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TECHNICAL REPORT

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Project Title: Development of Novel Copper-Based Sorbents for Hot Gas Cleanup
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ABSTRACT

The objective of this investigation is to evaluate two novel copper-based sorbents (i.e. copper-chromium and copper-cerium) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C.

In this program, structural and kinetic studies will be conducted on various compositions of the two selected copper-based sorbents to determine the optimum sorbent composition. The effect of operating conditions on the performance of the sorbents along with the stability and regenerability of the selected sorbents in successive sulfidation/regeneration operation will be determined.

New sorbent compositions from the selected Cu-Cr-O and Cu-Ce-O binary oxides were prepared this quarter and characterized by BET N₂-desorption for surface area measurement following various calcination/time-temperature exposures. The general trends reported last quarter (on 11 different compositions) were validated this quarter in that both binary oxides lose surface area as the amount of CuO is increased.

Time-resolved sulfidation tests were conducted at 850°C using the equimolar CuO.Cr₂O₃ composition. SEM/EDX particle analyses showed that, with progressive sulfidation, agglomeration of micron-sized grains and surface enrichment in chromium occurred, and that chromium oxide is inert to sulfidation under the conditions used in the test.

The two selected binary oxides prepared in larger quantities (for testing in a two-inch reactor) have physical properties typical of the sorbents prepared in past programs. Two multicycle desulfurization tests, conducted this quarter on the Cu-Ce-O sorbent at 850 °C, using a feed gas containing 5000 ppm H₂S, 10 vol % H₂ and 10 vol % H₂O at a space velocity (STP) of 2000 h⁻¹, demonstrated high sulfur removal efficiency for the first one or two cycles, and a significant reduction in efficiency in the following cycles.

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EXECUTIVE SUMMARY

Development of technology for coal gas desulfurization to sufficiently low levels at temperatures of 600° to 800 °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 H_2S (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 oxides have superior properties compared to single oxides for hot gas cleanup. Compounds of zinc and iron oxides, zinc ferrites, i.e. $ZnFe_2O_4$, and zinc and titanium oxides i.e. $ZnTiO_3$, have reached pilot-stage desulfurization testing. However, at sulfidation temperatures above 600° to 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 750°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. In a recently ICCI-funded program, the 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 650° to 850°C. The results of this study indicate that mixed binary oxides of copper with chromium ($CuCr_2O_4$) and cerium ($CuCeO_3$) are the most promising sorbents for such high temperature fuel gas cleanup applications. In various sulfidation/regeneration tests, both sorbents were capable of removing H_2S from a hot fuel gas to very low levels (<10 ppm) at temperatures as high as 850°C with good sorbent regenerability in cycling process. However, additional work is needed to achieve overall sorbent optimization.

This research program will evaluate two novel copper-based sorbents (i.e. copper-chromium and copper-cerium) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C.

In this two-year program, binary oxides of copper with oxides of chromium and cerium will be prepared at various sorbent compositions. The structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation will be determined. The effects of additive and operating conditions on the sulfidation kinetics will also be determined. This information will be used to determine the most effective sorbent composition for further studies related to detailed kinetics, stability, and regenerability. The results of

the proposed program will be used to determine the most effective copper-based sorbent for high temperature application that can be used as an alternative to the zinc-based sorbents.

During the previous quarter, six different compositions of Cu-Cr-O containing 25 to 99 mol % of Cr_2O_3 in CuO and five different compositions of Cu-Ce-O containing 33 to 90 mol % CeO_2 in CuO were prepared. After calcination at 500-1000°C it was found that the surface area of the Cu-Cr-O sorbents was invariant to composition at calcination temperatures higher than 700°C, except when excess CuO was used.

During this quarter new sorbent compositions from the selected binary oxides, i.e. Cu-Ce-O and Cu-Cr-O, were prepared according to the amorphous citrate technique and characterized by BET N_2 -desorption for surface area measurement following various calcination/time-temperature exposures. A few of the sorbent compositions that gave ambiguous data last quarter were remade and characterized again this quarter. The general trends reported last quarter were validated this quarter in that both binary oxides lose surface area as the amount of CuO is increased. This effect is very pronounced in calcination at 700°C for 2 hours, but less so at the high calcination temperatures of 850° and 1000°C. All sorbent compositions suffer large surface area loss between 700° and 850° C calcination temperature, the rate of loss being higher for low CuO-sorbent contents. Above 850°C, the rate of sintering (surface area loss) is approximately the same for all sorbent compositions.

Larger quantities (approx. 1 kg samples) of the precursor salts of the two selected binary oxides were synthesized for sulfidation testing in the two-inch reactor. The sorbent precursors, prepared according to the amorphous citrate technique, were calcined in various batches for one hour in a two-inch ID quartz reactor using air at 900°C-1000°C. The calcined Cu-Cr-O and Cu-Ce-O sorbents were analyzed and shown to have BET- N_2 surface areas ranging from 2.2-2.7 m^2/g , and 5.4-6.5 m^2/g , and bulk densities of 0.30-0.61 g/cm^3 , and 0.15-0.16 g/cm^3 , respectively. The porosity of the Cu-Ce-O sorbent varied from 1.7-2.5 cm^3/g . XRD analyses of these materials identified CuCr_2O_4 as the only phase present Cu-Cr-O sorbent, and separate CuO/ CeO_2 phases in the Cu-Ce-O sorbent.

Two multicycle (sulfidation/regeneration) desulfurization tests consisting of four and three cycles each were conducted on the Cu-Ce-O sorbent at 850°C using 5000 ppm H_2S . In the first test, performed in the upflow sulfidation mode, sulfidation cycle 1 showed typical results for this sorbent, reducing the H_2S exit gas concentration to less than 10 ppm for t/t^* from 0 to nearly 0.6. However, in the next two sulfidation cycles the H_2S exit gas concentration was below 10 ppm only for t/t^* from 0 to 0.12-0.18, with the H_2S rising to over 16 ppm at a t/t^* of 0.01 in the fourth cycle.

The second desulfurization test was conducted in the downflow mode

because there were some indications that fluidization and/or gas channeling may have occurred after the first cycle in the upflow sulfidation mode. This test, using fresh Cu-Ce-O sorbent, was conducted at the same reaction conditions as in the first upflow test except that the initial bed height was 1 inch. In the first sulfidation cycle the H_2S exit gas concentration was reduced to less than 10 ppm for a t/t^* from 0 to 0.7, and less than 50 ppm for a t/t^* up to 1.0. In the second sulfidation cycle less than 10 ppm H_2S was seen in the exit gas for a t/t^* from 0 to 0.35, and less than 50 ppm up to a t/t^* of 0.62, results similar to those obtained in the previous work using this sorbent. However, much higher pre-breakthrough H_2S levels were seen in the third cycle. The sorbents will be analyzed to determine the cause of the apparent decrease in sorbent activity.

Time-resolved sulfidation tests also began this quarter. These tests aim at studying structural changes in the sorbent caused by the progress of sulfidation both in the low-hydrogen and in highly reducing gas streams (to be tested next quarter). The equimolar $CuO.Cr_2O_3$ composition was chosen for time-resolved sulfidation testing. The tests were performed at 850°C using a gas mixture containing 2 mol % H_2S , 1 mol % H_2 and 97 mol% N_2 . Data were collected after 25, 50 and 100% sulfidation of the $CuO.Cr_2O_3$. SEM/EDX was used to follow surface morphology and phase composition changes in these samples. The H_2S content of the reactor exit gas was also measured.

Energy dispersive X-ray analysis (EDX) of fresh $CuO.Cr_2O_3$ particles verified the Cr/Cu atomic ratio of 2/1, in agreement with earlier XRD analysis performed last quarter which identified $CuCr_2O_4$ as the only phase present in this material. Three major effects can be reported from the SEM/EDX analyses of the partially and fully sulfided samples: (i) well-crystallized (sub-micron) grains, which formed on the surface of the 25% sulfided samples, changed over to broad-sized agglomerates progressively with the extent of sulfidation, (ii) the surface is progressively enriched in Cr from the stoichiometric 2/1 Cr/Cu ratio in the fresh and 25% sulfided material to 5/1 atomic ratio for the 100% sulfided sample, (iii) sulfur is only associated with copper, i.e. chromium oxide is inert to sulfidation under these conditions. This is verified by the EDX analysis where the atomic ratio of S/Cu is approximately equal to the stoichiometric ratio for Cu_2S in all samples.

OBJECTIVE

The overall objective of this program is to evaluate two novel copper-based sorbents (i.e. Cu-Cr-O and Cu-Ce-O) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 650° to 850°C. The specific objective of this two-year program is to optimize sorbent composition to determine 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 are 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 are to:

1. Prepare and characterize large quantities of two binary copper-based sorbents, namely copper-chromium and copper-cerium;
2. Determine the structural effects of cerium oxide and chromium oxide addition in copper oxide;
3. Determine the kinetic effects of additives in sulfidation;
4. Carry out a parametric study of sulfidation with both sorbents in a fixed bed to determine the effects of operating variables;
5. 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 emission. 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 800°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 H_2S (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 new generation gas turbines (with inlet temperatures exceeding 760°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 816°C or higher. In a recently ICCI-funded program, IGT and MIT (in a joint team 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 indicate that mixed binary oxides of copper with chromium (Cu-Cr-O) and cerium (Cu-Ce-O) are the most promising sorbents for such high temperature hot gas cleanup applications. In various sulfidation/regeneration tests, both sorbents were capable of removing H_2S from a hot fuel gas to very low levels (<10 ppm) at temperatures as high as 850°C with good sorbent regenerability in cycling process. However, additional work is needed to achieve overall sorbent optimization. The structural effects of CeO_2 and Cr_2O_3 addition in CuO and the effects of additives and operating conditions on sulfidation kinetics, stability and regenerability of the sorbent should be determined.

The objective of this investigation is to evaluate two novel copper-based sorbents (i.e. copper-chromium and copper-cerium) for their effectiveness in removing hydrogen sulfide from fuel gas in the temperature range of 600° to 850°C.

In this two-year program, binary oxides of copper with oxides of chromium and cerium will be prepared at various sorbent compositions. The structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation will be determined. The effects of additive and operating conditions on the sulfidation kinetics will also be

determined. This information will be used to determine the most effective sorbent composition for further studies related to detailed kinetics, stability, and regenerability. The results of the proposed program will be used to determine the most effective copper-based sorbent for high temperature application that can be used as an alternative to the zinc-based sorbents.

EXPERIMENTAL PROCEDURE

Sorbent Synthesis and Characterization

The objective of this task is to prepare several copper-based sorbents with different compositions for testing in this program.

During this quarter new sorbent compositions from the selected binary oxides, i.e. Cu-Ce-O and Cu-Cr-O, were prepared according to the amorphous citrate technique and characterized by BET N_2 -desorption for surface area measurement following various calcination/time-temperature exposures. A few of the sorbent compositions that gave ambiguous data last quarter were remade and characterized again this quarter.

Calcination of larger quantities (400-600 cm³) of the two selected binary oxide precursors (synthesized in the previous quarter) for sulfidation testing in the two-inch reactor was also completed this quarter. The sorbent precursors, prepared according to the amorphous citrate technique, were calcined in various batches for one hour in a two-inch ID quartz reactor using air at 900°-1000°C.

Each of the batches of calcined sorbent material was analyzed for one or more of the following physical properties: 1) BET- N_2 surface area, 2) XRD analysis, 3) Hg porosity, 4) bulk density, and 5) chemical composition.

Parametric Studies of Sulfidation

The objective of this task is to determine the effects of operating conditions on the performance of the selected sorbents.

Multicycle (sulfidation/regeneration) desulfurization tests were conducted on the Cu-Ce-O sorbent. The desulfurization tests were performed in a two-inch quartz reactor system shown in Figure 1 (configured in the Figure for sulfidation testing in the downflow mode and regeneration in the upflow mode). The 4-ft long, two-inch ID quartz reactor is housed in a two-zone furnace. Teflon tubing is used to convey H_2S -containing exit gas at temperatures lower than 200°C. A coarse porous quartz frit at the bottom of the sorbent bed is used to support the bed and as the gas distributor.

A syringe pump is used to introduce steam into the reactor through capillary tubing at the top of the reactor as shown in the Figure,

or at the bottom of the reactor in the upflow sulfidation mode. A thermocouple sheathed with a 1/8-inch closed-end quartz tube, that can be positioned within the bed or just above the bed, is used to measure temperature. A computerized data acquisition system is used to record bed temperatures as a function of time.

Partially cooled gases from the reactor are sent to either a glass condenser system or to a Balston coalescing filter in which all the exit gas is cooled by the use of an ice bath, and the water vapor condensed and collected. The Balston coalescing filter is also used to collect sulfur produced during sorbent regeneration.

The dry gases required for sulfidation and regeneration of the sorbent are obtained from cylinders. The gases are passed through pre-calibrated electronic mass flow controllers (set to give the desired level of H_2S and other gases) and mixed prior to entering the reactor. A purge gas, such as nitrogen, is used during the heating and cooling of the sorbent bed and during switching between sulfidation and regeneration cycles.

Sulfidation is carried out by flowing the H_2S -containing gas until the H_2S concentration in the reactor exit gas reaches approximately 500-600 ppm. Following the sulfidation, the reactor is switched to regeneration mode by stopping the flow of sulfidation gas to the reactor and heating the reactor to the desired reaction temperature again with continuous passage of nitrogen flowing through the reactor. Once the desired temperature is attained, the flow of regeneration gas is begun. Regeneration is performed using nitrogen as a diluent and air to give 3-6 vol % O_2 in the feed gas.

A slipstream of the gas from the reactor (after condensers) is diverted to the gas chromatograph for measurement of H_2S and SO_2 concentrations. The gas stream analysis is carried out using a Hewlett-Packard Gas Chromatograph equipped with flame photoionization (FPD) and thermal conductivity detectors. A Chromosil-310 column at $70^\circ C$ is used to separate the H_2S and SO_2 . Prior to each test, the gas chromatograph is calibrated using calibration standard gas samples.

Determination of Structural Effects

The objective of this task is to determine the effects of additive oxides (CeO_2 , Cr_2O_3) in reductive sulfidation.

Work on this task continued this quarter. These tests aim at studying structural changes in the sorbent caused by the progress of sulfidation both in the low-hydrogen and in highly reducing gas streams (to be tested next quarter). The equimolar $CuO.Cr_2O_3$ composition was chosen for time-resolved sulfidation testing. The sorbent was first calcined at $1000^\circ C$ for one hour. Time-resolved sulfidation tests were conducted in a 1-cm ID quartz reactor tube

with a shallow bed (1 cm tall) of -35+60 mesh sorbent particles. The tests were performed at 850°C using a gas mixture containing 2 mol % H_2S , 1 mol % H_2 and 97 mol% N_2 . Data were collected after 25, 50 and 100% sulfidation of the $\text{CuO} \cdot \text{Cr}_2\text{O}_3$. SEM/EDX was used to follow surface morphology and phase composition changes in these samples. The H_2S content of the reactor exit gas was also measured.

RESULTS AND DISCUSSION

Sorbent Synthesis and Characterization

Figures 2 and 3 show the measured surface areas as a function of mol % CuO in the $(\text{CuO})_x\text{-Cr}_2\text{O}_3$ and $(\text{CuO})_x\text{-CeO}_2$ binary oxides, respectively. The general trends reported last quarter were validated in that both binary oxides lose surface area as the amount of CuO is increased. This effect is very pronounced in calcination at 700°C for two hours, but less so at the high calcination temperatures of 850° and 1000°C. All sorbent compositions suffer large surface area loss between 700° and 850°C calcination temperature, the rate of loss being higher for low CuO-sorbent contents. Above 850°C, the rate of sintering (surface area loss) is approximately the same for all sorbent compositions.

The physical properties of the sorbents prepared in this task for testing in the two-inch reactor are summarized in Table 1. The calcined Cu-Cr-O and Cu-Ce-O sorbents have BET- N_2 surface areas ranging from 2.2-2.7 m^2/g , and 5.4-6.5 m^2/g , and bulk densities of 0.30-0.61 g/cm^3 , and 0.15-0.16 g/cm^3 , respectively. The porosity of the Cu-Ce-O sorbent varied from 1.7-2.5 cm^3/g . The physical properties of the two selected binary oxides are typical of the sorbents prepared in past programs in terms of their surface areas, bulk densities and XRD patterns. Examples of XRD graphs for the two selected sorbents are presented in Figure 4 and show that CuO and Cr_2O_3 formed the oxide compound CuCr_2O_4 , while CuO and CeO_2 existed only in individual phases.

Parametric Studies of Sulfidation

Two multicycle desulfurization tests, consisting of four and three cycles each, were conducted on the Cu-Ce-O sorbent (by combining the material from batches 9+10 in Table 1) at 850°C, using a 5000 ppm H_2S , 10 vol % H_2 , and 10 vol % H_2O feed gas mixture, and a space velocity of 2000 hr^{-1} . These tests were conducted in both the upflow and downflow sulfidation modes. Tests were conducted in the downflow mode because there were some indications that fluidization and/or gas channeling may have occurred during the upflow sulfidation mode.

Sulfidation cycle one (upflow mode) showed typical results for this sorbent, reducing the H_2S exit gas concentration to less than 10 ppm for t/t from 0 to nearly 0.6 (Figure 5). However, in the next two

sulfidation cycles the H_2S exit gas concentration was below 10 ppm only for t/t^* from 0 to 0.12-0.18, with the H_2S rising to over 16 ppm at a t/t^* of 0.01 in the fourth cycle. The sorbent was regenerated in the downflow mode at 750°C using a 3 vol % O_2 in N_2 gas. Regeneration was continued until the SO_2 level in the exit gas was less than 50 ppm. No elemental sulfur was trapped in the simple glass condenser during the regeneration of the sorbent, although significant amounts were trapped in the second (downflow) desulfurization test with the use of a Balston coalescing filter (cooled in an ice bath) when regeneration was conducted upflow. The results of the Cu-Ce-O sorbent regenerations for test one are shown in Figure 6.

A chemical analysis of the product solids after the first and third regeneration cycles (Table 2), indicates a nearly complete regeneration of the sorbent and no reduction in the surface area. A screen analysis of the bed solids after the fourth cycle did show significant reduction in sample particle size. This fact, in combination with the very low density of the sorbent and the fact that the bed shrinkage was about 20% after the fourth cycle, may have resulted in partial fluidization of the bed and/or gas channeling due to bed segregation thereby producing higher pre-breakthrough H_2S levels in the product gas.

A second test was conducted using fresh Cu-Ce-O sorbent with sulfidation in the downflow mode in an attempt to prevent the problems which may have occurred in the first test. The same reaction conditions as in the first upflow test (i.e. 850°C and a space velocity of 2000 hr^{-1}) were used except that the initial bed height was 1 inch. As shown in Figure 7, in the first sulfidation cycle the H_2S exit gas concentration was reduced to less than 10 ppm for a t/t^* from 0 to 0.7 and less than 50 ppm for a t/t^* up to 1.0. In the second sulfidation cycle less than 10 ppm H_2S was seen in the exit gas for a t/t^* from 0 to 0.35, and less than 50 ppm up to a t/t^* of 0.62, results similar to those obtained in the previous work using this sorbent. Much higher pre-breakthrough H_2S levels were seen in the third cycle. A fourth cycle was not completed due to a plug in the water delivery line at the beginning of the experiment.

Regeneration was conducted in the upflow mode at 750°C and 3-6 vol % O_2 in the first cycle and third cycles, and at 750 - 850°C using 6 vol % O_2 in the second cycle (Figure 8). Elemental sulfur was produced during each regeneration of the Cu-Ce-O sorbent, as was evidenced by the fact that it condensed on the upper, cooler part of the reactor early in the regeneration and volatilized as time progressed. Although not trapped in the glass condenser used in the first cycle, it was trapped in the next regeneration cycle by using a Balston coalescing filter cooled in an ice bath. Nearly 25% of the sulfur captured by the sorbent was released as sulfur

TABLE 1. SUMMARY OF PHYSICAL PROPERTIES OF SORBENTS FOR TESTING IN TWO-INCH REACTOR

Batch No.	1	2	3	4	5	6
Sorbent	Cr	Cr	Cr	Cr	Cr	Cr
Calcination Temp., °C	1000	1000	1000	900	900	900
Surface Area, m ² /g	2.2	2.4	2.7	2.6	2.4	2.5
Bulk Density, g/cm ³	0.43	0.37	0.30	0.94	0.47	0.38
Particle Size (mesh)	-35+60	-35+60	-35+60	-35+60	-35+80	-35+80
CA:TM Ratio ¹ , mol/mol	2	2	2	1 ²	2	2

Batch No.	7	8	9	10
Sorbent	Cr	Cr	Ce	Ce
Calcination Temp., °C	900	900	900	900
Surface Area, m ² /g	2.6	2.5	5.4	6.5
Bulk Density, g/cm ³	0.51	0.61	0.16	0.15
Particle Size (mesh)	-35+80	-35+80	-35+80	-35+80
CA:TM Ratio ¹ , mol/mol	2	2	2	2
Hg Porosity., cm ³ /g			1.66	2.50

¹Ratio of moles of citric acid to moles of Cu+Cr or Cu+Ce used in preparation of the precursor salts in the amorphous citrate technique
²Low CA:TM ratio used

TABLE 2. COMPARISON OF Cu-Ce-O FEED
AND DESULFURIZATION PRODUCT SOLIDS

	<u>Feed</u>	<u>Test 1 Product¹</u>	<u>Test 2 Product²</u>
Surface Area, m ² /g	5.9	5.1	--
Sulfate, wt %	--	0.18	--
Sulfide, wt %	--	<0.055	--
Cu, wt %	24.2	24.9	
<u>Particle Size (Mesh)</u>			
-20+35	55.0	35.3	28.2
-35+60	34.7	43.1	36.2
-60+80	10.3	14	15.3
-80	0	7.6	20.3

¹Sulfate/sulfide and Cu analyses after regeneration cycle 3
²and particle size analysis after sulfidation cycle 4.
 Particle size analysis after sulfidation cycle 4.

during the second regeneration. Only about 5% was trapped after the third regeneration.

As in the first test, significant bed shrinkage occurred. The bed shrinkage was approximately 25%, 14% and 11% after cycles 1, 2 and 3, respectively, about 2.5 times that seen in the first test. The product solids will be analyzed to determine if regeneration was complete and if changes occurred in the surface area or porosity. Further multicycle desulfurization tests will be conducted in the downflow mode using this sorbent at the same reaction conditions but using an initially larger bed volume.

Determination of Structural Effects

Figures 9 and 10 show SEM pictures of the fresh sorbent CuO.Cr₂O₃ used in the time-resolved sulfidation tests. Energy dispersive X-ray analysis (EDX) of these particles verified the Cr/Cu atomic ratio of 2/1, in agreement with earlier XRD analysis performed last quarter which identified CuCr₂O₄ as the only phase present in this material.

Figures 11-18 show the SEM pictures of the partially and fully sulfided samples, while Figures 19 and 20 show the corresponding ratio of Cr/Cu and S/Cu in the samples measured by EDX. Three major effects can be reported from this analyses: (i) well-crystallized (sub-micron) grains, which formed on the surface of the 25% sulfided samples (Figures 12 and 13), changed over to broad-sized agglomerates (Figure 18) progressively with the extent of sulfidation, (ii) the surface is progressively enriched in Cr (as shown in Figure 19) from the stoichiometric 2/1 Cr/Cu ratio in the fresh and 25% sulfided material to 5/1 atomic ratio for the 100% sulfided sample, (iii) sulfur is only associated with copper,

i.e. chromium oxide is inert to sulfidation under these conditions. This is shown in Figure 20 where the atomic ratio of S/Cu (measured by EDX) is approximately equal to the stoichiometric one for Cu_2S in all samples.

CONCLUSIONS AND RECOMMENDATIONS

New sorbent compositions from the selected Cu-Cr-O and Cu-Ce-O binary oxides were prepared this quarter and characterized by BET N_2 -desorption for surface area measurement following various calcination/time-temperature exposures. The typical trends reported last quarter (on 11 different compositions) were validated this quarter in that both binary oxides lose surface area as the amount of CuO is increased.

The two selected binary oxides prepared in larger quantities for desulfurization testing in the two-inch reactor have physical properties typical of the sorbents prepared in past programs in terms of their surface areas, bulk densities and XRD patterns.

In the two multicycle desulfurization tests (upflow and downflow modes) using the Cu-Ce-O sorbent, the H_2S exit gas concentration in sulfidation cycle 1 was reduced to less than 10 ppm for t/t. from 0 to 0.6-0.7, results similar to those obtained in the previous work using this sorbent. However, there was a significant reduction in H_2S removal efficiency in following cycles.

Further desulfurization tests will be conducted in the downflow mode using this sorbent at the same reaction conditions but using an initially larger bed volume. Tests will also be conducted to determine the effects of fuel gas composition, space velocity and sulfidation temperature.

Time-resolved sulfidation tests were conducted at 850°C using the equimolar $\text{Cu.Cr}_2\text{O}_3$ composition. SEM/EDX particle analyses showed that, with progressive sulfidation, agglomeration of micron-sized grains and surface enrichment in chromium occurred, and that chromium oxide is inert to sulfidation under the conditions used in the test. Tests will be conducted in highly reducing gas streams next quarter.

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FIGURE 1. BENCH-SCALE EXPERIMENTAL SETUP FOR TWO-INCH ID QUARTZ REACTOR

FIGURE 4. X-RAY DIFFRACTION GRAPHS OF
Cu-Cr-O AND Cu-Ce-O
a) Batch 1, b) Batches 9 and 11

FIGURE 5. H₂S BREAKTHROUGH PROFILES FOR Cu-Ce-O SORBENT (Upflow Mode)

FIGURE 7. H₂S BREAKTHROUGH PROFILES FOR Cu-Ce-O SORBENT (Downflow Mode)

FIGURE 6. CYCLIC REGENERATION OF Cu-Ce-O SORBENT (Test 1)

FIGURE 8. CYCLIC REGENERATION OF Cu-Ce-O SORBENT (Test 2)

FIGURE 9. SEM OF FRESH SORBENT $\text{CuO-Cr}_2\text{O}_3$

FIGURE 10. CLOSE-UP SEM OF FRESH SORBENT $\text{CuO-Cr}_2\text{O}_3$

FIGURE 11. SEM OF $\text{CuO-Cr}_2\text{O}_3$ AFTER 25% SULFIDATION

FIGURE 12. CLOSE-UP SEM OF $\text{CuO-Cr}_2\text{O}_3$ AFTER 25% SULFIDATION (For the Smoother Area A in Figure 11)

FIGURE 13. CLOSE-UP SEM OF CuO-Cr₂O₃
AFTER 25% SULFIDATION
(For the Rougher Area B in Figure 11)

FIGURE 14. SEM OF CuO-Cr₂O₃
AFTER 50% SULFIDATION

FIGURE 15. CLOSE-UP SEM OF CuO-Cr₂O₃
AFTER 50% SULFIDATION
(For the Smoother Area A in Figure 14)

FIGURE 16. CLOSE-UP SEM OF CuO-Cr₂O₃
AFTER 50% SULFIDATION
(For the Rougher Area B in Figure 14)

FIGURE 17. SEM OF $\text{CuO-Cr}_2\text{O}_3$
AFTER 100% SULFIDATION

FIGURE 18. CLOSE-UP SEM OF $\text{CuO-Cr}_2\text{O}_3$
AFTER 100% SULFIDATION

FIGURE 19. EDX DATA OF $\text{CuO-Cr}_2\text{O}_3$
SORBENT SULFIDATION (Cr:Cu Ratio)

FIGURE 20. EDX DATA OF $\text{CuO-Cr}_2\text{O}_3$
SORBENT SULFIDATION (S:Cu Ratio)

PROJECT MANAGEMENT REPORT
December 1, 1992 through February 28, 1993

Project Title: **Development of Novel Copper-Based Sorbents for Hot Gas Cleanup**

Principal Investigator: Andy H. Hill, Institute of Gas Technology

Co-Principal Investigator: Maria Flytzani-Stephanopoulos, Massachusetts Institute of Technology

Other Investigators: Javad Abbasian, Institute of Gas Technology
Luhong Bo, Massachusetts Institute of Technology
Li Li, Massachusetts Institute of Technology

Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS

Due to a personnel change at MIT, work was delayed but is expected to be back on schedule. Desulfurization testing at IGT is somewhat behind schedule due to longer than expected times required to prepare the sorbents but is also expected to be back on schedule.

DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT-GAS CLEANUP

Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1992 to Nov. 30, 1992	Projected	5,000	0	1,500		0	16,000	12,711	35,211
	Estimated	2,651		2,401			9,000	7,167	21,219
Sept. 1, 1992 to Feb. 28, 1993	Projected	11,500	0	2,500	1316	0	32,000	28,304	75,620
	Estimated	15,411		3,331			20,424	29,885	69,051
Sept. 1, 1992 to May 31, 1993	Projected	18,000	0	3,500	1316	0	48,000	43,621	114,437
	Estimated								
Sept. 1, 1992 to Aug. 31, 1993	Projected	21,609	0	4,000	1576	0	58,058	52,415	137,655
	Estimated								

*Cumulative by Quarter

Months and Quarters

0 = Projected Expenditures \$75,620

Δ = Estimated Actual Expenditures \$69,051

Total Illinois Clean Coal Institute Award \$137,655

DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT-GAS CLEANUP

SCHEDULE OF PROJECT MILESTONES

- A. Sorbents Synthesis and Characterization
- B. Parametric Studies of Sulfidation
- C. Determination of Structural Effects
- D. Study of Sulfidation Kinetics
- E. Sorbents Regenerability Studies
- F. Preparation of Technical Reports
- G. Preparation of Project Management Reports

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