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

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ABSTRACT

The objective of this investigation was to evaluate two novel copper-based sorbents, namely copper-chromium and copper-cerium, for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C. Such high temperatures will be required for the new generation of gas turbines (inlet >650°C) in Integrated Gasification Combined Cycle (IGCC) systems.

The results of extensive testing have shown that both binary copper-based sorbents can reduce the H₂S concentration of fuel gas from 5000 ppmv to less than 10 ppmv at high levels of sorbent conversion, sufficient for IGCC application. The sorbents were also able to reduce the H₂S concentration to less than 1 ppmv, sufficient for molten carbonate fuel cell application (MCFC). Desulfurization at lower temperatures improves sorbent conversion and efficiency in the range of 650° to 850°C. Copper chromite demonstrated better regenerability than copper-cerium sorbent at temperatures between 750°-850°C.

One of the formulations of copper chromite sorbent demonstrated high H₂S removal efficiency and high copper conversion levels with no evidence of sorbent degradation after 25 sulfidation-regeneration cycles at 750°C, making it a very promising sorbent material for high temperature fuel gas desulfurization for both IGCC and MCFC application.
EXECUTIVE SUMMARY

Development of technology for coal gas desulfurization to sufficiently low levels at temperatures of 600° to 850°C is now recognized as crucial to efficient and economic coal utilization in emerging technologies such as coal gasification-combined cycle power generation (using gas turbines) and gasifier/fuel cell power plants. The implementation of hot gas desulfurization technology relies heavily on the development of regenerable metal oxide sorbent materials which have high sulfur capacity and can efficiently remove H₂S (from several thousand ppm levels down to a few ppm) over many cycles of sulfidation/regeneration.

In recent years it has been shown that certain mixed metal oxides have superior properties compared to single metal oxides for hot gas cleanup. Compounds of zinc with iron and titanium oxides, such as zinc ferrites (ZnFe₂O₄), and zinc titanates (ZnTiO₃), have reached pilot-stage desulfurization testing. However, at sulfidation temperatures above 600°-700°C, zinc ferrites and titanates will suffer zinc losses. Such high temperatures will be required for the new generation gas turbines (with inlet temperatures exceeding 650°C). If gas cleanup can be performed at matching conditions, then higher power plant cycle efficiency gains will be realized.

Copper-based sorbents have been considered as a potential alternative to zinc-based sorbents for high-temperature gas desulfurization because they do not suffer from metal volatility problems. In a recently completed ICCI-funded program, a consolidated effort by IGT and the Massachusetts Institute of Technology 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 650° to 850°C. The results of this study indicated that mixed binary oxides of copper with chromium and cerium are the most promising sorbents for such high temperature fuel gas cleanup applications. In various sulfidation/regeneration tests, both sorbents were capable of removing H₂S from a hot fuel gas to very low levels (less than 10 ppmv) at temperatures as high as 850°C with good sorbent regenerability in cycling process. However, additional work was needed to achieve overall sorbent optimization.

The goal of this program was to develop a novel regenerable sorbent that is capable of reducing the H₂S level of fuel gas at elevated temperature (above 650°C) to very low levels of below 10 ppmv for IGCC and to levels below 1 ppmv for MCFC applications. The overall objective was to evaluate two novel copper-based sorbents (that is, copper-chromium and copper-cerium) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C.
The specific objectives were to optimize sorbent composition by determining the structural effects of cerium oxide and chromium oxide addition to copper oxide and to determine the performance of these sorbents at various operating conditions.

In the first year of the present two year program, binary oxides of copper with oxides of chromium and cerium were prepared at various sorbent compositions. The structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation were determined.

Parametric fixed-bed sulfidation-regeneration tests were conducted to determine the performance of the sorbents at various operating conditions. High desulfurization efficiencies were achieved at temperatures ranging from 750° to 850°C at relatively high space velocities. The copper chromite sorbent reduced the H₂S concentration of a fuel gas containing 5000 ppmv to less than 10 ppmv at 750°C at copper conversion levels up to 90% and to less than 1 ppmv at copper conversion levels up to 50% during multicyle testing. At 850°C, similarly very low H₂S levels were attained with lower copper conversion levels. The copper-cerium sorbent was also capable of removing H₂S to very low levels comparable to the copper chromite sorbent but generally only for the first cycle. Sorbent performance generally deteriorated with respect to both efficiency and capacity with cycling, which may be attributed to the effects of sulfate formation during regeneration of the sorbent.

Both sorbents were found to reduce rapidly during sulfidation, although H₂ is later released through the reaction of the metallic copper with the H₂S. For both sorbents it appears that sufficient residual oxidic copper remains to effect high desulfurization efficiencies at high levels of copper conversion as evidenced by the fact that the H₂S pre-breakthrough concentrations are much below the values for metallic copper sulfidation.

In the second year of this program, work continued on development of the sorbents, including detailed kinetic and parametric studies of sulfidation and regeneration as well as addressing issues raised during the first year. Toward this end, sulfidation-regeneration testing was conducted in fixed-bed and thermogravimetric analyzer (TGA) reactors to determine the effects of: 1) gas composition, 2) pre-reduction of the sorbents with H₂/CO, 3) regeneration conditions (for Cu-Ce only), and 4) sorbents composition on the sorbents performance.

In tests conducted to determine the effect of gas composition on the performance of the copper chromite sorbent, results indicated that sorbent utilization increased with a decrease
in the \( \text{H}_2/\text{CO} \) content of the gas mixture. The copper-cerium sorbent utilization increased with an increase in the \( \text{H}_2/\text{CO} \) concentration of the gas mixture, however, sorbent utilization as well as \( \text{H}_2\text{S} \) removal efficiency dropped significantly in succeeding cycles. Regeneration of the sulfided copper-cerium sorbent was conducted at various conditions to improve the \( \text{H}_2\text{S} \) removal efficiency of the sorbent. Higher temperature and/or reductive regeneration improved sorbent performance slightly in some cases and worsened it in others. Test results also indicated that pre-reduction did not effect the performance of either sorbent for \( \text{H}_2\text{S} \) removal at levels below 10 ppmv or below 1 ppmv.

Sulfidation-regeneration testing was also conducted using copper-rich and additive-rich sorbents in the fixed-bed reactor. The \( \text{H}_2\text{S} \) removal performance of the chromium-rich copper chromite sorbent was found to be slightly better than that of the 1:1 molar composition sorbent over three cycles. The cerium-rich copper-cerium sorbent also performed slightly better than that of the 1:1 composition, but degradation in sorbent performance was seen in the succeeding cycles, although not as severe as with the 1:1 sorbent. Both copper-rich sorbents demonstrated \( \text{H}_2\text{S} \) removal performance inferior to that of the respective 1:1 molar compositions.

The effects of operating conditions (i.e., pre-reduction, gas composition, and temperature) on the rate of reduction, sulfidation and regeneration of both sorbents were also studied in the TGA system and the kinetic rate expressions were derived. Test results indicated no deleterious effects of pre-reduction on the rate of sulfidation of both sorbents with cycling. The rate of reduction for copper chromite was significantly slower at 650°C than at 750° or 850°C. During regeneration, results for copper-cerium sorbent suggested that some copper or cerium sulfates may have formed.

Based on the results of the extensive testing conducted in this program, a chromium-rich formulation of copper chromite sorbent, offering the potential of both high sulfur removal efficiency and stable reactivity in cyclic sulfidation-regeneration, was considered to be the best candidate for long-term testing. "Life-cycle" testing was conducted with this sorbent to determine its physical and chemical durability in long cycling process.

The \( \text{H}_2\text{S} \) removal performance over 25 cycles for a chromium-rich formulation of copper chromite sorbent indicated that although the reactivity of the sorbent gradually decreased with cycling, after 25 cycles the reactivity of the sorbent was still sufficient to reduce the \( \text{H}_2\text{S} \) in fuel gas from 5000 ppmv to very low levels (less than 10 ppmv) while still utilizing about 60% of the copper before breakthrough. This indicates that this sorbent is quite suitable for hot gas
desulfurization in IGCC application. The sorbent was also able to reduce the \( \text{H}_2\text{S} \) to below 1 ppmv suitable for MCFC application. The \( \text{H}_2\text{S} \) removal efficiencies of the chromium-rich copper chromite at 750°C are better than, while sulfur loadings are comparable to those of zinc titanate at the lower temperature of 550°C in cyclic desulfurization.

Future work should include performing multicycle sulfidation-regeneration tests of copper chromite at lower temperatures and elevated pressures and enhancing sorbent durability. Operation at a lower temperature has the potential to reduce the decline in reactivity of the sorbent under cycling conditions, and increase copper utilization over that obtained at 750°C for \( \text{H}_2\text{S} \) reduction below both 10 and 1 ppmv. Other sorbent-binder formulations may enhance sorbent durability and possibly stabilize the sorbent reactivity in cyclic operation.
OBJECTIVE

The goal of this program was to develop a novel regenerable sorbent that is capable of reducing the H₂S level of fuel gas at elevated temperature (above 650°C) to very low levels (below 10 ppmv) to be used in IGCC and (below 1 ppmv) in MCFC power plants. The overall objective of this research program was to evaluate two novel copper-based sorbents (that is, copper-chromium and copper-cerium) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C.

The specific objective was to optimize sorbent composition by determining the structural effects of CeO₂ and Cr₂O₃ addition to copper oxide and to determine the performance of these sorbents at various operating conditions.

The program goals were specifically directed toward gas cleanup priority section 6.1B: Removal of Sulfur-Containing Gases From the Hot Gases Produced by Gasification of High Sulfur Illinois Coal.

The specific goals of this project were to:

1. Carry out a parametric study of sulfidation with both sorbents in a fixed bed to determine the effects of operating variables;

2. Determine the kinetic effects of additives in sulfidation;

3. Determine the stability and regenerability of the sorbents in successive cyclic operation.

INTRODUCTION AND BACKGROUND

The main goal of the ICCI sponsored research on sulfur in coal is to increase the utilization of high-sulfur Illinois coals using a method that is both economical and environmentally acceptable. The market share of high-sulfur coal has suffered losses because of the trend toward more stringent government-imposed limitations on sulfur emissions. Thus, there is a real need to develop technologies for reducing sulfur emissions while minimizing solid wastes for disposal.

Integrated Gasification Combined-Cycle (IGCC) Power Plants and Fuel Cell Power Generation Technologies are among the leading contenders for coal conversion. Coal gas desulfurization to sufficiently low levels at temperatures of 650° to 850°C is now recognized as crucial to efficient and economic coal utilization in IGCC power generation (using gas turbines) and
gasifier/fuel cell power plants. The implementation of hot coal gas desulfurization relies heavily on the development of regenerable sorbent materials which have high sulfur capacity and 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.

Various transition metal oxides have been studied as regenerable high-temperature desulfurization sorbents. In recent years it has been shown that certain mixed oxides, namely zinc ferrites and zinc titanates, have superior properties compared to single oxides for hot gas cleanup. However, at sulfidation temperatures above 600°-700°C, these materials suffer zinc losses. Such high temperatures will be required for the next generation gas turbines (with inlet temperatures exceeding 650°C). If gas cleanup can be performed at matching conditions, then higher power plant cycle efficiency gains will be realized.

Copper oxide-based sorbents have been examined to a lesser extent than zinc oxide sorbents for high-temperature gas desulfurization. As copper-based sorbents do not suffer from metal volatility problems, they could be used at temperatures up to 850°C.

In a recent ICCI-funded program, the Institute of Gas Technology and the Massachusetts Institute of Technology (in a joint effort) 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 650° 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.

In the first year of the present two year program, binary oxides of copper with oxides of chromium and cerium were prepared at various sorbent compositions. The structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation were determined. Parametric fixed-bed sulfidation-regeneration tests were conducted to determine the performance of the sorbents at various operating conditions. High desulfurization efficiencies were achieved at temperatures ranging from 750° to 850°C at relatively high space velocities. The copper-cerium sorbent was also capable of
removing H$_2$S to very low levels comparable to the copper chromite sorbent but generally only for the first cycle. Sorbent performance generally deteriorated with respect to both efficiency and capacity with cycling, which may be attributable to the effects of sulfate formed during regeneration of the sorbent. Both sorbents were found to reduce rapidly (H$_2$ is later released through the reaction of the metallic copper with the H$_2$S, however).

In the second year of this program work continued on development of the sorbents, including detailed kinetic and parametric studies of sulfidation and regeneration as well as addressing issues raised during the first year. Toward this end, sulfidation-regeneration testing was conducted in fixed-bed and thermogravimetric analyzer (TGA) reactors to determine the effects of: 1) gas composition, 2) pre-reduction of the sorbents with H$_2$/CO, 3) regeneration conditions (for Cu-Ce only), and 4) sorbents composition on the sorbents performance.

Detailed studies of the sulfidation/regeneration kinetics of the two sorbents were conducted in the TGA system over the temperature range of 650°-850°C. The effects of operating conditions (i.e., pre-reduction, gas composition, and temperature) on the rate of reduction, sulfidation and regeneration of both sorbents were determined and the kinetic rate expressions were derived.

Based on the results of the fixed-bed and TGA reactor testing, "life-cycle" testing was conducted with the sorbent formulation that demonstrated the optimum sulfidation efficiency and capacity, regenerability and potentially stable reactivity with cycling, to determine its physical and chemical durability in long cycling process. This testing determined the suitability of this sorbent for hot gas desulfurization in IGCC or MCFC application.

**EXPERIMENTAL PROCEDURE**

**Fixed-Bed Desulfurization Tests**

Fixed-bed multicycle desulfurization testing was conducted in the quartz reactor system shown in Figure 1(a). at a space velocity of 2000 hr$^{-1}$ (STP) using the 250-850 micron fraction of the sorbents. Pre-reduction and sulfidation of the sorbents was conducted at 750°C using various H$_2$ and fuel gas mixtures while regeneration of the sulfided sorbents was conducted at 750°-850°C in various air-N$_2$ gas mixtures.

The reactor system was configured for flowing gas downwards for both sulfidation and regeneration. A coarse porous quartz
frit near the middle of the 2.5-cm ID by 0.8-m tall reactor was used to support the sorbent bed. A thermocouple sheathed with a 3-mm closed-end alumina tube, the end of which was positioned within the bed, was used to measure temperature. Temperature was recorded as a function of time using a computerized data acquisition system. Teflon tubing was used to convey SO₂/H₂S-containing exit gas at temperatures lower than 200°C. Reactor exit gas was sent to a glass condenser system in which all the exit gas was cooled in an ice bath.

The dry gases required for sulfidation and regeneration of the sorbent were obtained from pressurized cylinders. The gases were passed through pre-calibrated electronic mass flow controllers or rotameters (set to give the desired level of H₂S and other gases) and mixed prior to entering the reactor. A syringe pump was used to introduce water through capillary tubing into the reactor.

Sulfidation of the sorbent was carried out by feeding the H₂S-containing gas until the H₂S concentration in the reactor exit gas reached approximately 500 ppmv. Following sulfidation, the reactor was 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 was attained, the flow of regeneration gas was begun. A slipstream of the gas from the reactor was diverted to the gas chromatograph for measurement of H₂S and SO₂ concentrations. Prior to each test, the gas chromatograph was calibrated using calibration standard gas samples.

Regeneration of the sorbent was conducted by first heating the bed in flowing N₂ and then adding air to the N₂. Regeneration was considered complete after the SO₂ concentration in the exit gas reached less than about 50 ppmv.

All copper chromite and copper-cerium sorbents were prepared by the amorphous citrate technique for synthesizing highly dispersed solids. Sorbents were calcined at 500°C-1000°C for 1-3 hours. A chromium-rich copper chromite sorbent formulation was prepared for use in the 25-cycle test.

**Thermogravimetric Analyzer Reactor Tests**

Reduction-sulfidation-regeneration kinetics tests were conducted in a Cahn System 113-X thermogravimetric analyzer (TGA) reactor system as shown in Figure 1(b). Approximately 2 mg of the 125-180 micrometer fraction of the sorbents was used in all tests. Feed gas flowrates were sufficiently high to eliminate changes in the gas composition due to reaction with the solids.
Sorbent Characterization

Fresh, reduced, sulfided and regenerated samples were characterized by various analytical methods. These included specific surface area measurement with a BET surface analyzer using N₂, X-ray diffraction for identification of crystalline phases, and scanning electron microscopy to observe the surface morphology.

RESULTS AND DISCUSSION

Parametric Studies of Sulfidation

The H₂S removal performance of the copper chromite and copper-cerium sorbents are presented below in terms of breakthrough curves, which show the H₂S exit gas concentration as a function of normalized absorption time, t/t'. Here t is the actual reaction time and t' is the theoretical time required for complete conversion of the copper in the sorbent to Cu₂S. The breakthrough time is the time when the H₂S concentration rises sharply to the inlet value. The fractional conversion at the breakthrough time is a measure of the sorbent utilization, while the pre-breakthrough H₂S level is a measure of the sorbent performance or removal efficiency.

Effect of Operating Conditions

The H₂S removal performance for the (1:1 CuO:Cr₂O₃ or CuO:CeO₂ molar ratio) copper chromite and copper-cerium sorbents for a fuel gas containing 5000 ppmv H₂S, 10 vol% H₂, 22 % CO, 10 % CO₂, 10 % H₂O in N₂ is shown in Figure 2. Results at 850°C are shown for comparison in Figure 3. The sorbent utilization was considerably higher at 750°C than at 850°C for H₂S levels less than 10 ppmv. At 750°C, copper chromite was able to reduce the H₂S in fuel gas to less than 10 ppmv while utilizing up to 75% of the copper over three cycles. The copper chromite was also able to reduce the H₂S concentration to less than 1 ppmv for copper conversions of 60-70% as shown in the inset graph in Figure 2. Regeneration of the copper chromite sorbent at 750°C-850°C in a 30% air-N₂ mixture was rapid and complete as shown in Figure 4.

The copper-cerium sorbent performance generally deteriorated with respect to capacity and efficiency after the first cycle. Although low H₂S pre-breakthrough levels and high sorbent utilization, comparable to those using copper chromite, were obtained in the first cycles under all test conditions, much higher H₂S pre-breakthrough concentrations were obtained in succeeding cycles, possibly due to the evolution of H₂S produced from the reaction of H₂ in the fuel gas with sulfates.
of copper or cerium formed during regeneration of the sorbent. Regeneration of the sulfided copper-cerium sorbent was conducted at various conditions to attempt to improve the \( \text{H}_2\text{S} \) removal efficiency of the sorbent. Higher temperature and/or reductive regeneration improved sorbent performance slightly in some cases and worsened it in others.

In tests conducted to determine the effect of gas composition on the performance of the sorbents, results indicated that sorbent utilization and efficiency for the copper chromite generally increased with a decrease in the \( \text{H}_2/\text{CO} \) content of the gas mixture. Copper conversion of up to 99% was obtained in a 10 vol% \( \text{H}_2 \) gas mixture at 750°C. The copper-cerium sorbent utilization increased with an increase in the \( \text{H}_2/\text{CO} \) concentration of the gas mixture. Sorbent sulfur loadings of more than twice the saturation value for copper were obtained in the first cycle, suggesting the participation of cerium during sulfidation. However, sorbent utilization as well as \( \text{H}_2\text{S} \) removal efficiency dropped significantly in succeeding cycles. A decrease of about 50% in both the BET surface area and total pore volume was indicated for the regenerated sorbent after the third cycle.

Tests conducted to determine the effect of sorbent composition on the sorbent's \( \text{H}_2\text{S} \) removal performance indicated low \( \text{H}_2\text{S} \) pre-breakthrough levels (less than 10 ppmv) during sulfidation of a chromium-rich copper chromite sorbent (Figure 5) in 5000 ppmv \( \text{H}_2\text{S} \) fuel gas. Reduction to less than 1 ppmv was obtained for longer periods of time than in the 1:1 molar composition before gradually increasing to 10 ppmv. Because of the additional chromium oxide additive in the chromium-rich copper chromite, sulfur loadings are lower than in the 1:1 molar composition as shown in Figure 6. On the other hand, the higher additive content may serve to stabilize or enhance sorbent reactivity and durability with repeated sorption-regeneration cycling, and thereby compensate for the lower loading. A copper-rich copper chromite sorbent demonstrated \( \text{H}_2\text{S} \) removal performance inferior to that of the 1:1 molar composition.

The performance of the copper- and cerium-rich copper-cerium sorbents over three cycles in a 5000 ppmv fuel gas demonstrated high \( \text{H}_2\text{S} \) removal efficiencies in the first cycle, comparable to those with the 1:1 molar composition. However, much higher \( \text{H}_2\text{S} \) pre-breakthrough levels were observed in the next two succeeding cycles. As with the other copper-cerium sorbent compositions, various regeneration schemes conducted in the next two cycles did not restore the reactivity of the sorbent to the high level obtained in the first cycle.

Product gas composition data during fixed-bed testing as well
as TGA data indicated that both sorbents were generally reduced prior to sulfidation. Sulfidation-regeneration tests with and without pre-reduction of the sorbents indicated no adverse effect of pre-reduction on the H₂S removal performance of either sorbent, and for the copper-cerium oxide sorbent, pre-reduction enhanced the overall conversion of the sorbent. For both sorbents it appeared that sufficient residual oxidic copper remained to effect high desulfurization efficiencies at high levels of copper conversion as evidenced by the fact that the H₂S pre-breakthrough concentrations were much below the values for metallic copper sulfidation which, depending on the H₂ concentration, range from 50-250 ppmv in the temperature range studied.

Product gas composition data also indicated that the water-gas shift reaction reached equilibrium for both sorbents under all test conditions.

**Study of Sulfidation Kinetics**

The effects of operating conditions on the sulfidation and regeneration of the copper chromite and copper-cerium sorbents were studied in the TGA system and the kinetic rate expressions were derived.

A typical plot of the sorbent weight changes (normalized by the initial weight) for the sulfidation-regeneration of the copper chromite sorbent in a 10 vol% H₂, 10 vol% H₂O in N₂ feed gas mixture at 750°C is shown in Figure 7. The curves reveal that sulfidation of the sorbent actually consists of two stages: a reduction-dominating stage, that is, weight loss segments in the curves, and a sulfidation-dominating stage, that is, weight increasing segments. It should be noted that on the basis of stoichiometry of Cu₂S→2CuO, no weight change is expected in either sulfidation or regeneration. During the first stage, Cu²⁺ is reduced to Cu⁺ or metal Cu, by reactions:

\[
\begin{align*}
CuO + H_2 &= Cu + H_2O \\
2CuO + H_2 &= Cu_2O + H_2O \\
Cu_2O + H_2 &= Cu + H_2O
\end{align*}
\]

resulting in a weight loss.

During the weight increase segment, metal copper or copper oxides are sulfided to copper sulfides. Due to the stoichiometry of the reactions involved, the normalized weight of the sample after sulfidation returns to the original normalized weight if Cu₂S is formed. Because the final normalized weight exceeded 1 after sulfidation, non-stoichiometric copper sulfides may have formed. Similar curves were obtained for the copper-cerium sorbent during
sulfidation, except that cerium sulfides may have also formed.

If the regeneration of the sulfided sorbent proceeds as given in Equation (4),

$$\text{Cu}_2\text{S} + \text{O}_2 = \text{CuO} + \text{SO}_2$$  \hspace{1cm} (4)

then the normalized weight change after regeneration would equal 1, the original weight of the sample. For the 1:1 copper chromite sorbent, the normalized weight reached 1 or below, suggesting that copper sulfides were not all oxidized to CuO--other copper chromium oxides may have also formed. For the copper-cerium sorbent, the normalized weight increased above 1 during regeneration, implying that copper or cerium sulfates might have formed besides CuO.

Figures 8 and 9 compare the normalized weight changes of the 1:1 and 1:3 copper-chromium sorbent compositions, respectively, during pre-reduction in H$_2$/H$_2$O, sulfidation and regeneration. Pre-reduction and sulfidation of both sorbents is rapid and complete. No significant effect of pre-reduction on the H$_2$S removal performance was observed when the sorbents were pre-reduced before sulfidation. As to regeneration of these two sorbents, both show similar regenerability. As was seen in the test for the 1:1 sorbent during direct sulfidation, the normalized weight during regeneration in the test with pre-reduction also reached 1 or below, suggesting again that copper sulfides were not all oxidized to CuO--other copper chromium oxides may have also formed. For the copper-rich sorbent similar results were obtained for pre-reduction and sulfidation. During regeneration a decrease in weight in the first few minutes was seen after which the weight increased back up to near 1. This implies that its regeneration involves other reactions than (4).

As for the copper-cerium sorbents, the results for pre-reduction and sulfidation are similar to those for the copper chromite sorbents. However, normalized weights above 1 during regeneration were obtained, again suggesting that copper or cerium sulfates may have formed besides CuO.

**Determination of Kinetic Equations**

Based on the weight changes recorded in the TGA tests, the reaction rate at time $t=t'$, was calculated using the following equations:

For pre-reduction, CuO + H$_2$ = Cu + H$_2$O:

$$R_t = \frac{(dW/dt)|_{t=t'}}{M_{\text{CuO}} \cdot A} = \frac{(dW/dt)|_{t=t'}}{M_{\text{CuO}} \cdot S \cdot W_0} \text{ mmol CuO/cm}^2 \cdot \text{s} \hspace{1cm} (5)$$
For sulfidation reaction, \(2\text{Cu} + \text{H}_2\text{S} = \text{Cu}_2\text{S} + \text{H}_2\): \[ R_s = \frac{(dW/dt)|_{t=t'}}{(\Delta W/\Delta t)|_{t-t'}} \quad \text{mmol Cu/cm}_2\cdot\text{s} \] (6)

where:

\[(\Delta W/\Delta t)|_{t=t'} = \text{Slope of the weight vs. time profile at time } t', \text{ mg/s;}
M_{\text{CuO}} = \text{Molecular weight of CuO, mg/mmol}
M_{\text{Cu}} = \text{Molecular weight of Cu, mg/mmol}
A = \text{Total surface area of sorbent, cm}^2
S = \text{Specific surface area of sorbent, cm}^2/\text{mg}
W_0 = \text{Initial sample weight, mg.}

When time \(t'=0\), initial reaction rates were obtained.

**Pre-Reduction**

During pre-reduction of the 1:1 molar ratio copper chromite and copper-cerium sorbents by \(\text{H}_2\), only Reaction (1) was assumed to occur. In the absence of bulk and pore diffusion and mass transfer resistance, the intrinsic initial heterogeneous reaction rate can be expressed as:

\[ R_{r_0} = K \cdot (C_{\text{H}_2})^n \] (7)

where:

\[ R_{r_0} = \text{Initial reaction rate, mmol/cm}^2; \]
\[ K = \text{Intrinsic rate constant;} \]
\[ C_{\text{H}_2} = \text{Molar concentration of } \text{H}_2, \text{ mmol/cm}^3; \]
\[ n = \text{Reaction order with respect to } \text{H}_2; \]
\[ T = \text{Absolute temperature, K.} \]

In Equation (7), the intrinsic rate constant, \(K\), can be further expressed by the Arrhenius equation:

\[ K = K_0 \exp(-E/RT) \] (8)

where:

\[ K_0 = \text{Reaction frequency constant} \]
\[ E = \text{Activation energy, J/mol} \]
\[ R = \text{Ideal gas constant, J/mol} \cdot \text{K} \]

\(R_{r_0}\) at various \(\text{H}_2\) concentrations and temperatures were calculated from the TGA data by using Equation (1), and then were used to determine the reaction order, \(n\), and activation energy, \(E\), according to Equations (7) and (8). For copper chromite, \(n=0.619\) and \(E=79 \text{ kJ/mol}\), while \(n=0.456\) and \(E=36 \text{ for copper-cerium sorbent. Thus, for the two sorbents, equations}
(7) and (8) can be re-written as:

For copper chromite:

$$R_{r_0} = 9.76 \times 10^{-1} \cdot \exp\left((-79000/RT) \cdot (C_{H_2})^{0.610}\right)$$  \hspace{1cm} (9)

For copper-cerium:

$$R_{r_0} = 1.76 \times 10^{-3} \cdot \exp\left((-36000/RT) \cdot (C_{H_2})^{0.465}\right)$$  \hspace{1cm} (10)

The reduction rates for both sorbents increased with an increase of H$_2$ concentration in the inlet gas. Figure 10 shows that the pre-reduction of copper chromite sorbent at 650°C is very slow compared to 750°C and 850°C. In contrast, the reduction of copper cerium is quite fast at all three temperatures.

**Sulfidation Following Pre-Reduction**

By using the same method, kinetic equations for expressing initial sulfidation rates of the copper chromite and copper-cerium sorbents were obtained as follows:

For copper chromite:

$$R_{r_0} = 2.80 \times 10^{-4} \cdot \exp\left((-19000/RT) \cdot (C_{H_2S})^{0.42}\right)$$  \hspace{1cm} (11)

For copper-cerium:

$$R_{r_0} = 3.88 \times 10^{-3} \cdot \exp\left((-15000/RT)^{0.60}\right)$$  \hspace{1cm} (12)

At the tested conditions, the initial sulfidation rates for both sorbents are much smaller than the initial reduction rates, which is consistent with the fact that the reduction of CuO is much faster than sulfidation. For both sorbents, the activation energy and reaction frequency constants for sulfidation are almost the same meaning that after fully reduced the sulfidation kinetics of metal copper in both sorbents were almost the same. The activation energy of sulfidation is smaller than that for reduction, implying temperature has little effect on sulfidation. Increasing the H$_2$S concentration also led to an increase in the sulfidation rate. Little influence of H$_2$O on the initial sulfidation rate was found.

**Direct Sulfidation**

Although, as demonstrated above, direct sulfidation includes two stages or segments: the reduction-dominated stage and sulfidation-dominated stage, reduction and sulfidation actually occur simultaneously when the sorbents contact the
inlet gas containing both H₂ and H₂S. By fitting the experimental data using the same method as above, the kinetic parameters listed in Table 1 were obtained.

Because reaction temperature has a stronger effect on reduction than on sulfidation, as stated previously, the influence of temperature on direct sulfidation is mainly determined by the reduction, as shown in Figure 11. For the copper chromite sorbent at 650°C, reduction was very slow compared to 750°C and 850°C, and therefore, more CuO or Cu₂O were involved in sulfidation. This suggests that desulfurization at temperatures less than 750°C may be beneficial. The presence of more oxide was also responsible for the different sulfidation activation energies obtained at the low and high temperature ranges.

For the copper-cerium sorbent, because temperature has little effect on both reduction and sulfidation, direct sulfidation at these three temperatures exhibited almost the same behavior: reduction approaching completion and sulfidation occurring at about the same rate.

The reduction rate increased and the reduction became more complete for both sorbents with an increase in the H₂ inlet concentration. Sulfidation rate increased with an increase in the H₂ inlet concentration, due to the faster sulfidation of copper metal than the oxide. Water vapor had no significant effect on the reduction rate or on sulfidation rate. Although increasing the H₂S concentration also led to an increase in the sulfidation rate, its effect was much less than for sulfidation with pre-reduction, which involves the sulfidation of copper metal which is much faster than sulfidation of copper oxide.

<table>
<thead>
<tr>
<th>Table 1. KINETIC PARAMETERS FOR DIRECT SULFIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Copper chromite</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>E, kJ/mol</td>
</tr>
<tr>
<td>n</td>
</tr>
</tbody>
</table>

*Not available

**Data were estimated separately for the two temperature ranges due to large change of slope. The first value is for high temperature range, 750-850°C, and the second for the low temperature range, 650°C-750°C.
Sorbent Regenerability Studies

Based on the results of the extensive testing conducted in this program, copper chromite sorbent is the best candidate for high temperature fuel gas desulfurization. Of the various copper chromite compositions tested, the chromium-rich copper chromite offers both high sulfur removal efficiency, stable reactivity and durability in cyclic sulfidation-regeneration. Therefore, this sorbent composition was considered to be the best candidate for long-term testing. "Life-cycle" testing was conducted using a formulation of this sorbent to determine its physical and chemical durability in long cycling process.

Figure 12 shows the H$_2$S breakthrough profiles over 25 cycles for this chromium-rich copper chromite sorbent. Although the reactivity of the sorbent gradually decreased with cycling, it's reactivity with cycling remained high. In the 25th cycle, for example, the H$_2$S exit gas concentration was reduced to less than 10 ppmv while still utilizing over 60% of the copper before breakthrough and H$_2$S exit gas levels below 1 ppmv were seen up to copper conversions as high as 90% extending into the 11th cycle. No cracking or spalling of the sorbent was evident even with the repeated high sulfur loadings. Both the BET surface area and the total pore volume of the regenerated sorbent were slightly higher after the 25th cycle as compared to the fresh sorbent.

The performance of the copper chromite can be compared with that of zinc titanate sorbent during cyclic fluidized-bed desulfurization as shown in Figure 13. Desulfurization with zinc ferrite showed similar results to that of zinc titanate. As can be seen in the figure, this zinc titanate sorbent, one of the optimum formulations after years of development of this type of sorbent, also demonstrates a decline in reactivity with cycling, but at a much lower temperature of 550°C. At higher temperatures, results for zinc titanate show similar or potentially greater reactivity declines. It is anticipated that the cyclic desulfurization performance of the copper chromite sorbent will improve at lower temperatures of around 650°C. A reduction in the rate of decline of the reactivity of copper chromite and enhancement of the ability of the sorbent to reduce H$_2$S levels below 1 ppmv for longer periods of time may also be expected.

The decline in zinc titanate sorbent reactivity with cycling seen in these and other results, has apparently prompted a recent DOE "Request For Proposal" (No. DE-RP21-94MC31089) "to develop regenerable sorbents for use in the much lower temperature range of 343°-538°C." In this temperature range
the reactivity of the sorbent may be more stable but at the expense of the thermal efficiency of the hot gas desulfurization process. The H$_2$S removal efficiencies of the chromium-rich copper chromite at 750°C are better than while sulfur loadings are comparable to those of zinc titanate at 550°C in cyclic desulfurization making it suitable for hot gas desulfurization in both IGCC (<10 ppmv) and MCFC (<1 ppmv) application. Enhancing the copper chromite sorbent durability and operation at a lower temperature of 650°C have the potential to improve the sorbent reactivity/stability and capacity even further.

CONCLUSIONS AND RECOMMENDATIONS

Based on the test results obtained in this program, it can be concluded that:

- Both copper-chromium and copper-cerium sorbents can reduce the H$_2$S exit gas concentration to less than 10 ppmv for IGCC application, and to less than 1 ppmv for MCFC application at high sorbent utilization.

- Copper chromite demonstrated better regenerability than copper-cerium at temperatures between 750°-850°C.

- The H$_2$S removal performance of additive-rich copper chromite sorbent is slightly better than while the copper-rich is worse than that of the 1:1 molar composition.

- Both copper chromite and copper-cerium sorbents are generally reduced prior to sulfidation; however, it appears that sufficient residual oxidic copper remains to reduce the H$_2$S to levels far below the equilibrium values for metallic copper sulfidation.

- Pre-reduction does not appear to effect the H$_2$S removal performance of either sorbent.

- Sorbent utilization in the copper chromite sorbent during pre-breakthrough increased with a decrease in the H$_2$/CO concentration of the feed gas mixture.

- During sulfidation of the copper-cerium sorbents, various cerium and/or copper sulfides may have formed; during regeneration, sulfates of copper or cerium may have formed which decomposed when exposed to a reducing gas (producing H$_2$S) and thereby decreasing the apparent H$_2$S removal efficiency of the sorbent.

Based on the results of the extensive testing conducted in this program, copper-chromite sorbent was considered to be the
best candidate for long-term testing. "Life-cycle" testing was therefore conducted using a chromium-rich copper chromite sorbent formulation because it demonstrated high sulfur removal efficiency and, due to the possible stabilizing effects of the additional chromium oxide additive, has the potential for more stable reactivity/durability in cyclic operation.

In cyclic sulfidation-regeneration testing of the chromium-rich copper chromite sorbent at 750°, it demonstrated very high H₂S removal efficiency, high copper conversion levels after 25 cycles and no degradation of the sorbent. The H₂S removal efficiencies of the chromium-rich copper chromite at 750°C are better than, while sulfur loadings are comparable to those of zinc titanate at 550°C in cyclic desulfurization. The ability of the sorbent to reduce the H₂S in fuel gas at 750°C to levels less than 10 ppmv makes the sorbent suitable for hot gas desulfurization in IGCC and to less than 1 ppmv for MCFC applications.

Recommendations for future work include testing of copper chromite at lower temperatures and elevated pressures and enhancing sorbent durability. Operation at a lower temperature may reduce the decline in reactivity of the sorbent with cycling and increase the H₂S removal efficiency over that obtained at 750°C. Other sorbent-binder formulations may enhance sorbent durability and possibly stabilize the sorbent reactivity in cyclic operation.

REFERENCES CITED


This work was prepared with the support, in part, by grants made possible by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Illinois Clean Coal Institute, and by the U.S. Department of Energy. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of IDENR, ICCI, and the DOE.
Figure 1. EXPERIMENTAL SETUP FOR THE (A) 2.5-CM ID QUARTZ REACTOR AND (B) THERMOBALANCE REACTOR SYSTEMS
Figure 2. H$_2$S BREAKTHROUGH PROFILES FOR PRE-REDUCED (A) COPPER CHROMITE AND (B) COPPER-CERIUM AT 750°C IN SYNGAS
Figure 3. H₂S BREAKTHROUGH PROFILES FOR (A) COPPER CHROMITE AND (B) COPPER-CERIUM AT 850°C IN SYNGAS
Figure 4. REGENERATION OF COPPER CHROMITE AT 750°C IN AIR-N₂ MIXTURE

Figure 5. H₂S BREAKTHROUGH PROFILES FOR PRE-REDUCED CHROMIUM-RICH COPPER CHROMITE AT 750°C IN SYNGAS
FIGURE 6. SORBENT SULFUR LOADING FOR (A) COPPER CHROMITE AND (B) CHROMIUM-RICH COPPER CHROMITE
Figure 7. WEIGHT CHANGES OF COPPER CHROMITE IN TGA AT 750°C DURING (A) DIRECT SULFIDATION AND (B) REGENERATION
Figure 8. WEIGHT CHANGES OF COPPER CHROMITE IN TGA AT 750°C WITH PRE-REDUCTION (A) PRE-REDUCTION (B) SULFIDATION AND (C) REGENERATION
Figure 9. WEIGHT CHANGES OF CHROMIUM-RICH COPPER CHROMITE IN TGA AT 750°C WITH PRE-REDUCTION (A) PRE-REDUCTION (B) SULFIDATION (C) REGENERATION
Figure 10. REDUCTION OF COPPER CHROMITE SORBENT AT VARIOUS TEMPERATURES

Figure 11. SULFIDATION (WITHOUT PRE-REDUCTION) OF COPPER CHROMITE SORBENT AT VARIOUS TEMPERATURES
Figure 12. AVERAGE H₂S BREAKTHROUGH PROFILES FOR CHROMIUM-RICH COPPER CHROMITE AT 750°C IN SYNGAS

Figure 13. AVERAGE H₂S BREAKTHROUGH PROFILES FOR ZINC TITANATE AT 550°C IN SYNGAS
PROJECT MANAGEMENT REPORT
June 1 through August 31, 1994

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

DOE Grant Number: DE-FC22-92PC92521 (Second Year)
ICCI Project Number: R92-1/6.1B-3M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Co-Principal Investigator: Maria Flytzani-Stephanopoulos, Tufts University
Other Investigators: Andy H. Hill, Institute of Gas Technology, Zhijiang Li, Tufts University
ICCI Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS

The project was completed on schedule and all objectives were achieved.
## DEVELOPMENT OF COPPER-BASED SORBENTS FOR HOT GAS CLEAN-UP

### EXPENDITURES - EXHIBIT B

#### CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Types of Cost</th>
<th>Direct Labor</th>
<th>Fringe Benefits</th>
<th>Materials &amp; Supplies</th>
<th>Travel</th>
<th>Major Equipment</th>
<th>Other Direct Costs</th>
<th>Indirect Costs</th>
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<td></td>
<td>16,701</td>
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<td>36,741</td>
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<td>56,781</td>
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<td></td>
<td>2,500</td>
<td>508</td>
<td></td>
<td>56,781</td>
<td>42,479</td>
<td>118,957</td>
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<td>4,000</td>
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<td>66,805</td>
<td>55,047</td>
<td>150,000</td>
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<tr>
<td>Aug. 31, 1994</td>
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<td></td>
<td>4,000</td>
<td>560</td>
<td></td>
<td>66,805</td>
<td>55,809</td>
<td>150,000</td>
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*Cumulative by Quarter
CUMULATIVE COSTS BY QUARTER - EXHIBIT C

Development of Novel Copper-Based Sorbents for Hot Gas Cleanup.

(IN THOUSANDS)

Months and Quarters

O = Projected Expenditures $150,000
Δ = Actual Expenditures $150,000

Total ICCI Award $150,000
DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT GAS CLEAN-UP

A
B
C
D
E

Begins S O N D J F M A M J J A
Sept. 1, 1993

A. Parametric Studies of Sulfidation
B. Study of Sulfidation Kinetics
C. Sorbents Regenerability Studies
D. Preparation of Technical Reports
E. Preparation of Project Management Reports

SCHEDULE OF PROJECT MILESTONES
HAZARDOUS WASTE REPORT
September 1, 1993 through August 31, 1994

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

DOE Grant Number: DE-FC22-92PC92521 (Second Year)
ICCI Project Number: R92-1/6.1B-3M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Co-Principal Investigator: Maria Flytzani-Stephanopoulos, Tufts University
Other Investigators: Andy H. Hill, Institute of Gas Technology, Zhijiang Li, Tufts University
ICCI Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS

None of the hazardous substances defined under 40CFR261, Subpart D, entitled "List of Hazardous Wastes," were purchased, utilized, or generated in this project.
EQUIPMENT INVENTORY LIST
September 1, 1993 through August 31, 1994

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

DOE Grant Number: DE-FC22-92PC92521 (Second Year)
ICCI Project Number: R92-1/6.1B-3M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Co-Principal Investigator: Maria Flytzani-Stephanopoulos, Tufts University
Other Investigators: Andy H. Hill, Institute of Gas Technology, Zhijiang Li, Tufts University
ICCI Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS

No equipment with a life expectancy of one year of more was purchased in this project.
LIST OF PUBLICATIONS AND PRESENTATIONS
September 1, 1993 through August 31, 1994

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

DOE Grant Number: DE-FC22-92PC92521 (Second Year)
ICCI Project Number: R92-1/6.1B-3M
Principal Investigator: Javad Abbasian, Institute of Gas Technology
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Other Investigators: Andy H. Hill, Institute of Gas Technology, Zhijiang Li, Tufts University
ICCI Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS


DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS
FOR HOT GAS DESULFURIZATION

Javad Abbasi and Andy Hill, Institute of Gas Technology
Maria F. Stephenopoulos, Massachusetts Institute of Technology
Franklin I. Honea, Illinois Clean Coal Institute

ABSTRACT

Development of technology for coal gas desulfurization to sufficiently low levels at temperatures above 650°C is now recognized as an important factor for efficient and economic coal utilization in emerging technologies such as integrated gasification-combined cycle (IGCC) power generation (using gas turbines) and integrated gasification fuel cell (IGFC) power plants. The implementation of hot gas desulfurization technology heavily relies on the development of regenerable sorbent materials which have high sulfur capacity and can efficiently remove H₂S (from several hundred ppm levels down to a few ppm for IGCC application and to below ppm levels for IGFC application) over many sulfidation/regeneration cycles. Structural stability and good mechanical strength are additional desired features of the sorbents.

At sulfidation temperatures above 650°C, zinc-based sorbents will suffer zinc losses (via zinc vaporization) that reduces sorbent reactivities and structural stability in the cyclic process. Also, zinc-based sorbents, because of thermodynamic equilibrium limitations, are not suitable for fuel cell application where very low levels of H₂S (below ppmv) in the fuel gas is required. Copper-based sorbents do not suffer from metal volatility problems at temperatures well above 650°C, and have excellent sulfidation equilibria which make them ideal candidates for fuel cell application.

Several novel binary copper-based sorbents have been evaluated by the IGT/MIT team, and ranked in terms of their sulfidation equilibria, reduction stability, sulfidation reactivity and regenerability in the temperature range of 650°C to 850°C. The results of this study indicate that mixed binary oxide of copper with chromium (Cu-Cr-O) and Cerium (Cu-Ce-O) are the most promising sorbents for such high temperature coal gas desulfurization application. The effects of operating conditions and sorbent composition on the performance of the two selected binary oxide sorbents will be discussed in this paper.
DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT GAS CLEANUP

Javad Abbasi and Andy H. Hill
Institute of Gas Technology

Maria Flytzani-Stephanopoulos and Zhijiang Li
Tuft University

ICCI Project Manager: Franklin H. Honea

ABSTRACT

Development of the technology for coal gas desulfurization to sufficiently low levels at temperatures above 650°C is now recognized as crucial to efficient and economic coal utilization in emerging technologies such as coal gasification-combined cycle power generation (using gas turbines) and coal gasification/fuel cell power plants. The implementation of hot gas desulfurization technology relies heavily on the development of regenerable metal oxide sorbent materials which have high sulfur capacity and can efficiently remove H₂S (from several thousand ppm levels down to a few ppm) over many cycles of sulfidation/regeneration.

The objective of this study was to evaluate two novel copper-based sorbents (i.e., copper-chromium and copper-cerium) for hot gas desulfurization application at elevated temperatures. To achieve this objective, the effects of operating variables such as calcination temperature, calcination time, sorbents composition, and coal gas composition on the sorbent performance were evaluated. The physical/chemical properties of the sorbent undergoing various sulfidation/regeneration process were also determined. Based on the results of these analyses, the optimum sorbent composition and operating conditions were determined. The physical and chemical durability of the sorbents in the long "life" cycle test have also been determined.

The effectiveness of various sorbent composition over a wide range of operating conditions were determined in the thermogravimetric analyzer (TGA) and a fixed-bed reactor. Both sorbents appear to be very effective at 750°C with good capacity and regenerability. The effect of prereduction on the sorbents performance was also studied.

The results obtained in this study indicated that the copper-chromite sorbent (chromium-rich composition) is the best candidate for hot gas cleanup application at 750°C. The results obtained so far in the "life cycle" tests indicate that the reactivity of the sorbents is essentially maintained through successive sulfidation/regeneration process.