr-36) in pellet form (i.e., dp = 1-5 mm) was also selected for testing in this task. Depending on the sorbent performance, the number of cycles completed with these sorbents ranged from 5 to 14 cycles.

The effect of sulfidation temperature on the reactivity of the CuCr-29 sorbent was determined in the temperature range of 550° to 650°C at a space velocity of 2000 hr⁻¹ using a simulated coal gas containing 2% H₂S. The effect of prereduction on the sorbent performance was determined by reducing the sorbent prior to sulfidation using different gas mixtures. The results of these tests are presented in the section “RESULTS AND DISCUSSION”.

HPTGA Studies

The reactivity of the “best” sorbent formulation identified in task 3 (i.e., CuCr-29) during sulfidation and reduction reactions was determined at the optimum temperatures at elevated pressure (i.e., T=600°C and P=10-20 bar) in the high pressure thermogravimetric analyzer (HPTGA) unit. This state-of-the-art HPTGA unit is capable of operation at 100 bar and 1000°C 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 were 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 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)

\[ Cu_2O + H_2S = Cu_2S + H_2O \] (Sulfidation) (1b)

or

\[ 2CuO + 2H_2 = 2Cu + 2H_2O \] (Complete Reduction) (2a)

\[ 2Cu + H_2S = Cu_2S + H_2 \] (Sulfidation) (2b)

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

\[ 2CuO + H_2S + H_2 = Cu_2S + 2H_2O \] (3)

If the reduction reactions occur faster than the sulfidation reactions, 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_2S) 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 the regeneration reaction:

\[ Cu_2S + O_2 = 2CuO + SO_2 \] (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.

The CuCr-29 sorbent was reacted with a reducing gas containing H_2S, whereby the sorbent underwent simultaneous reduction and sulfidation reactions. The regenerated CuCr-29 sorbent was also subjected to a sequential reduction-sulfidation test in the HPTGA unit. The results of these tests are presented in the section “RESULTS AND DISCUSSION”.

**Preliminary Testing of Sorbent Pellets**

Given the excellent performance of the CuCr-29 granules, the same chemical composition and preparation technique were used to prepare the copper-chromite CuCr-36 sorbent in
pellet form (i.e., dp=1-5 mm). This sorbent was tested in the ambient pressure packed-bed unit over 9 cycles at operating conditions identical to those used during testing with the granules. The motivation for these tests was to determine the suitability of the copper chromite sorbent for moving-bed application. The results of these tests are presented in the section “RESULTS AND DISCUSSION”.

Task 3. “Long-Term” Durability Studies

The objective of this task was to determine the suitability of the sorbent for long-term application in hot gas cleanup processes.

Based on the HPTGA test results as well as data generated in Task 2, the CuCr-29 copper chromite sorbent was then subjected to 25 cycles of sulfidation/regeneration tests at process conditions in the high-pressure high-temperature fluidized bed reactor (HPTR) unit.

A schematic diagram of the (HPTR) unit is given in Figure 6. The unit is suitable for packed-bed and fluidized-bed mode of operation and is designed for operation at a maximum temperature of 1000°C and a pressure of 30 bar. The reactor is capable of handling corrosive gas mixtures including hydrogen sulfide (H₂S) and sulfur dioxide (SO₂). 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 SO₂ 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 “Long-Term” durability cyclic tests in this task were conducted at 600°C at 20 bar to provide the necessary information for estimating the rate of fresh sorbent make-up, as described in Task 4. The results of this series of tests are presented in the section “RESULTS AND DISCUSSION”.

Task 4. Data Analyses and Reactor Modeling

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

The experimental data obtained in Task 3 were used to estimate the extent of desulfurization in larger commercial equipment. The analyses were based on the comparison of the reactivities of the copper chromite CuCr-29 and commercial zinc titanate UCI-3718 sorbent. These analyses provided 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 were also used to estimate the “fresh sorbent make-up rate” in the desulfurization process.
RESULTS AND DISCUSSION

A total of thirty six (36) different formulations of copper chromite based sorbents were prepared in the form of granules (i.e., dp = 0.02-0.08 cm) and pellets (i.e., dp = 1-5 mm). The sulfur capacities of these sorbents ranged from 2% to 11.5%. Three (3) formulations of attrition resistant granules of the copper chromite sorbents (i.e., CuCr-10, CuCr-21, and CuCr-29) as well as one (1) copper chromite sorbent in pellet form (i.e., CuCr-36) which had reasonably high compressive crush strength were selected for cyclic desulfurization tests in tasks 2 and 3. In addition to the four selected sorbents, two additional copper chromite sorbents (i.e., CuCr-34 and CuCr-35) were also prepared to assess the effect of preparation technique on sorbent resistance to attrition. The motivation for the preparation of these sorbents was to determine if an improvement in the effective capacity of the CuCr-29 sorbent could be made without compromising the attrition resistance of the sorbent.

The \( \text{H}_2\text{S} \) breakthrough curves for the CuCr-10 and CuCr-21 sorbents are shown in Figures 8 and 9, respectively. The results indicate that both sorbents are reactive toward \( \text{H}_2\text{S} \) at 650 °C and that the reactivities of the sorbents are relatively constant over the first 5 to 6 cycles tested. The \( \text{H}_2\text{S} \) prebreakthrough concentrations were generally about 20 to 30 ppm, making them suitable for IGCC application. However, because the theoretical sulfur capacities of these sorbents were relatively low, no further tests were performed with these sorbents.

The attrition resistance of a number of sorbents are presented Figure 10 in terms of % fines generated as a function of duration to which each sorbent was subjected to attrition resistance testing. As shown in this figure, CuCr-29 sorbent performed much better than all sorbents tested, except limestone, with percent fines generated varying between 4 and 7% for exposure times ranging from 0.5 to 2 hours. Unlike the UCI-4169 zinc titanate sorbent, the attrition resistance of the CuCr-29 copper chromite sorbent appears to be much less sensitive to exposure times. The performance of CuCr-35 does not appear to be as good as the CuCr-29 sorbent, with the percent fines generated being about 7% after one hour and about 11% after two hours. Although not shown on Figure 10, the performance of CuCr-34 sorbent was also evaluated. The percent fines generated were about 24% and 38% after one hour and two hours, respectively, which is believed to be unacceptable for fluidized-bed operation. Therefore, the CuCr-29 sorbent was selected for more detailed testing in this study.

The results of the first 4 sulfdation/regeneration cycles conducted with the CuCr-29 sorbent are shown in Figure 11 which also shows the level of \( \text{H}_2\text{S} \) that should be expected in the clean gas, had the equilibrium been dictated by the Cu metal. This sorbent has a theoretical sulfur capacity of approximately 11% such that at a space velocity of 2000 hr\(^{-1}\) and a \( \text{H}_2\text{S} \) content in the feed sulfdation gas of 2%, the theoretical time to breakthrough can be estimated as 270 minutes. These results corroborate the results obtained at 650°C with CuCr-10 and CuCr-21 copper chromite sorbents. These results also suggest that the
first few cycles are not usually indicative of sorbent performance in long-term testing, as will be shown subsequently. For example, certain sorbents, especially those meeting attrition resistance criteria for a fluidized-bed environment, may require an activation phase during which sorbent performance improves as the sorbent is being conditioned by a series of oxidation/reduction tests.

A fortuitous feature of the CuCr-29 sorbent is its capability to achieve extremely low levels of H₂S in the cleaned fuel gas even at high temperatures, indicating that the sorbent is stabilized against complete reduction to elemental copper. Therefore, it was considered essential to determine the optimum sulfidation temperature which would improve sorbent reactivity and utilization. The effect of temperature on sorbent desulfurization performance in the range 550° to 650°C is shown in Figure 12. This figure clearly indicates that superior desulfurization efficiency (<1 ppm H₂S) and the highest sulfur capacity can be achieved at a sulfidation temperature of 600°C.

In order to eliminate temperature excursions due to exothermic sorbent reduction during the sulfidation stage, pre-reduction was performed in certain cycles. In one cycle, the pre-reduction was conducted for 30 minutes using a 10%CO-CO₂ gas mixture; in another cycle, a H₂S-free sulfidation gas was used prior to the sulfidation stage. As shown in Figure 13, in both cases pre-reduction adversely affected sorbent efficiency during sulfidation to the same extent, regardless of the nature of reducing gas. However, H₂S levels less than 5 ppm were still achieved in corresponding sulfidation tests. A slight improvement of the sorbent effective sulfur capacity was obtained in the sulfidation test following the CO-CO₂ pre-reduction period, while a somewhat significant decrease in sulfur capacity was caused by the pre-reduction using the H₂S-free sulfidation gas.

A 14-cycle series of tests was then completed to demonstrate the durability and regenerability of the CuCr-29 sorbent. The results from cycles 7 through 14 are reported in Figure 14. All tests were conducted at a sulfidation temperature of 600°C and a regeneration temperature of 750°C. The results indicate that the sorbent sulfur capacity significantly improved with each cycle. This effect is noticeable up to the 12th cycle, but is much less pronounced beyond this cycle, as can be noted with reference to Figure 14.

A second series of tests was conducted with the CuCr-29 sorbent (-20 +40 mesh size fraction) to determine the effects of cycling on the reactivity of the sorbent at different temperatures. The results of the tests conducted at 550°C and 600°C are shown in figures 15 and 16, respectively. The results confirm that the sorbent sulfur capacity significantly improved with each cycle at both temperatures. Comparison of the results in Figures 15 and 16 confirm that higher desulfurization efficiency (<5 ppm H₂S) and sulfur capacity can be achieved at the sulfidation temperature of 600°C. Therefore, this temperature was adopted as a desired sulfidation temperature in “long-term” multicycle testing in the HPTR unit.
The results of regeneration tests shown in Figure 17 indicate that a 6% O$_2$-N$_2$ gas mixture and a starting temperature of 750°C are sufficient for complete sorbent regeneration without sulfate formation or reactivity deterioration in subsequent cycles. The SO$_2$ concentration in the regeneration product gas is shown in Figure 17 as a function of reaction time. The theoretical maximum SO$_2$ concentration in the product gas shown in Figure 17 corresponds to the complete consumption of oxygen in the 6% O$_2$-N$_2$ regeneration gas mixture, as may be calculated from the following overall regeneration reaction:

$$\text{Cu}_2\text{S} + 2\text{O}_2 = 2\text{CuO} + \text{SO}_2 \quad \text{(Regeneration)}$$

(4)

Given that the areas under the curves in Figure 17 represent the total amount of SO$_2$ released during each regeneration (or sulfur absorbed during sulfidation), the results of regeneration tests also confirm that the sulfur capacity of the sorbent has improved in successive cycles. Another very favorable feature of the CuCr-29 sorbent is that breakthrough occurred rapidly when the bed was completely regenerated, indicating that the sorbent can be regenerated at high space velocities in a relatively small reactor (in a commercial process).

During the induration (i.e., thermal treatment) of copper chromite sorbents, the following species may form through solid-state reactions: CuO•Cr$_2$O$_3$ (CuCr$_2$O$_4$), Cu$_2$O•Cr$_2$O$_3$ (CuCrO$_2$), or both. The most stable copper sulfide is Cu$_2$S; therefore, the sulfidation reactions involving the above copper chromite species are as follows:

$$2[\text{CuO}•\text{Cr}_2\text{O}_3] + (\text{H}_2\text{S}) + (\text{H}_2) = [\text{Cu}_2\text{S}•\text{Cr}_2\text{O}_3] + [\text{Cr}_2\text{O}_3] + 2(\text{H}_2\text{O})$$

(5)

$$[\text{Cu}_2\text{O}•\text{Cr}_2\text{O}_3] + (\text{H}_2\text{S}) = [\text{Cu}_2\text{S}•\text{Cr}_2\text{O}_3] + (\text{H}_2\text{O})$$

(6)

Reaction (6) is perhaps more appropriately written in the following fashion:

$$2[\text{CuCrO}_2] + (\text{H}_2\text{S}) = [\text{Cu}_2\text{S}•\text{Cr}_2\text{O}_3] + (\text{H}_2\text{O})$$

(6a)

In the above reactions, [ ] and ( ) designate solid and gas phases, respectively. For Reaction (5), the total weights of solid reactants and solid products are the same; therefore, during the overall reduction/sulfidation reaction, no weight change should be observed during HPTG testing. While for Reactions (6) or (6a), according to the weights of solid reactants and products, the sample weight during HPTG testing should increase with time, with $W_f/W_0 \approx 1 + 1.263 \times 10^{-3}(% \text{Cu})$, where %Cu is the weight percent copper in indurated CuCr-29 sorbent material.
Several tests were conducted in the HPTGA unit to determine the relative rates of reduction and sulfidation reactions. Figure 18 shows the results of two high pressure tests in which the CuCr-29 sorbent was exposed to a reducing gas containing 1% \( \text{H}_2\text{S} \), indicating that the rate of sulfidation at least equals that of the reduction reaction, because unlike the results shown in Figure 3, the sample weight does not decrease during the test (i.e., an indication of dominating reduction reaction). Furthermore, the sample weight gradually increased, when the sample was exposed to \( \text{H}_2\text{S} \), indicating that the fresh sorbent may be at least in partially reduced state (i.e., some \( \text{Cu}_2\text{O} \) was present).

The regenerated CuCr-29 sorbent was also subjected to a sequential reduction-sulfidation test in the HPTGA unit. The results are shown in Figure 19, confirming that the rate of the sulfidation reaction is about two orders of magnitude faster than that of the reduction reaction at similar conditions.

A 9-cycle series of tests was conducted with the CuCr-36 sorbent to demonstrate the durability and regenerability of the copper chromite sorbent pellets. The \( \text{H}_2\text{S} \) breakthrough curves for this series of tests are presented in Figure 20. These tests were conducted at a sulfidation temperature of 600\(^\circ\)C to 650\(^\circ\)C and a regeneration temperature of 750\(^\circ\)C. The results indicate that similar to the CuCr-29 copper chromite granules, the sorbent sulfur capacity improved with each cycle. However, as expected, because of the larger size and lower packing density of the pellets, the effective sorbent capacity of the pellets is much lower than that of the granules.

Based on the results obtained in this project, sufficient quantities of the CuCr-29 sorbent were prepared and sized appropriately for fluidized-bed testing in IGT's High Pressure High Temperature Reactor (HPTR) unit. The particle size distribution of the CuCr-29 sorbent is given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. PARTICLE SIZE DISTRIBUTION OF CuCr-29 SORBENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (mesh)</td>
</tr>
<tr>
<td>+20</td>
</tr>
<tr>
<td>-20 +30</td>
</tr>
<tr>
<td>-30 +40</td>
</tr>
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</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

A series of tests consisting of 25 sulfidation/regeneration cycles was conducted with the CuCr-29 sorbent in the HPTR unit. The \( \text{H}_2\text{S} \) breakthrough curves for a selected number of cycles are presented in Figure 21. These tests were conducted at a sulfidation
temperature of 600°C and a regeneration temperature of 750°C, with the exception of the last two cycles (i.e., cycles 24 and 25) which were conducted at slightly different operating conditions. The results indicate that, similar to the tests conducted at ambient pressure in task 3, the reactivity and sulfur capacity of the sorbent gradually improve during the first 25 cycles, which may be attributed to the creation of “new” secondary pores during the cyclic process.

The H₂S breakthrough concentration curves for a commercial zinc titanate sorbent tested in the HPTR unit at the same operating conditions for 30 cycles in a different project (19) are shown in Figure 22. This zinc titanate sorbent, designated as ZnTi (UCI-3140), has been extensively tested in IGT’s bench scale high-pressure/high-temperature reactor (HPTR) as well as Enviropower’s pilot-scale desulfurization units and has been shown to have acceptable reactivity and sorbent capacity for fluidized bed operation. Comparison of the results in Figures 21 and 22 indicates that CuCr-29 has higher reactivity and sulfur capacity than UCI-4169 sorbent.

The SO₂ concentration in the regeneration product gas in one of the tests conducted on the copper chromite sorbent is shown in Figure 23 as a function of reaction time. The sharp decline in the concentration of SO₂ to below 10 ppm (as shown in Figure 23) is a good indication of complete regeneration of the sorbent. Furthermore, the H₂S breakthrough and SO₂ concentration profiles in Figures 21 and 23 indicate that excellent regeneration of the CuCr-29 sorbent was achieved at elevated pressure and temperature without sulfate formation.

Because of the lack of intrinsic reaction rate data of the copper-chromite CuCr-29 sorbent, a comparative analysis was performed, involving UCI-3718 zinc titanate sorbent to predict the performance of the CuCr-29 sorbent in larger commercial equipment. The predicted performance of the UCI-3718 zinc titanate sorbent (after 30 sulfidation/regeneration cycles) in a pilot scale fluidized-bed reactor is presented in Figure 24. Details on the procedure adopted to generate Figure 4 can be found elsewhere (19, 20). The reactor was assumed to operate at the same fluidization conditions as the tests conducted in task 3. The results in Figure 24 indicate that the reactivity of the zinc titanate sorbent after 30 cycles was high enough to reduce the H₂S level of the coal gas to below 20 ppm in a very small reactor. These results were also confirmed in the pilot scale test performed at Enviropower Inc. (20).

Given that the reactivity of the CuCr-29 after 25 cycles is significantly higher than that of the UCI-3718 sorbent, it can be concluded that the CuCr-29 sorbent will perform very well in commercial scale reactors. Because the results of long-term durability tests with the CuCr-29 sorbent did not indicate any decline in the sorbent reactivity during the 25 cycles, the estimated “fresh sorbent makeup rate” in the desulfurization process (based on the result of 25-cycle test) is zero. However, because it is believed that the sorbent reactivity will eventually decline during the cyclic process, it must be concluded that the “fresh sorbent makeup rate” for the CuCr-29 copper chromite sorbent will be significantly lower than that for the UCI-3718 zinc titanate sorbent.
CONCLUSIONS AND RECOMMENDATIONS

The results obtained from the work performed in this project indicate that the CuCr-29 sorbent has excellent attrition resistance, which is far superior to that of a commercial zinc titanate sorbent (i.e., UCI-4169). Furthermore, the CuCr-29 sorbent has superior desulfurization performance, achieving less than 5 ppm H₂S concentration in the cleaned fuel gas. The optimum desulfurization temperature in terms of sorbent efficiency (terminal H₂S levels in the cleaned fuel gas) and utilization (sulfur capacity at breakthrough or effective capacity) appears to be about 600°C. Sorbent regeneration at 750°C ensured complete conversion of the copper sulfide to oxide without sulfate formation or reactivity deterioration in subsequent cycles. The sulfidation reactivity and sulfur capacity of the CuCr-29 sorbent consistently improved during the first 25 cycles. The CuCr-36 sorbent pellets also exhibited excellent desulfurization performance making this formulation a good candidate for moving-bed application.

REFERENCES CITED


Figure 1. AVERAGE H₂S 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
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Figure 14. EFFECT OF MULTICYCLE TESTING ON DESULFURIZATION PERFORMANCE OF CuCr-29 SORBENT
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Figure 16. H$_2$S BREAKTHROUGH CURVES FOR CuCr-29 SORBENT AT 600°C
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Figure 21. H$_2$S BREAKTHROUGH CURVES FOR CuCr-29 COPPER CHROMITE SORBENT IN THE HPTR FLUIDIZED-BED REACTOR

Figure 22. H$_2$S BREAKTHROUGH CURVES FOR UCI-3718 ZINC TITANATE SORBENT IN THE HPTR FLUIDIZED-BED REACTOR
Figure 23. CONCENTRATION OF SO₂ PRODUCED DURING REGENERATION OF CuCr-29 SORBENT AT 750°C AND 20 BAR (IN THE HPTR UNIT)

Figure 24. PREDICTED PERFORMANCE OF THE UCI-3718 ZINC TITANATE SORBENTS IN PILOT-SCALE FLUIDIZED BED REACTOR
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PROJECT MANAGEMENT REPORT
June 1, 1996, through August 31, 1996

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

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/2.2A-5M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Other Investigators: Rachid B. Slimane and James R. Wangerow
Institute of Gas Technology
Project Manager: Daniel D. Banerjee, ICCI

COMMENTS

The Project was completed on schedule and all project objectives were achieved.
EXPENDITURE - EXHIBIT B

CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURE BY QUARTER

Development of Regenerable Copper-Sorbents for Hot Gas Cleanup

<table>
<thead>
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<th>Quarter*</th>
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<th>Travel</th>
<th>Major Equipment</th>
<th>Other Direct Costs</th>
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* Cumulative by Quarter
CUMULATIVE COSTS BY QUARTER - EXHIBIT C

Development of Regenerable Copper-Sorbents for Hot Gas Cleanup

(In Thousands)

$150
$125
$100
$75
$50
$25
$

Months and Quarters

$ = Projected Expenditure $147,000

Δ = Actual Expenditure $148,035

Total ICCI Award $147,000
PROJECT SCHEDULE AND MILESTONE CHART

Development of Regenerable Copper-Sorbents for Hot Gas Cleanup

A  

B

C  X

D

E

F

S  O  N  D  J  F  M  A  M  J  J  A

Begin
Sept. 1
1996

A. Sorbent Synthesis and Characterization
B. Parametric Studies
C. Long Term Durability Studies
D. Data Analysis and Reactor Modeling
E. Quarterly and annual technical reports prepared and submitted
F. Quarterly management reports prepared and submitted
EQUIPMENT INVENTORY LIST
September 1, 1995, through August 31, 1996

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

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/2.2A-5M
Principal Investigator: Javad Abbasi, Institute of Gas Technology
Other Investigators: Rachid B. Slimane and James R. Wangerow
Institute of Gas Technology
Project Manager: Daniel D. Banerjee, ICCI

COMMENTS

No equipment with life expectancy of one year or more was purchased in this project.
HAZARDOUS WASTE REPORT
September 1, 1995, through August 31, 1996

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

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/2.2A-5M
Principal Investigator: Javad Abbasion, Institute of Gas Technology
Other Investigators: Rachid B. Slimane and James R. Wangerow
Institute of Gas Technology
Project Manager: Daniel D. Banerjee, ICCI

COMMENTS

None of the hazardous substances defined under 40 CFR 261, Subpart D, entitled “List of Hazardous Wastes,” were purchased, utilized, or generated in this project.
LIST OF PUBLICATIONS AND PRESENTATIONS
September 1, 1995, through August 31, 1996

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

DOE Cooperative Agreement Number: DE-FC22-92PC92521(Year 4)
ICCI Project Number: 95-1/2.2A-5M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Other Investigators: Rachid B. Slimane and James R. Wangerow
Institute of Gas Technology
Project Manager: Daniel D. Banerjee, ICCI

COMMENTS


DEVELOPMENT OF REGENERABLE COPPER-BASED SORBENTS FOR HOT GAS CLEANUP

Javad Abbasi, Rachid B. Slimane, and James R. Wangerow
Institute of Gas Technology

ICCI Project Manager: Daniel D. Banerjee

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 project includes testing the sorbent in pellet and granular forms in packed- and fluidized-bed reactors.

A number of highly durable copper chromite based sorbents have been produced in this project. A high capacity sorbent formulation that has excellent crush strength, designated as CuCr-29, was tested over 14 cycles. The results indicate that the optimum sulfdation temperature for this sorbent is about 600°C. At this temperature, the CuCr-29 sorbent is very reactive toward H₂S, resulting in H₂S prebreakthrough concentrations in the range of 1 to 5 ppm. Sorbent reduction prior to sulfdation slightly increases the H₂S prebreakthrough concentration to 5-10 ppm. The sorbent reactivity appears to increase during the first 10 cycles and stabilizes thereafter, making this sorbent suitable for IGCC application. The results of attrition tests conducted with CuCr-29 indicate higher resistance to attrition compared to commercial zinc titanate sorbent. This sorbent is currently undergoing “life-cycle” testing in the high pressure fluidized bed reactor.
DEVELOPMENT OF REGENERABLE COPPER-BASED SORBENTS FOR HOT GAS DESULFURIZATION

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ABSTRACT

Integrated gasification combined cycle (IGCC) processes are considered to be among the most promising power generation technologies for the 21st century. In these processes, solid fuels such as coals are gasified and the fuel gas is cleaned and combusted in a gas turbine. IGCC plants with hot fuel gas cleanup systems are superior to conventional pulverized coal-fired power plants because they offer higher power generation efficiency, higher power-to-heat ratio for cogeneration, superior environmental performance, and simple plant configuration and modularity.

The implementation of hot gas cleanup systems heavily depends on the development of regenerable sorbent material for removal of sulfur-containing species from the fuel gas stream at elevated temperature (i.e. higher than 350 °C) from several thousand ppm level down to a few ppm (suitable for gas turbine application) over many sulfidation/regeneration cycles. High Sulfur Capacity, good sulfidation kinetics, good mechanical strength, as well as good chemical and structural stability are additional desires features of the sorbents.

Zinc-based sorbents such as zinc titanates are the leading sorbents for hot gas desulfurizations. However, these sorbents have been shown to suffer from zinc volatilization at elevated temperatures, resulting in sorbent deterioration, loss of reactivity and attrition losses, leading to increasing sorbent replacement costs and overall cost of electricity. Copper-based sorbents, because of the high melting point of the metal, do not suffer from this problem. Bulk copper oxide is reduced to metallic copper in reducing fuel gas environment, leading to thermodynamic limitations, resulting in insufficient level of desulfurization. However, the sorbent performance can be improved by combining copper oxide with other oxides to improve the sorbent reduction stability in reducing atmosphere.
This paper will address the results of a systematic study of several novel copper based sorbents for hot gas cleanup application. The evaluation criteria included reduction stability, sulfidation reactivity and regenerability at elevated temperatures. Performance of the most promising sorbent in long duration cyclic sulfidation/regeneration tests will also be presented and discussed.