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Project Title: **DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS
 FOR HOT-GAS CLEANUP** DE-FC22-92PC 92521

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ABSTRACT

The objective of this investigation is 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 >750°C) in Integrated Gasification Combined Cycle (IGCC) systems.

Structural and kinetic studies were conducted on various compositions of the two 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 were determined. Overall, the CuO-lean binaries (with Cr₂O₃ or CeO₂) may benefit the H₂S breakthrough levels. While this is at the expense of sulfur capacity for the Cu-Cr-O sorbents (Cr₂O₃ is inert), it may not affect the capacity of the Cu-Ce-O sorbents (CeO₂-participation).

Parametric multicycle desulfurization tests were conducted in a bench-scale quartz reactor at one atmosphere using the CuCr₂O₄ and CuO-CeO₂ sorbents. The parameters studied included temperature, space velocity, and feed gas composition. Both sorbents were able to reduce the H₂S concentration of the reactor feed gas from 5000 ppmv to less than 1 ppmv to 10 ppmv at 750° to 850°C.

Both sorbents were found to consume H₂ and produce SO₂ during the initial stages of sulfidation. Analysis of partially sulfided samples identified predominantly Cu metal, the additive oxide (either Cr₂O₃ or CeO₂) and small amounts of oxidic copper. For the Cu-Cr-O sorbents, the latter is apparently sufficient to keep the H₂S pre-breakthrough levels as low as has been reported in this work. For the Cu-Ce-O sorbents, in which very little or no oxidic copper remained, the low H₂S levels may be due to the participation of CeO₂, whose sulfidation is promoted by copper.

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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 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 oxides have superior properties compared to single oxides for hot gas cleanup. Compounds of zinc and iron oxides, zinc ferrites, such as ZnFe₂O₄, and zinc and titanium oxides, such as ZnTiO₃, 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 completed 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 (CuCr₂O₄) and cerium (CuO-CeO₂) 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 (<10 ppm) 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 objective of this research program is 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.

In this two year program, binary oxides of copper with oxides of chromium and cerium are prepared at various sorbent compositions. The structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation are determined. The results of this program will be used to identify the most promising copper-based sorbent for high temperature application that can be further developed as an alternative to the zinc-based sorbents.

Mixed sorbent oxides containing 20 mol% to 75 mol% copper with CeO_2 and Cr_2O_3 were prepared and the surface areas of these sorbents were determined after calcination at various conditions. At calcination temperatures of 550° to 1000°C and calcination times of 0.5 to 1 hour, the surface areas of the Cu-Cr-O sorbents, as determined by N_2 -desorption, decrease as the amount of CuO is increased, especially at lower calcination temperatures while a maximum in surface area for the 50:50 molar mixture of CuO: CeO_2 was identified.

Sulfidation tests were conducted on the various compositions of the two sorbents to study structural changes in the sorbents caused by the progress of sulfidation in both low-hydrogen and highly reducing gas streams. After 25, 50, 75 and 100% sulfidation of the calcined sorbents, little change in the surface area was indicated with the extent of sulfidation. For all sorbents, breakthrough of H_2S occurred earlier when the 20% H_2 gas mixture was used. Overall, the CuO-lean binaries (with Cr_2O_3 or CeO_2) may benefit the H_2S breakthrough levels. While this is at the expense of sulfur capacity for the Cu-Cr-O sorbents (Cr_2O_3 is inert), it may not affect the capacity of the Cu-Ce-O sorbents (CeO_2 -participation). Further refinements require more detailed studies of regeneration performance (including regeneration off-gas composition) and mechanical strength studies, in addition to detailed kinetic studies of sorbent reduction and sulfidation.

Parametric multicycle desulfurization tests were conducted in a bench-scale (5-cm-diameter) quartz reactor at one atmosphere using the CuCr_2O_4 and CuO- CeO_2 sorbents. The test conditions included two temperatures (750° and 850°C), two space velocities, and three gas compositions.

In the baseline sulfidation tests at 850°C , with a space velocity of 2000 hr^{-1} and a 10 vol% H_2 , 10 vol% H_2O , N_2 -feed gas mixture, the CuCr_2O_4 reduced the H_2S concentration of the feed gas from 5000 ppmv to less than 1 to 10 ppmv, in all three cycles conducted. Two distinct H_2S pre-breakthrough levels were obtained, an initially very low H_2S level and a second higher level. The second H_2S pre-breakthrough level corresponds to the sulfidation equilibrium of metallic copper (to Cu_2S) while the first corresponds closely to that of CuO.

Similar breakthrough curves were obtained at double the space velocity, suggesting that it may be possible to increase the space velocity even further and still obtain high H_2S removal efficiencies. Using syngas as the sulfidation feed gas did not appear to significantly affect the performance of the sorbent except to increase the second pre-breakthrough H_2S level which may be attributed to a slightly higher H_2 concentration due to some water-gas shift. The sorbent performance improved dramatically in the tests conducted at 750°C , in that very low levels of H_2S were seen until most of the copper was utilized. Increasing the H_2 concentration in the feed gas from 10 vol% to 20 vol% significantly

reduced the effectiveness of the sorbent. Regeneration of the CuCr_2O_4 at 750°C using 6 vol% O_2 in N_2 was rapid and apparently complete in all tests.

The CuO-CeO_2 sorbent was also capable of removing the H_2S to very low levels comparable to the CuCr_2O_4 sorbent. The CuO-CeO_2 sorbent appeared to be less effective after the first cycle at all conditions tested, which may be attributable to sulfate formation during the regeneration of the CuO-CeO_2 or to the presence of some remaining elemental sulfur produced during the regeneration of the sorbent. Sulfided CuO-CeO_2 generally required longer regeneration times than the CuCr_2O_4 sorbent to reach very low SO_2 exit gas concentrations. With the 20 vol% H_2 gas, very low H_2S exit gas concentrations were obtained in the first sulfidation/regeneration cycle with a corresponding increase in the total capacity of the sorbent. In the two subsequent cycles, however, the performance of the sorbent decreased significantly.

Both sorbents were found to consume H_2 and produce SO_2 during the initial stages of sulfidation. Analysis of partially sulfided samples identified predominantly Cu metal, the additive oxide (either Cr_2O_3 or CeO_2) and small amounts of oxidic copper. For the Cu-Cr-O sorbents, the latter is apparently sufficient to keep the H_2S pre-breakthrough levels as low as has been reported in this work. For the Cu-Ce-O sorbents, in which very little or no oxidic copper remained, the low H_2S levels may be due to the participation of CeO_2 , whose sulfidation is promoted by copper.

OBJECTIVE

The overall objective of this program is 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 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.¹³ 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.^{4,10} 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 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. 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,¹¹ IGT and MIT (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 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 (that is, 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 the structural effects of chromium oxide and cerium oxide (additives) to copper oxide in sorbent synthesis and reductive sulfidation are determined. The effects of additive and operating conditions on the performance of the sorbents are also determined. The results of the proposed program will be used to identify the most effective copper-based sorbent for high

temperature application that can be further developed as an alternative to the zinc-based sorbents.

EXPERIMENTAL PROCEDURE

Sorbent Synthesis and Characterization

Batches of Cu-Cr-O and Cu-Ce-O sorbent oxides with different compositions were prepared (using the amorphous citrate technique¹²) for testing in the 1-cm-diameter microreactor. The surface areas of these sorbents were determined using BET N₂-desorption after calcination from 0.5 to 2 hours at 500°-1000°C.

Larger batches of CuCr₂O₄ and CuO-CeO₂ sorbents were prepared (also using the amorphous citrate technique) for testing in the bench-scale unit. The calcined sorbents were analyzed by XRD for crystalline phase identification, surface area and Hg-porosity.

Parametric Studies of Sulfidation

Multicycle desulfurization tests were conducted in the bench-scale (5-cm-diameter) reactor at one atmosphere using the CuCr₂O₄ and CuO-CeO₂ sorbents. The bench-scale quartz reactor system, shown in Figure 1, is configured for sulfidation testing in the downflow mode and regeneration in the upflow mode. The 1.2 m long, 5-cm ID quartz reactor is heated by a two-zone furnace. A coarse porous quartz frit near the middle of the reactor is used to support the sorbent bed and as the gas distributor. A thermocouple sheathed with a 3-mm closed-end quartz tube, that can be positioned within the bed or just above the bed, is used to measure temperature. Bed temperatures are recorded as a function of time using a computerized data acquisition system. Teflon[®] tubing is used to convey SO₂/H₂S-containing exit gas at temperatures lower than 200°C. 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 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 pressurized cylinders. The gases are passed through pre-calibrated electronic mass flow controllers (set to give the desired level of H₂S and other gases) and mixed prior to entering the reactor. A syringe pump is used to introduce steam into the reactor through capillary tubing at the top of the reactor. A nitrogen purge gas 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 H₂S-containing gas until the H₂S concentration in the reactor exit gas reaches approximately

500 ppmv. Following 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 with continuous passage of nitrogen flowing through the reactor. Once the desired temperature is attained, the flow of regeneration gas is begun. A slipstream of the gas from the reactor (after condensers) is diverted to the gas chromatograph for measurement of H₂S and SO₂ concentrations. Prior to each test, the gas chromatograph is calibrated using calibration standard gas samples.

The test conditions included: 1) two temperatures: 750° and 850°C, 2) three different feed gases: one containing 5000 ppm H₂S, 10 vol% H₂ and 10 vol% H₂O in N₂, a second with 5000 ppm H₂S, 10 vol% H₂, 10 vol% H₂O, 20 vol% CO and 10 vol% CO₂ in N₂, and a third containing 5000 ppm H₂S, 20 vol% H₂ and 10 vol% H₂O in N₂, and 3) two space velocities: 2000 and 4000 hr⁻¹ (STP). Regeneration of the sulfided sorbents was conducted at 750°C and one atmosphere, using a 3%-6% O₂ in N₂ gas. Reductive regenerations using 10 vol% H₂ and 10 vol% H₂O in N₂ were also performed on the Cu-CeO₂ sorbent in some tests.

Determination of Structural Effects

These tests aimed at studying structural changes in the sorbents caused by the progress of sulfidation both in the low-hydrogen (1%) and in the highly reducing gas streams containing 20% H₂. Time-resolved sulfidation experiments were conducted with the various Cu-Cr-O and Cu-Ce-O sorbent compositions at 850°C in which fresh sorbents were sulfided to predetermined levels. The tests were conducted in a 1-cm ID quartz reactor tube with a shallow bed (1 cm tall) of -35+60 mesh (0.03-0.05 cm diameter) sorbent particles, and a space velocity of 3000 hr⁻¹ using two different gas mixtures: one containing 2 vol% H₂S, 1 vol% H₂ and 97 vol% N₂, and the second gas mixture containing 2 vol % H₂S, 20 vol% H₂ and 78 vol% N₂. The levels of sulfidation selected were 25, 50, 75 and 100%.

X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used to follow surface morphology and phase composition changes in the sorbents. The H₂S contents of the reactor exit gas were also measured.

To determine the effects of excess ceria on the performance of the Cu-Ce-O sorbent, additional multicycle desulfurization tests were also conducted in the microreactor using two CeO₂-rich Cu-Ce-O sorbents, namely, Cu-2Ce and Cu-4Ce with molar ratios of CuO:CeO₂ = 1:2 and 1:4, respectively. These tests were conducted at 850°C and a space velocity of 2000 hr⁻¹, with a gas mixture containing 5000 ppmv H₂S, 18 vol% H₂O, 10 vol% H₂ and N₂. The Cu-2Ce sorbent was calcined at 990°C and the Cu-4Ce was calcined at 880°C.

RESULTS AND DISCUSSION

Sorbent Synthesis and Characterization

Figures 2 and 3 show the surface areas of the 3Cu-2Cr, Cu-2Cr, Cu-6Cr, 3Cu-Ce, Cu-Ce and Cu-3Ce sorbent oxides after calcination. All the Cu-Cr-O oxides lose surface area as the amount of CuO is increased, especially at the lower calcination temperatures, with the rate of loss being higher at the higher Cu concentrations (Figure 2). For the Cu-Ce-O sorbents, Figure 3 shows a clear maximum in surface area for the 50:50 molar mixture of CuO:CeO₂, at all temperatures below 1000°C.

The physical properties of the sorbents prepared for bench-scale testing are summarized in Table 1. The characteristics of the sorbent samples are highly dependent on the preparation technique. The calcined Cu-Cr-O and Cu-Ce-O sorbents have BET-N₂ surface areas ranging from 2.2-2.7 m²/g, and 5.4-6.5 m²/g, and bulk densities of 0.30-0.61 g/cm³, and 0.15-0.16 g/cm³, respectively. The porosity of the Cu-Ce-O sorbent varied from 1.7-2.5 cm³/g. XRD diffraction spectra for the two sorbents selected for bench-scale testing show that CuO and Cr₂O₃ formed the oxide compound CuCr₂O₄, while CuO and CeO₂ existed only in individual phases.

Parametric Studies of Sulfidation

CuCr₂O₄ Sorbent

The H₂S breakthrough profiles over three cycles for the CuCr₂O₄ sorbent at the baseline conditions of 850°C, a space velocity of 2000 hr⁻¹ with a feed gas containing 5000 ppmv H₂S, 10 vol% H₂ and 10 vol% H₂O in N₂ are shown in Figure 4. Here t/t^{*} is the normalized conversion where t^{*} is the theoretical breakthrough time calculated by assuming copper oxide as the only active phase sulfided by H₂S to Cu₂S. Two distinct H₂S pre-breakthrough levels can be seen in the figure, an initially very low H₂S level and a second higher level. The second H₂S pre-breakthrough level corresponds to the sulfidation equilibrium of metallic copper (to Cu₂S) while the first corresponds closely to that of CuO.

When the space velocity was doubled (Figure 5) very low H₂S concentrations were again obtained suggesting that it may be possible to further increase the space velocity while maintaining high H₂S removal efficiencies.

Results using a simulated coal gasification product gas (syngas) as the feed gas mixture at 850°C are shown in Figure 6. The higher second H₂S pre-breakthrough value (compared to that seen in the test without CO/CO₂ in the feed gas mixture) is probably due to a slightly higher H₂ concentration produced by the water-gas shift

reaction. The syngas does not appear to adversely affect the high reactivity of the sorbent at 850°C.

Figure 7 shows that operating at 750°C can reduce the H₂S in the exit gas to less than 1 to 10 ppmv for up to a normalized conversion of 0.70 or nearly twice the normalized conversion as that obtained at 850°C for the same level of H₂S removal.

Increasing the H₂ concentration in the feed gas from 10 to 20 vol% significantly reduced the conversion level before the first breakthrough as well as the total capacity of the sorbent for all three cycles, as shown in Figure 8.

Regeneration of the sulfided sorbents was conducted in the upflow mode at 750°C and 3-6 vol % O₂-N₂. Regeneration of the CuCr₂O₄ was rapid and apparently complete in that very low SO₂ levels were seen in the regeneration off-gas soon after the majority of the SO₂ was eluted.

CuO-CeO₂ Sorbent

The H₂S breakthrough profiles for three sulfidation/regeneration cycles conducted using the CuO-CeO₂ sorbent at the baseline sulfidation conditions are shown in Figure 9. The sorbent was able to reduce the H₂S in the feed gas to below 10 ppmv in the first two cycles, but did not maintain the same high reactivity level in the third cycle. The lower H₂S removal efficiency of the sorbent seen in the third cycle may be due to incomplete regeneration of the sorbent as is shown in Figure 10. SO₂ levels in the regeneration off-gas did not fall to the same low levels as rapidly as was seen with the CuCr₂O₄ sorbent (Figure 11) and when the air was stopped and replaced with N₂ high levels of SO₂ eluted from the regenerated sorbent. This may be attributed to the decomposition of copper or cerium sulfates, which is inhibited in the presence of O₂. The normalized conversion > 1.0 suggests the possible formation of cerium sulfides. Additionally, upon exposure of the regenerated CuO-CeO₂ sorbent to a H₂/H₂O-containing gas at 850°C, significant quantities of H₂S eluted from the sorbent, possibly due to metal sulfate reduction. It is also possible that the elemental sulfur produced during regeneration may have been the source of the H₂S.

In an attempt to prevent H₂S formation at the beginning of the sulfidation tests, the next two tests included a pre-treatment step, in which the regenerated sorbent was exposed to a 10 vol% H₂/10 vol% H₂O in N₂ gas mixture until the H₂S concentration in the exit gas was below 10 ppmv. This pre-treatment often required a number of hours after which the sorbent was re-oxidized with a 6 vol% O₂-N₂ gas mixture. In all cases there was considerable bed shrinkage and particle size reduction with each succeeding cycle which was not seen in the tests with the CuCr₂O₄ sorbent.

Figure 12 shows that, as with the CuCr_2O_4 sorbent, the fresh CuO-CeO_2 sorbent maintains its high reactivity for H_2S removal when the space velocity is doubled from 2000 to 4000 hr^{-1} . However, the reactivity declined significantly in the second and third cycles. Because the first sulfidation cycle demonstrated high H_2S removal efficiency, it is possible that the poor performance of the CuO-CeO_2 in the second and third sulfidation cycles may be due to incomplete regeneration, or to the reductive pre-treatment step used for the first time in this test and/or that an insufficient amount of time was used to re-oxidize the sorbent.

The results of the sulfidation test conducted over three cycles with the syngas at 850°C are shown in Figure 13. For the fresh sorbent, it appears that the high reactivity of the sorbent is maintained and that the syngas may even increase the total capacity of the sorbent by favoring the conditions for the possible formation of other sulfur containing copper or cerium compounds.

In the test at 750°C (Figure 14), the fresh sorbent reduced the H_2S exit gas concentration to <10 ppmv up to a normalized conversion of 0.70, followed by a sharp breakthrough to the inlet H_2S concentration. There was a considerable increase in the pre-breakthrough H_2S levels in the two succeeding cycles due to the same factors discussed above.

The effect of higher H_2 concentration in the feed gas on the sulfidation performance of the CuO-CeO_2 sorbent is shown in Figure 15. In the first sulfidation/regeneration cycle, no effect on the first H_2S pre-breakthrough or conversion level is shown, although the total capacity of the sorbent increased to a t/t' of greater than 2.1. In the two subsequent cycles, however, the first pre-breakthrough conversion level of the sorbent as well as the overall capacity decreased dramatically.

Sorbent Reduction and SO_2 Production

Flowrate measurements during sulfidation testing revealed that the exit gas flowrate decreased immediately upon introduction of the feed gas by an amount corresponding to the H_2 flowrate. The exit gas flowrate then rapidly increased to the feed gas flowrate value after a length of time corresponding approximately to that required to reduce all of the copper oxide in the sorbent to metallic copper by the feed gas H_2 . The absence of H_2 in the exit gas was confirmed by an independent analysis of exit gas samples taken at various times during the test. To confirm copper oxide reduction to metallic copper, sulfidation tests were conducted in which the test was terminated shortly after the exit gas flowrate measurement indicated that no further H_2 was being consumed, but well before the first H_2S breakthrough was reached. Samples of the top and bottom of the bed were analyzed by XRD for crystalline phase identification. Sulfidation tests were conducted in both the

bench-scale reactor and microreactor with both sorbents at 850°C using a feed gas containing 5000 ppmv H₂S, 10 vol% H₂, 10 vol% H₂O in N₂, and at 650°C (in the bench-scale reactor only) using 5000 ppmv H₂S, 10 vol% H₂, and 20 vol% H₂O in N₂. In all tests, less than 1 ppmv of H₂S was detected in the reactor exit gas up to the point at which the test was terminated.

The XRD diffraction spectra of the CuCr₂O₄ sorbent partially sulfided to a $t/t^* = 0.16$ at 850°C in the bench-scale reactor indicates predominantly metallic copper and Cr₂O₃, with significantly smaller amounts of Cu₂O and Cu₂S in both the top and bottom bed samples. The 650°C samples ($t/t^* = 0.25$) show the presence of Cu, Cr₂O₃ and oxidic copper as CuCrO₂, instead of Cu₂O in both bed samples, suggesting that copper reduction is slower at 650°C.

The diffraction spectra of the CuO-CeO₂ sorbent partially sulfided to a $t/t^* = 0.36$ at 850°C (in the bench-scale reactor) indicates phases present as Cu and CeO₂, and some Cu₂S and CeS₂ in the top bed sample. Only Cu and CeO₂ were seen in the bottom sample at 850°C. At 650°C ($t/t^* = 0.39$) the top bed sample shows phases present as predominantly CeO₂, Cu and Cu₂S. The bottom bed sample shows mainly CeO₂, Cu and a very small amount of Cu₂O. The presence of some copper oxide suggests that reduction is also slower for the CuO-CeO₂ sorbent at 650°C.

During sulfidation testing, SO₂ is produced (to a maximum of 100-200 ppmv) immediately after introduction of the H₂S feed gas. Although the SO₂ drops off rapidly to very low levels (1 ppmv or less) in some tests it persists at this low level to the end of the test. The time at which the sharp drop-off in the SO₂ concentration occurs coincides approximately with the time required to reduce all of the copper oxide in the sorbent to metallic copper at the prevailing H₂ gas flowrate. This suggests that the SO₂ may be produced by the reaction of H₂S with the metal oxides, or possibly by some solid-solid reactions.

Analysis, by XRD, of the samples from the tests conducted in the microreactor, identified Cu metal and CeO₂ in the Cu-Ce sorbents, while the partially sulfided CuCr₂O₄ samples showed Cu, Cr₂O₃ and oxidic copper (in a bound form: CuCrO₂, CuCr₂O₄). Minor unidentified peaks may correspond to sulfide phases.

What is interesting in terms of structural information is that, apparently, in the CuO-CeO₂ system, the reduction of CuO to Cu metal is fast and complete. However, the CuCr₂O₄ sorbent retains some copper in oxide compound form (with chromium) even after 30-35% sulfidation. The latter is sufficient to keep the H₂S pre-breakthrough levels as low as has been reported in this work. The explanation for the former probably resides with the participation of the CeO₂, whose sulfidation is promoted by copper.

Alternatively, some partially oxidized copper may exist in association with the CeO_2 -lattice oxygen, so the end effect is again low pre-breakthrough levels of H_2S (lower than for Cu metal sulfidation).

In regards to SO_2 production, the above analyses indicate that the Cu-Ce-O sorbents are less prone to reactions of oxidic copper with H_2S to produce SO_2 . This is because the CuO in the Cu-Ce-O sorbents will rapidly reduce to Cu metal. On the other hand, the reverse is true for Cu-Cr-O materials, which show considerable SO_2 production under certain conditions (low H_2 , low H_2O).

Determination of Structural Effects

Cu-Cr-O Sorbent

Figure 16 shows the surface area change with extent of sulfidation for the Cu-Cr-O sorbents. Little surface area change was observed up to 100% sulfidation.

Figure 17 shows the H_2S breakthrough profiles for the Cu-2Cr (CuCr_2O_4) sorbent. In the 1% H_2 gas, breakthrough of H_2S occurred at a normalized conversion of nearly two, or double that observed in the 20% H_2 gas, suggesting the formation of CuS.

For the copper-rich 3Cu-2Cr sorbent (Figure 18) in the 20% H_2 gas, low H_2S levels were seen for a shorter duration and without the plateau in the H_2S concentration as seen with the Cu-2Cr. In the 1% H_2 gas, after an initially low H_2S exit gas concentration, the H_2S concentration increased gradually to the inlet H_2S value which is probably due to the higher H_2S equilibrium of metallic copper formed from the excess CuO.

For the Cr_2O_3 -rich Cu-6Cr sorbent (Figure 19), in which the copper is highly dispersed, very low levels of H_2S in the exit gas were observed for longer periods of time than in either of the other two Cu-Cr sorbents. The normalized conversions for the Cu-6Cr sorbent reached 1.4 in the 20% H_2 gas to 3.6-4.3 in the 1% H_2 gas. A sharp breakthrough to the inlet H_2S values occurred in both gases indicating that the copper is not as easily reduced to metallic copper in this sorbent.

Table 2 shows the X-ray diffraction data obtained for fresh and fully sulfided Cu-6Cr and for the fully sulfided Cu-2Cr sorbents. CuO and Cr_2O_3 formed oxide compounds CuCr_2O_4 and CuCrO_2 , when Cr_2O_3 and CuO, respectively, were in excess. For sulfidation in 20% H_2 , with the Cu-6Cr material, only oxide phases could be identified, but considerably shifted, indicative of oxide solid solution or oxysulfide solid solution formation masking the sulfide phase. Mixed copper-chromium sulfides are seen for the case of sulfidation

of the same material in low hydrogen (1%).

Figure 20 shows EDX data for sulfided Cu-Cr-O sorbents in terms of Cr/Cu atomic ratios. These data are for overall scans of particles, which are occasionally inhomogeneous. For the equimolar Cu-2Cr material, EDX data at 100% sulfidation show minor enrichment in chromium over the stoichiometric 2:1. The 3Cu-2Cr material shows no enrichment, while the Cu-6Cr shows Cu-enrichment in the calcined (fresh) material changing over to Cr-rich surfaces after 100% sulfidation in H₂-rich gas (20% H₂). The sample sulfided in 1% H₂ remained rich in copper.

Although Cu-2Cr showed little enrichment overall, certain areas of the Cu-2Cr (appeared "rough" in SEM pictures) were shown by EDX to be rich in Cr₂O₃. The effect of higher H₂ in the gas is dramatic for this material. Two types of crystals were seen in the SEM: the light is Cr₂O₃-rich and has low sulfur, while the dark corresponds to large, triangular copper-rich crystals with high sulfur content.

SEM pictures of the 3Cu-2Cr sorbent showed sintered crystals of CuO and CuCrO₂ constituting the fresh material. After complete sulfidation in 1% H₂, agglomerated large crystals ($\approx 2 \mu\text{m}$) were seen with evidence of grain sintering and partial melting. The surface of the 100% sulfided material in 20% H₂ appeared highly crystalline.

For specific areas of the chromium-rich Cu-6Cr sorbent samples, SEM pictures and EDX data reveal the development of two types of crystals in gas mixtures with low H₂ (1%): "dark", large copper sulfide crystals and smaller "light" areas consisting of mixed chromium-copper sulfide phases with higher than 0.5 S/Cu ratio. In 20% H₂ more uniform surfaces were seen consisting of sub-micron crystallites, rich in chromium.

Cu-Ce-O Sorbent

Figure 21 shows the surface area change with extent of sulfidation for the various copper-cerium sorbents. As with the copper-chromium sorbents, little surface area change was observed with the extent of sulfidation for all compositions.

Figure 22 shows the H₂S breakthrough profiles of Cu-Ce (1:1) sorbent. In the 1% H₂ gas, breakthrough of H₂S occurred at a conversion slightly higher than that observed in the 20% H₂ gas.

For the 3Cu-Ce sorbent (Figure 23), in the 20% H₂-gas, very low H₂S levels were seen for a shorter duration than was seen with the Cu-Ce (1:1) sorbent. In the 1% H₂ gas, after an initially low H₂S exit gas concentration lasting somewhat longer than in the 20% H₂ gas, the H₂S concentration increased more gradually to the inlet H₂S value than in the 20% H₂ gas. The results obtained with this sorbent are similar to the 3Cu-2Cr sorbent for which lower levels

of conversion were attributed to the reduction of the excess copper oxide in the sorbent.

For the Cu-3Ce sorbent (Figure 24), in which the copper is highly dispersed, very low H₂S exit gas concentrations were obtained for longer periods of time than in the other two copper-cerium sorbents. The very low H₂S level lasted twice as long in the 1% H₂ gas as in the 20% H₂ gas. This is again similar to the Cu-6Cr sorbent where excess chromium may improve sorbent performance in terms of conversion.

Figures 25-27 summarize the EDX analysis of the 50% and 100% sulfided Cu-Ce and Cu-3Ce samples. As shown in Figure 25, upon sulfidation, the surface of the Cu-Ce sorbents becomes Ce-rich (30-50% over stoichiometric). An exception is the 100% sulfided Cu-3Ce sample (in 20% H₂), but this may be due to particle variability. The partially sulfided samples had a reddish color, indicative of Cu metal presence. The S/Cu atomic ratio (Figures 26 and 27) in partially sulfided samples was very low (< 0.1) supporting the hypothesis of copper metal formation as the first step during sulfidation. A peculiar finding of zero sulfur on the surface of the fully sulfided Cu-Ce sorbent cannot be explained at the present time. The samples Cu-3Ce show S:Cu ratio higher than 0.5 in their fully sulfided form indicating again possible sulfidation of CeO₂.

Results of the multicycle sulfidation/regeneration tests using the two CeO₂-rich Cu-Ce-O sorbents are shown in Figures 28 and 29. Figure 28 for Cu-2Ce shows three cycles of sulfidation with intermittent regeneration at 750°C with 30 vol% air-N₂ gas mixture. After the third sulfidation cycle, the surface area of this sorbent was slightly higher (1.7 m²/g) than the fresh material (1.4 m²/g). XRD analysis of the sulfided material identified Cu₃S₂ as a major phase, CeS₂, CeO₂ and minor amounts of other Cu_{2-x}S phases. Figure 29 shows three sulfidation cycles with the Cu-4Ce material at similar conditions. Both Figures 28 and 29 indicate the pre-breakthrough H₂S levels in CeO₂-rich Cu-Ce-O sorbents are well below the corresponding equilibrium values, based on copper metal sulfidation. Because the CeS₂ phase has consistently appeared in sulfided Cu-Ce-O sorbents analyzed by XRD, it appears that copper enhances the sulfidation of cerium oxide. The equilibrium data for cerous oxide, Ce₂O₃, are superior to copper metal. It is not known at this point whether a partially reduced ceria, CeO_{2-x}, or a concerted effect of partially reduced copper and cerium oxides, is responsible for the low pre-breakthrough values of H₂S in these tests. However, it is clearly shown in this work that the presence of copper in cerium oxide enables the partial sulfidation of ceria. CeO₂ is known to be inactive under the conditions of these tests. Pre-reduction with H₂ or CO at high temperature is required to activate ceria. Therefore, the effect of copper in CeO₂ is that of a reduction sulfidation promoter.

CONCLUSIONS AND RECOMMENDATIONS

The results of the parametric multicycle sulfidation/regeneration tests conducted in the bench-scale reactor indicate that the reactivity of both the CuCr_2O_4 and CuO-CeO_2 sorbents are high enough to reduce the H_2S content of coal gasification product gas to below 1 to 10 ppmv at temperatures from 650° to 850°C. The effectiveness of the CuCr_2O_4 was lower than that of the CuO-CeO_2 sorbent when using a feed gas containing a higher H_2 concentration in the feed gas. The CuCr_2O_4 sorbent was easily regenerated with a 6 vol% air/ N_2 gas at 750°C while the copper cerium sorbent appears to require a longer regeneration time and/or higher temperatures or alternate methods for complete regeneration.

From the study of structural effects of additives, it has been found that, overall, the CuO -lean binaries (with Cr_2O_3 or CeO_2) may benefit the H_2S breakthrough levels. While this is at the expense of sulfur capacity for the Cu-Cr-O sorbents (Cr_2O_3 is inert), it may not affect the capacity of the Cu-Ce-O sorbents (CeO_2 -participation). Further refinements require more detailed studies of regeneration performance (including regeneration off-gas composition) and mechanical strength studies, in addition to the detailed kinetic studies of reduction and sulfidation.

It was also discovered during the course of this study that the H_2 in the feed gas reacts rapidly with both the CuCr_2O_4 and CuO-CeO_2 sorbents at 650° to 850°C during the initial stages of sorbent sulfidation to produce metallic copper, the additive oxides and smaller amounts of oxidic copper. Apparently, however, the remaining oxidic copper is in sufficient quantities to be able reduce the H_2S to the very low levels seen in this work. Detailed kinetic studies of competing reactions may be needed to determine the optimum process configuration of a hot-gas cleanup system for application of CuO -based sorbents.

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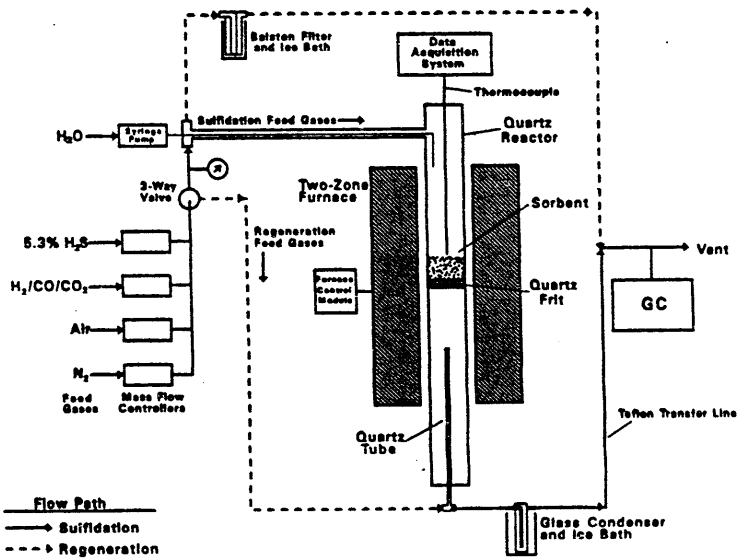


Figure 1. BENCH-SCALE EXPERIMENTAL SETUP FOR THE 5-CM ID QUARTZ REACTOR

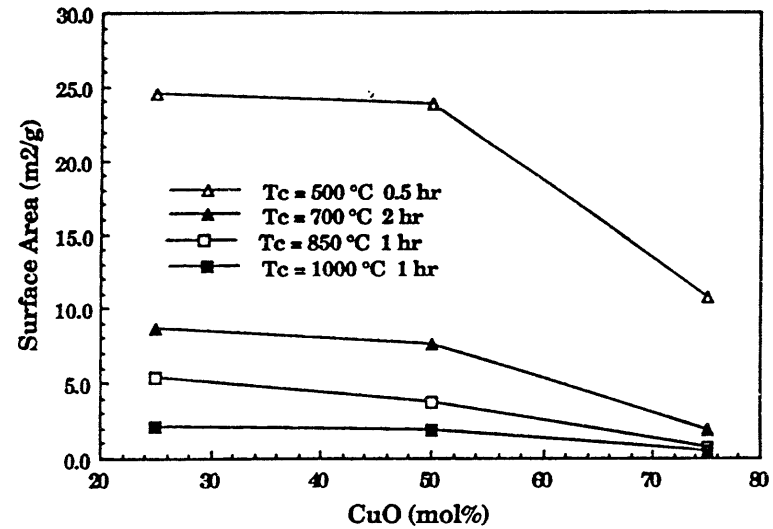


Figure 2. SURFACE AREAS OF Cu-Cr-O MIXED OXIDES AFTER CALCINATION AT DIFFERENT TEMPERATURES

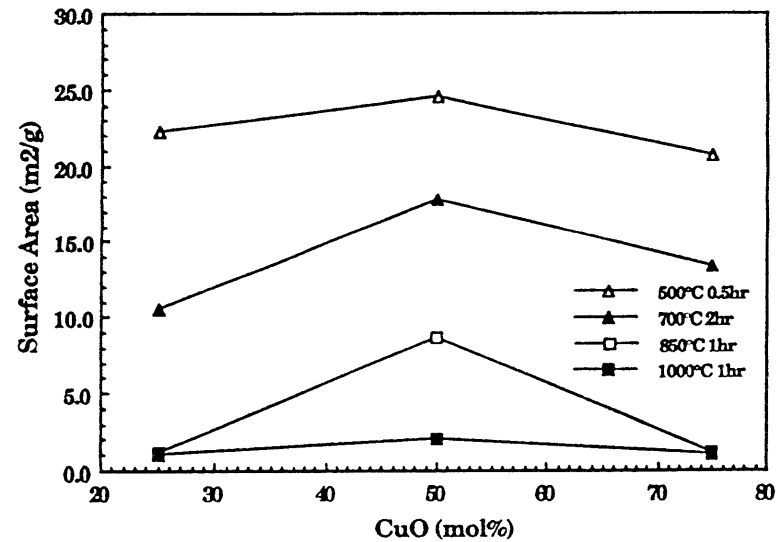


Figure 3. SURFACE AREAS OF Cu-Ce-O MIXED OXIDES AFTER CALCINATION AT DIFFERENT TEMPERATURES

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
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

Table 1. SUMMARY OF PHYSICAL PROPERTIES OF SORBENTS FOR TESTING IN BENCH-SCALE REACTOR

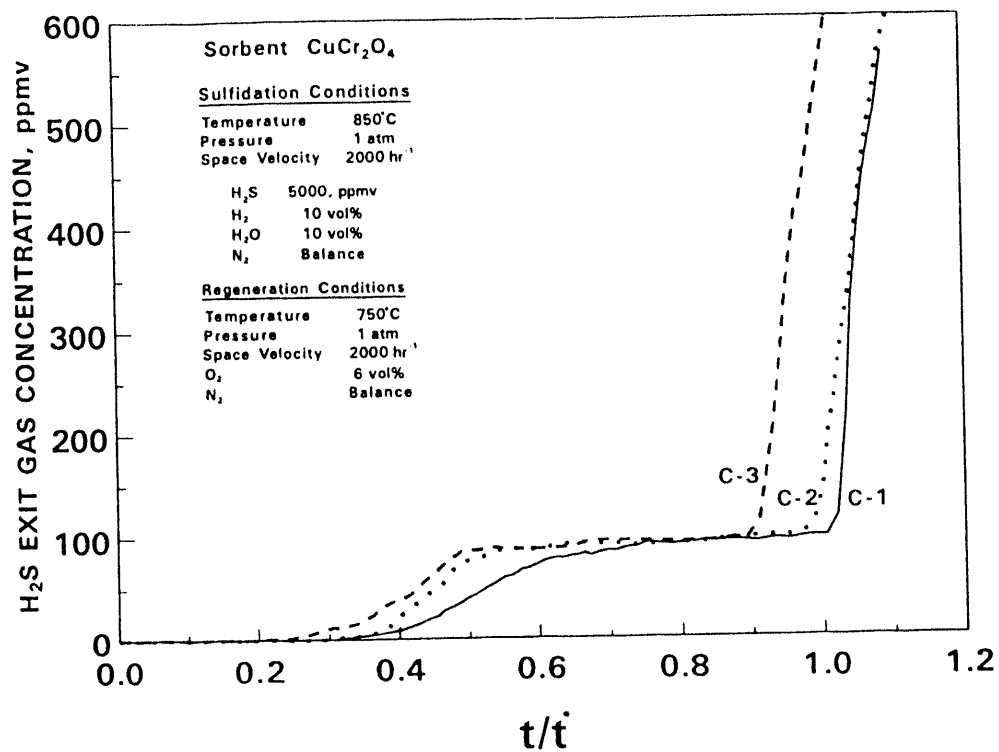


Figure 4. H₂S BREAKTHROUGH PROFILES FOR CuCr_2O_4 AT 850°C AND A SPACE VELOCITY OF 2000 hr⁻¹

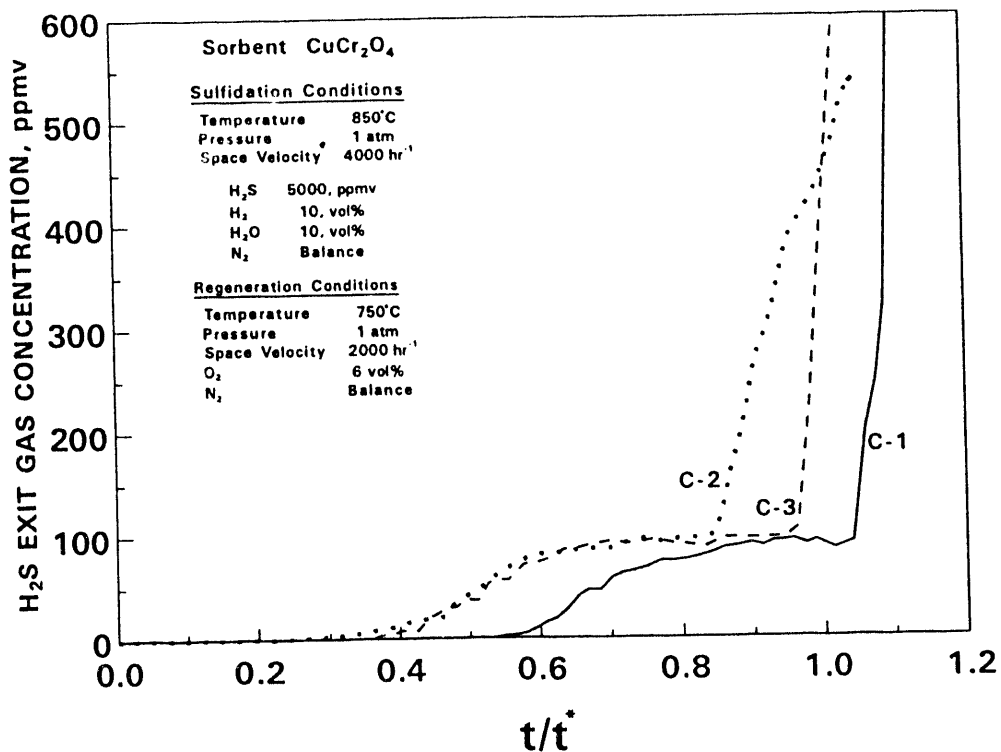


Figure 5. H₂S BREAKTHROUGH PROFILES FOR CuCr_2O_4 AT 850°C AND A SPACE VELOCITY OF 4000 hr⁻¹

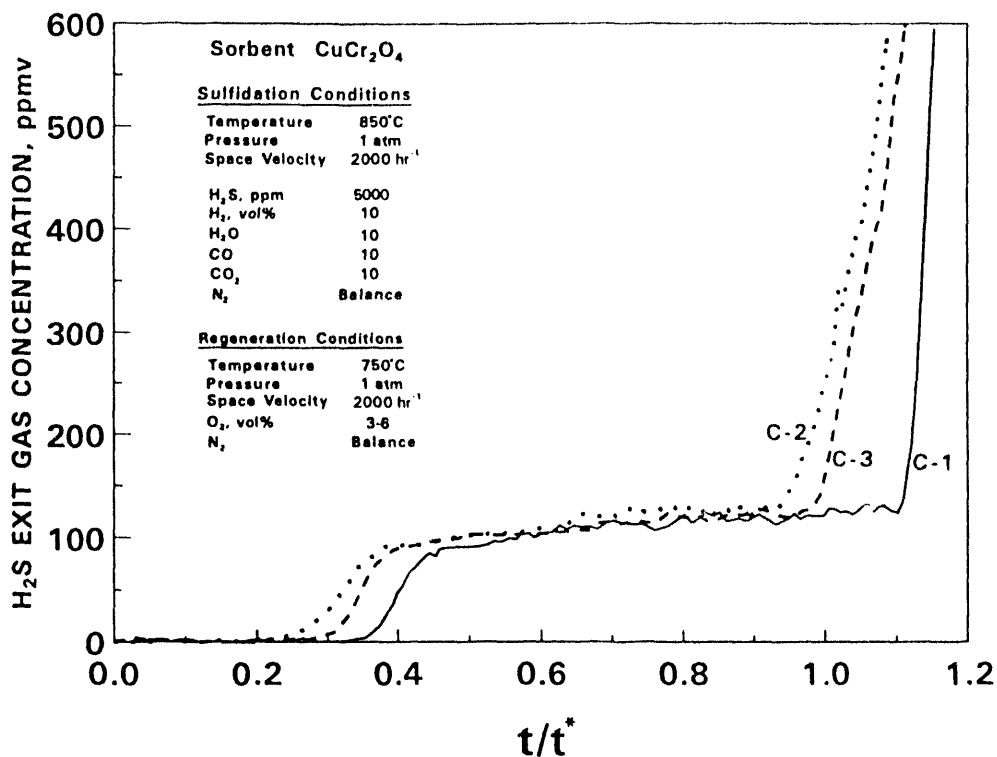


Figure 6. H₂S BREAKTHROUGH PROFILES FOR CuCr_2O_4 AT 850°C IN SYNGAS

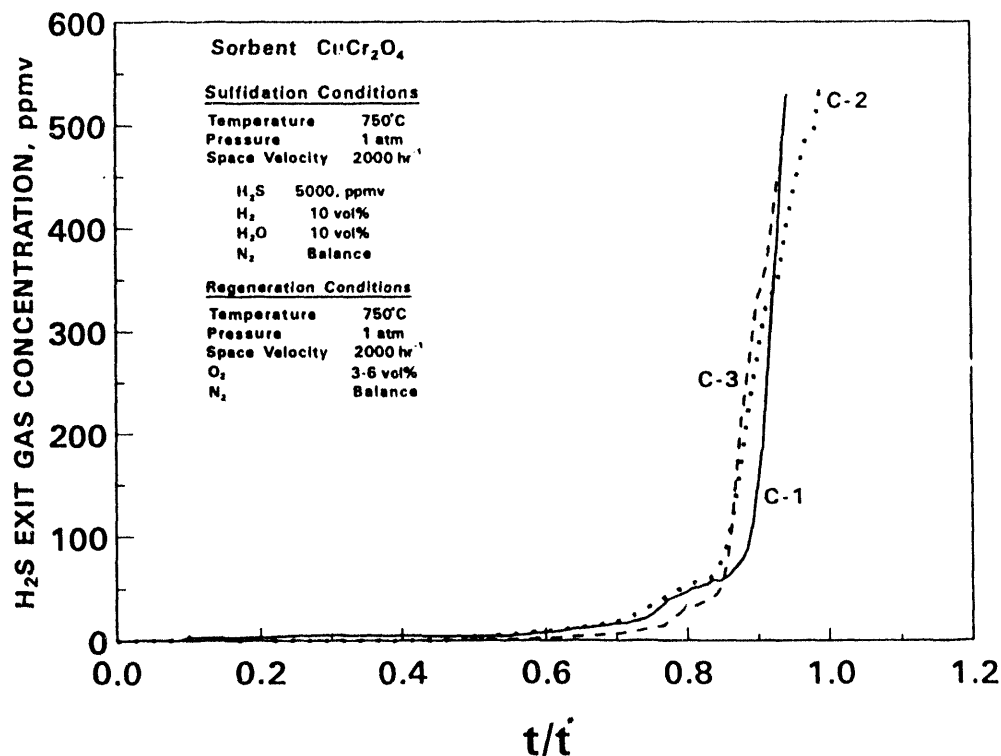


Figure 7. H₂S BREAKTHROUGH PROFILES FOR CuCr_2O_4 AT 750°C

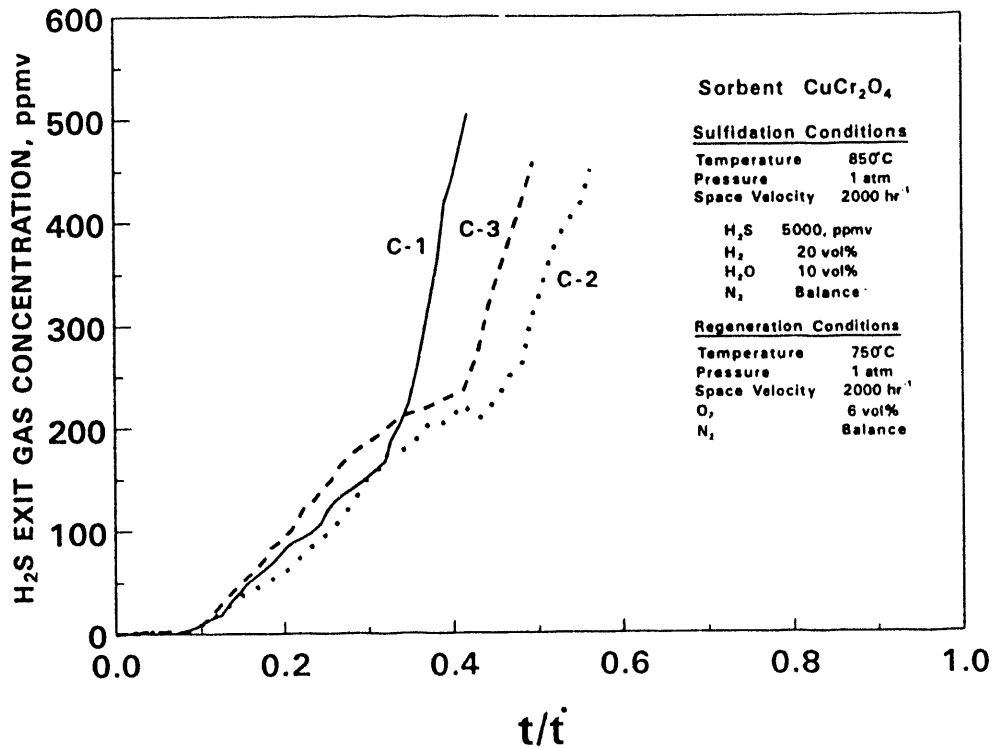


Figure 8. H₂S BREAKTHROUGH PROFILES FOR CuCr_2O_4 AT 850°C IN 20 VOL% H₂

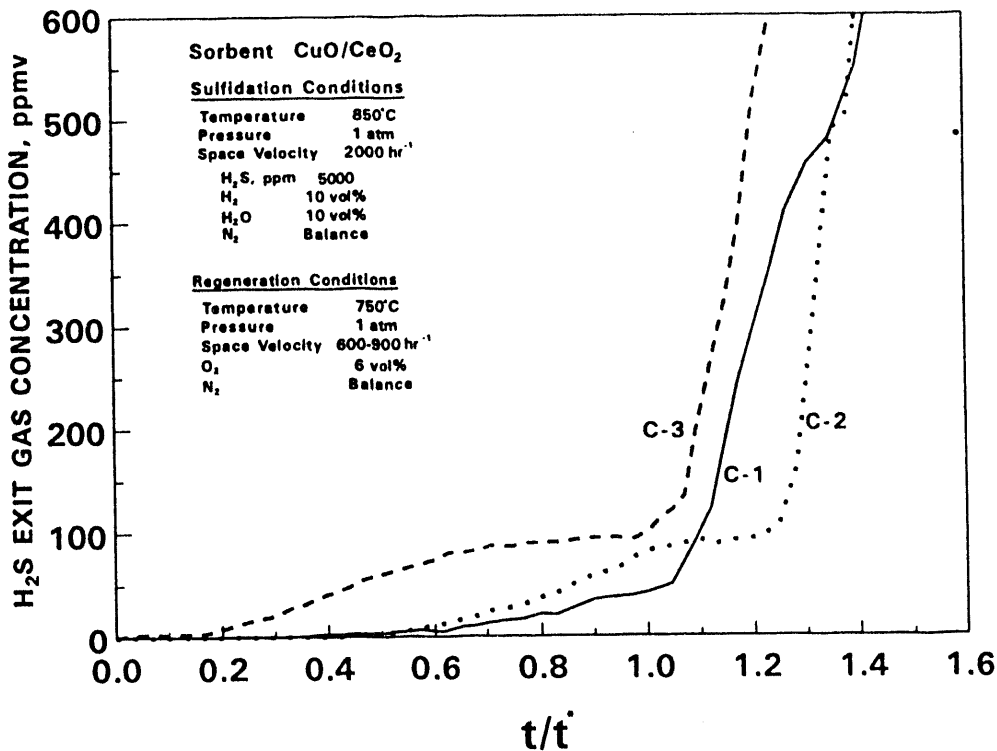


Figure 9. H₂S BREAKTHROUGH PROFILES FOR CuO-CeO_2 AT 850°C AND A SPACE VELOCITY OF 2000 hr⁻¹

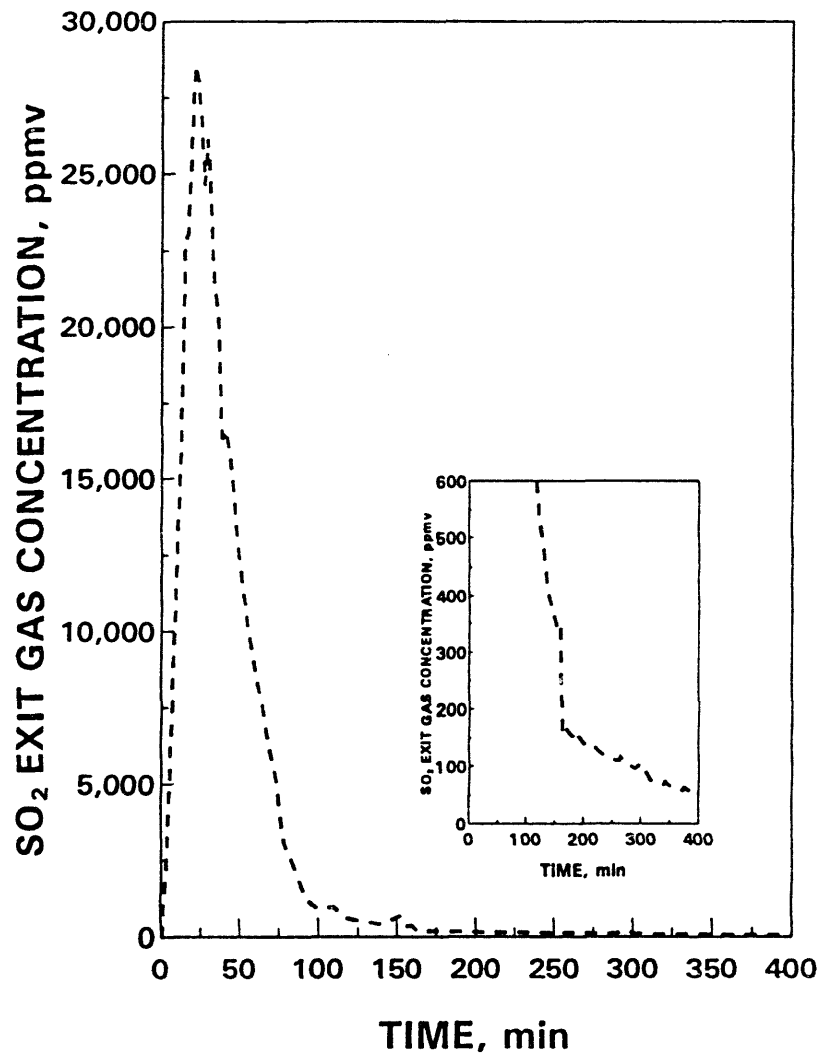


Figure 10. REGENERATION OF CuO-CeO₂
AT 750°C IN 6% O₂-N₂ MIXTURE

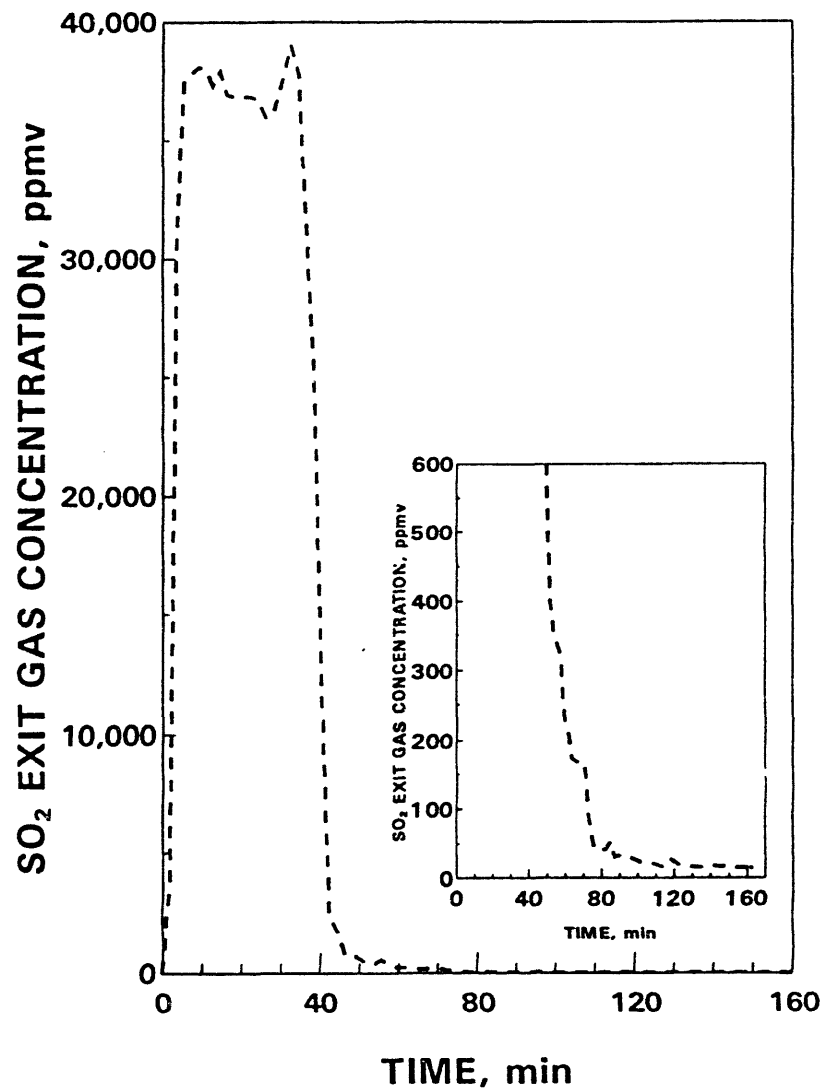


Figure 11. REGENERATION OF CuCr₂O₄
AT 750°C IN 6% O₂-N₂ MIXTURE

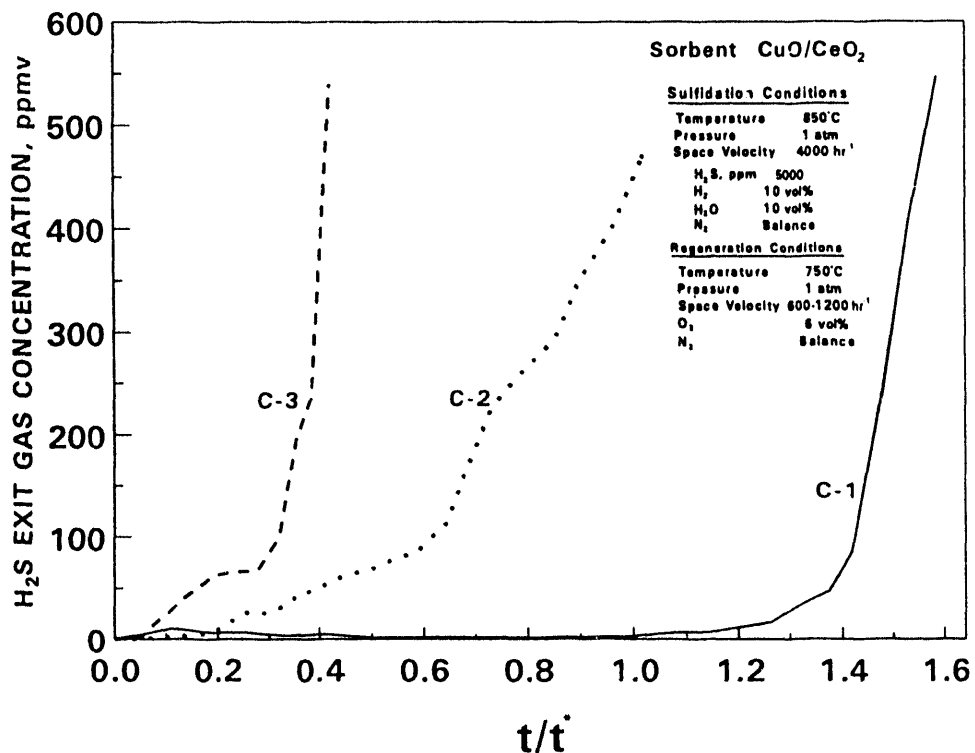


Figure 12. H₂S BREAKTHROUGH PROFILES FOR CuO-CeO₂ AT 850°C AND A SPACE VELOCITY OF 4000 hr⁻¹

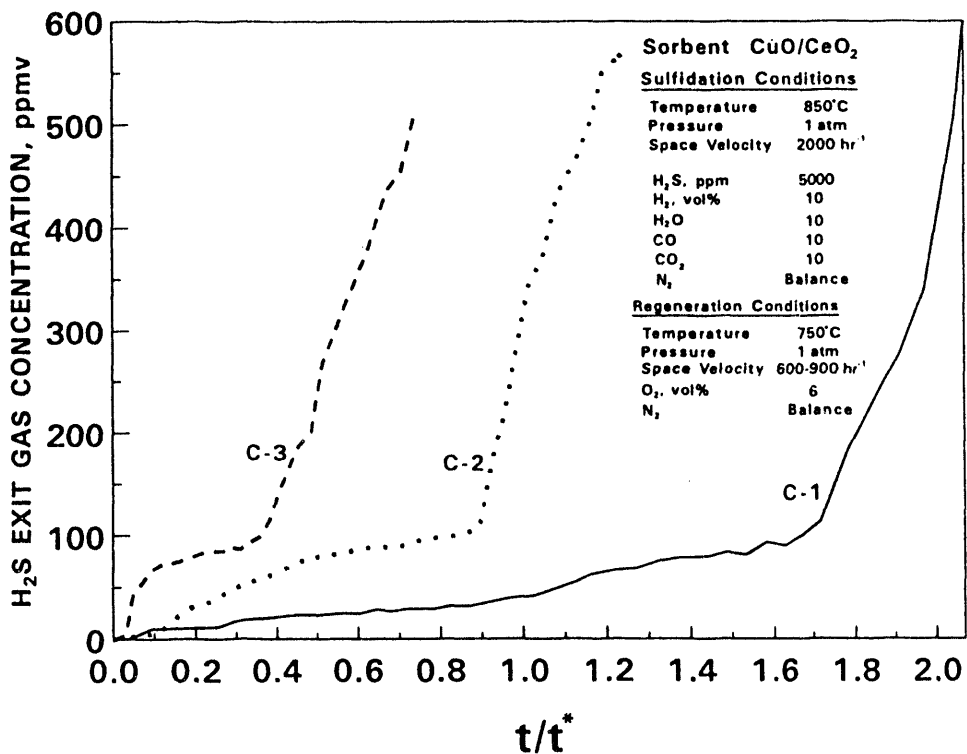


Figure 13. H₂S BREAKTHROUGH PROFILES FOR CuO-CeO₂ AT 850°C IN SYNGAS

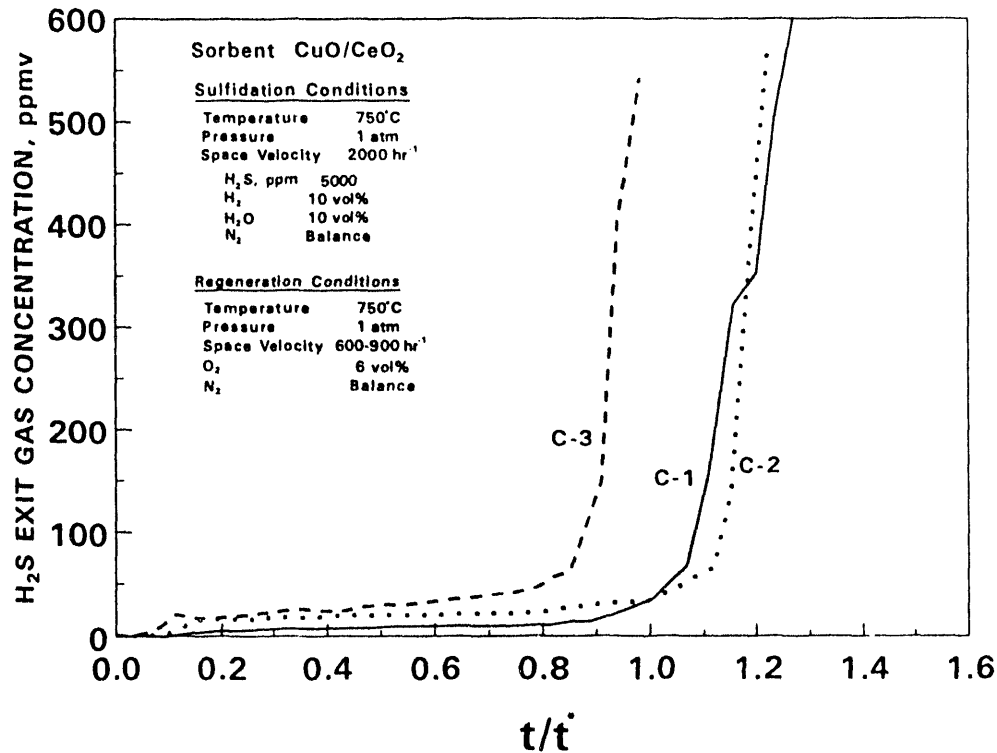


Figure 14. H₂S BREAKTHROUGH PROFILES FOR CuO-CeO₂ AT 750°C

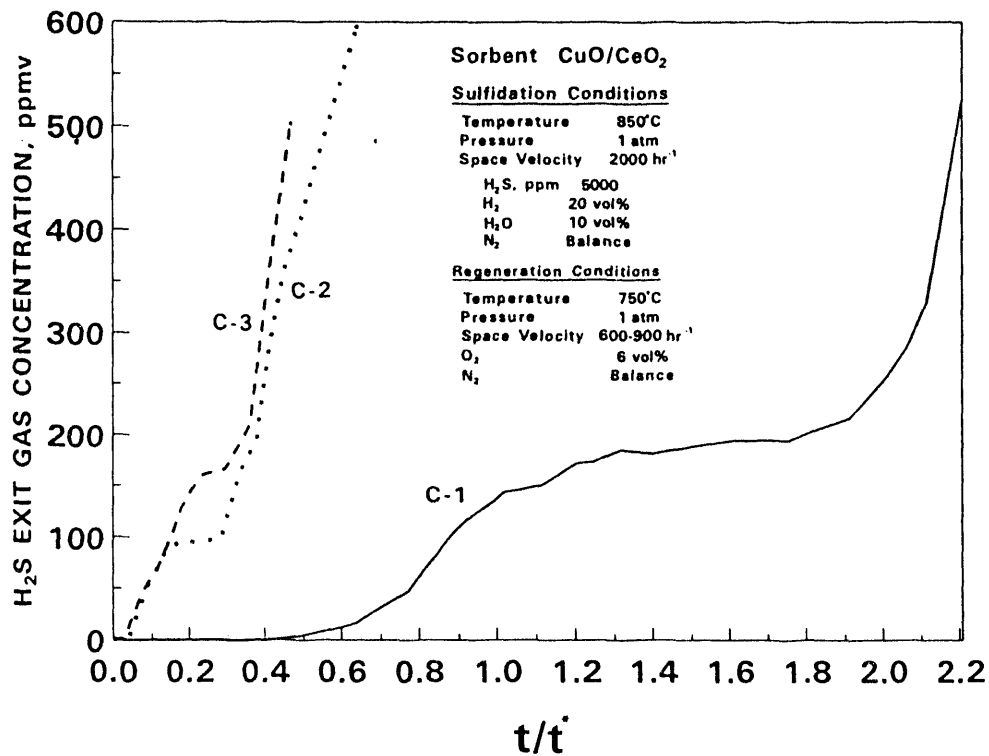


Figure 15. H₂S BREAKTHROUGH PROFILES FOR CuO-CeO₂ AT 850°C IN 20 VOL% H₂

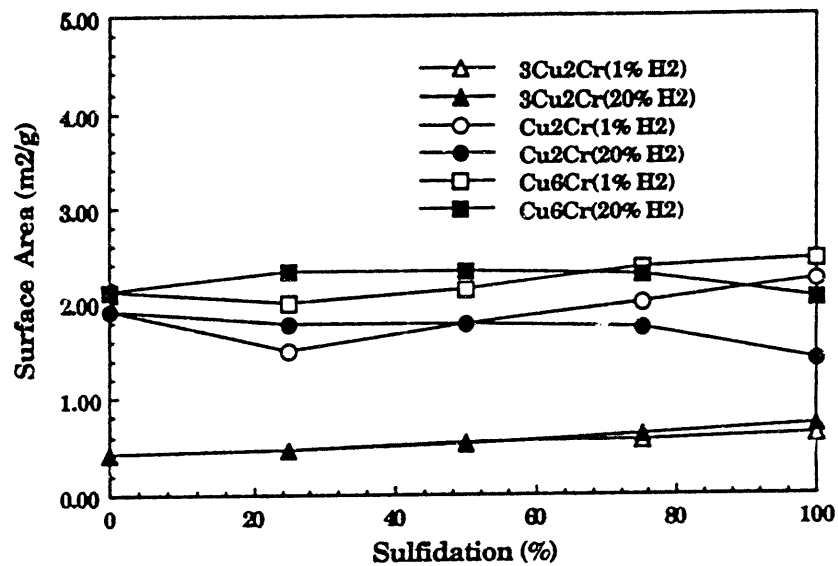


Figure 16. SURFACE AREAS OF SULFIDED Cu-Cr OXIDES

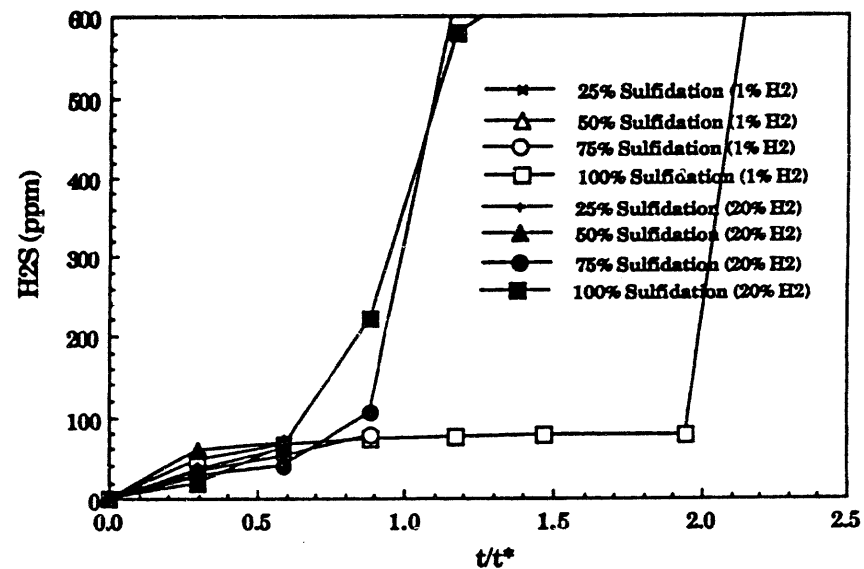


Figure 17. SULFIDATION OF Cu-2Cr SORBENT AT 850°C

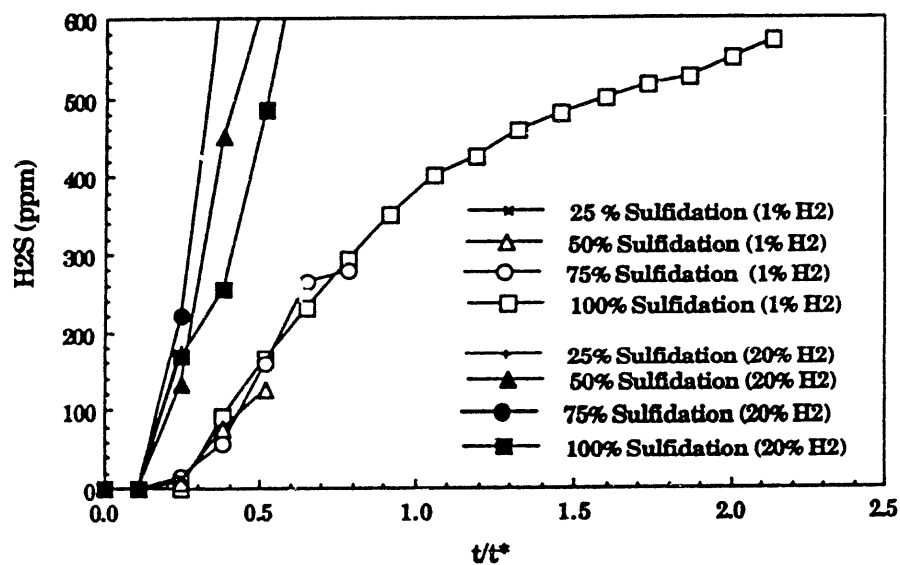


Figure 18. SULFIDATION OF 3Cu-2Cr SORBENT AT 850°C

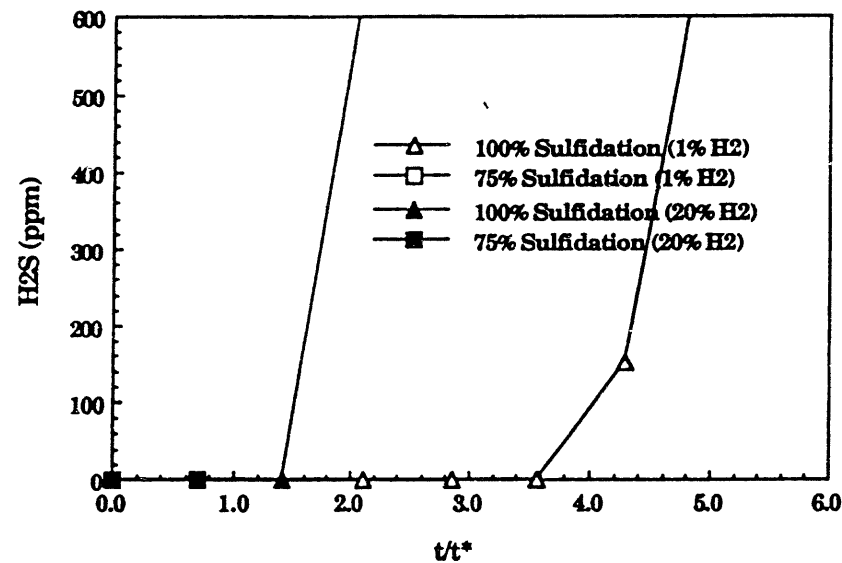


Figure 19. SULFIDATION OF Cu-6Cr SORBENT AT 850°C

Table 2. PHASE IDENTIFICATION (XRD)

Sorbent	Molar Ratio <u>CuO/Cr₂O₃</u>	H ₂ (%)	Sulfidation (%)	Phases
Cu-6Cr	1:3	0	0	Cr ₂ O ₃ CuCr ₂ O ₄
Cu-6Cr	1:3	1	100	Cr ₂ O ₃ CuCrS ₂ Cr ₂ .73Cu ₃ .05S ₆ Cu ₄ O ₃
Cu-6Cr	1:3	20	100	Cr ₂ O ₃ Cu ₄ O ₃
Cu-2Cr	1:1	20	100	Cr ₂ O ₃ Cu ₄ O ₃ Cu ₂ S CrS

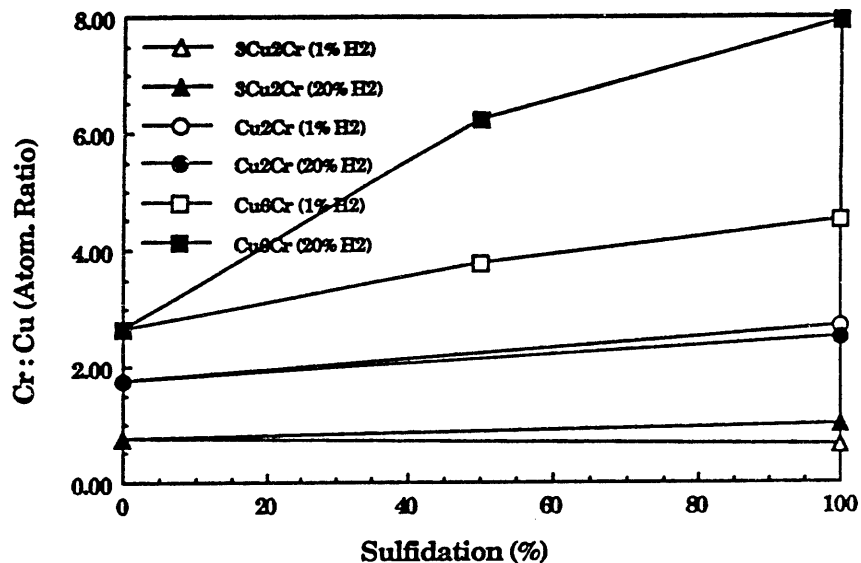


Figure 20. EDX DATA (OVERALL) OF Cu-Cr MIXED OXIDES SULFIDATION

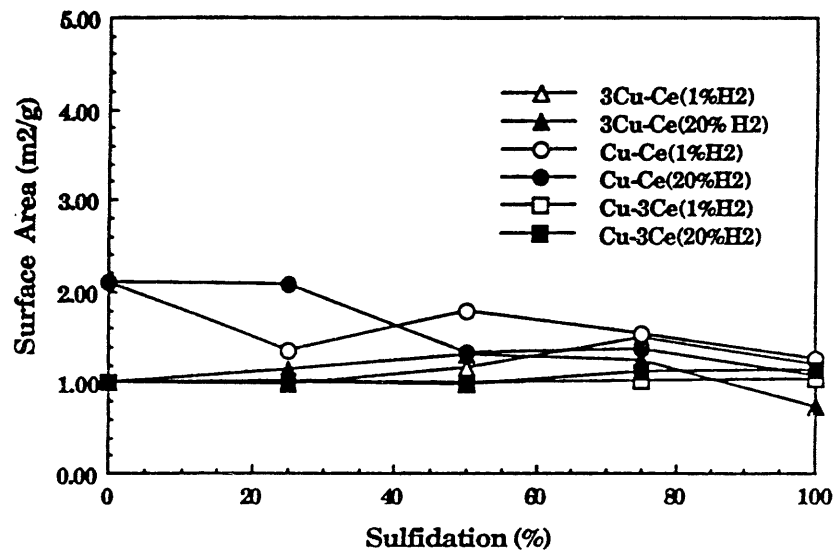


Figure 21. SURFACE AREAS OF SULFIDED Cu-Ce MIXED OXIDES

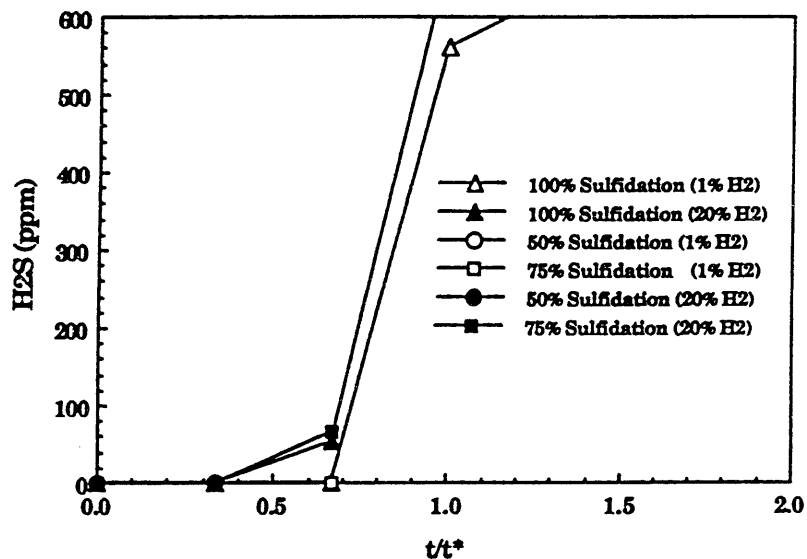


Figure 22. SULFIDATION OF Cu-Ce AT 850°C

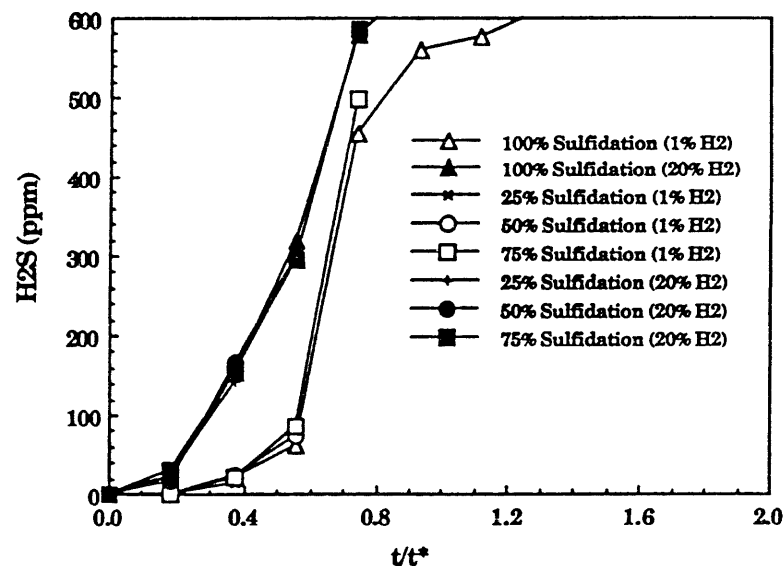


Figure 23. SULFIDATION OF 3Cu-Ce SORBENT AT 850°C

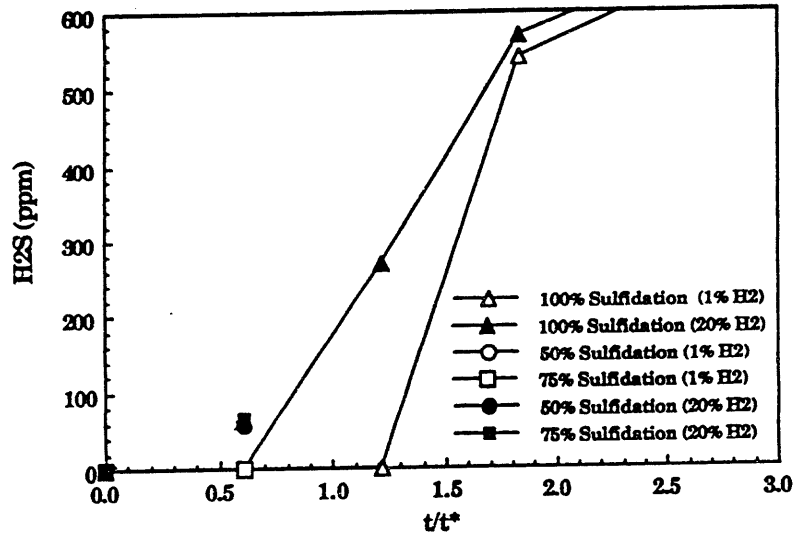


Figure 24. SULFIDATION OF Cu-3Ce SORBENT AT 850°C

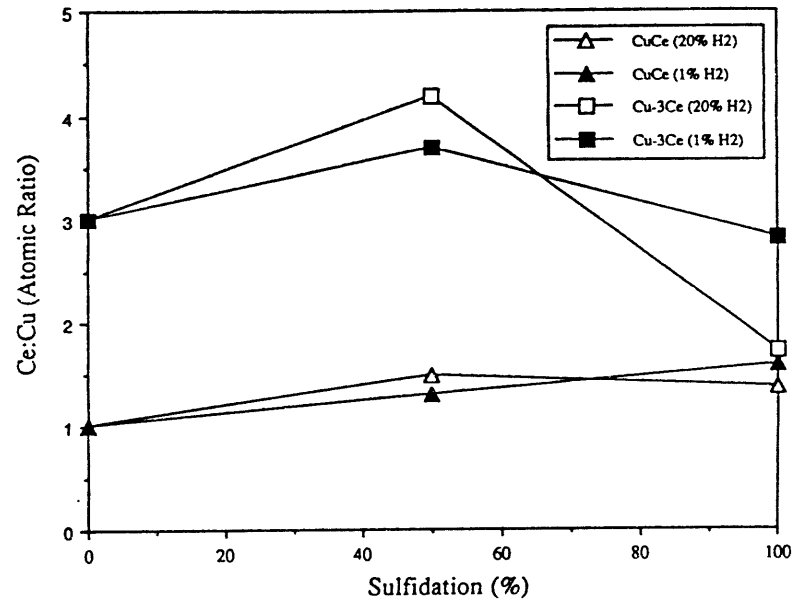


Figure 25. EDX DATA OF Cu-Ce MIXED OXIDES SULFIDATION

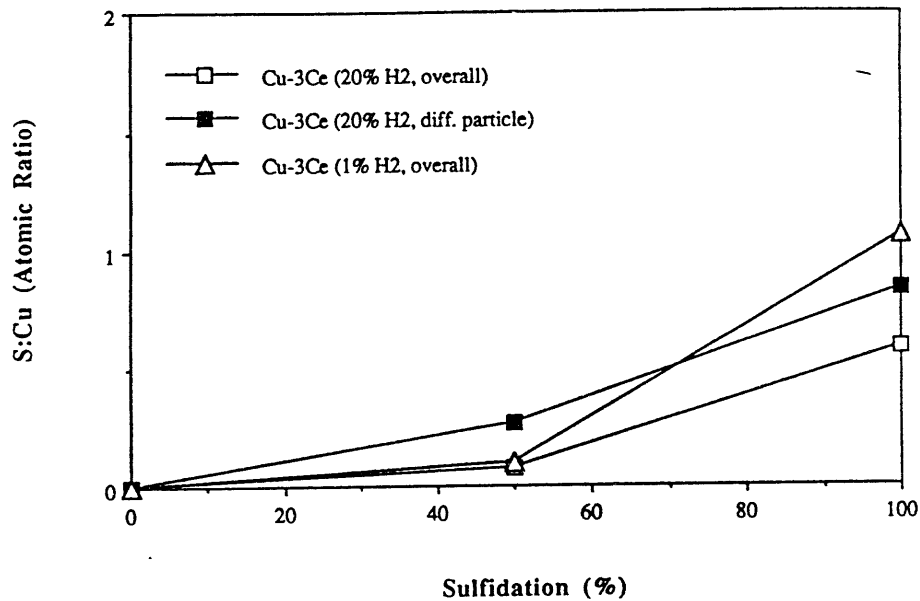


Figure 26. EDX DATA OF Cu-3Ce MIXED OXIDE SULFIDATION

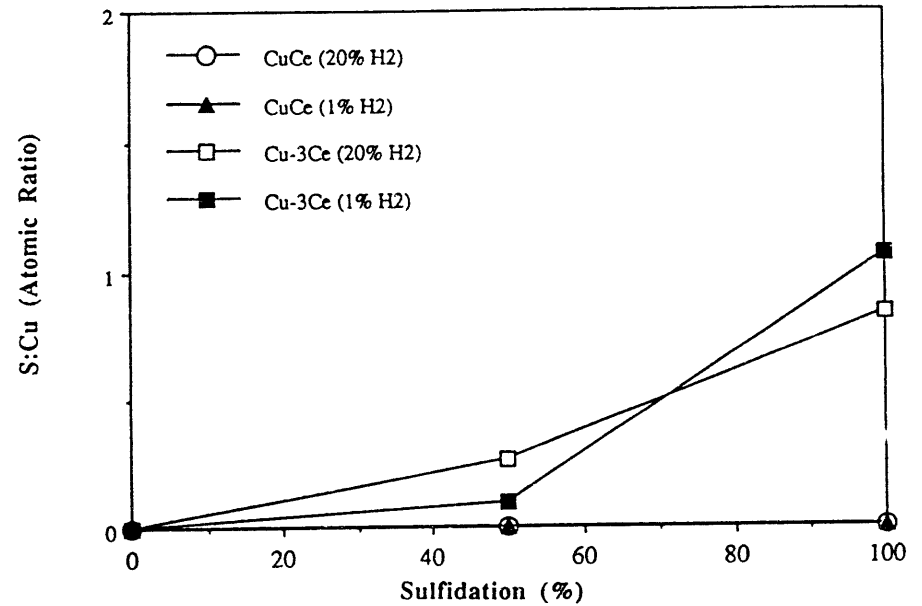


Figure 27. EDX DATA OF Cu-Ce AND Cu-3Ce OXIDE SULFIDATION

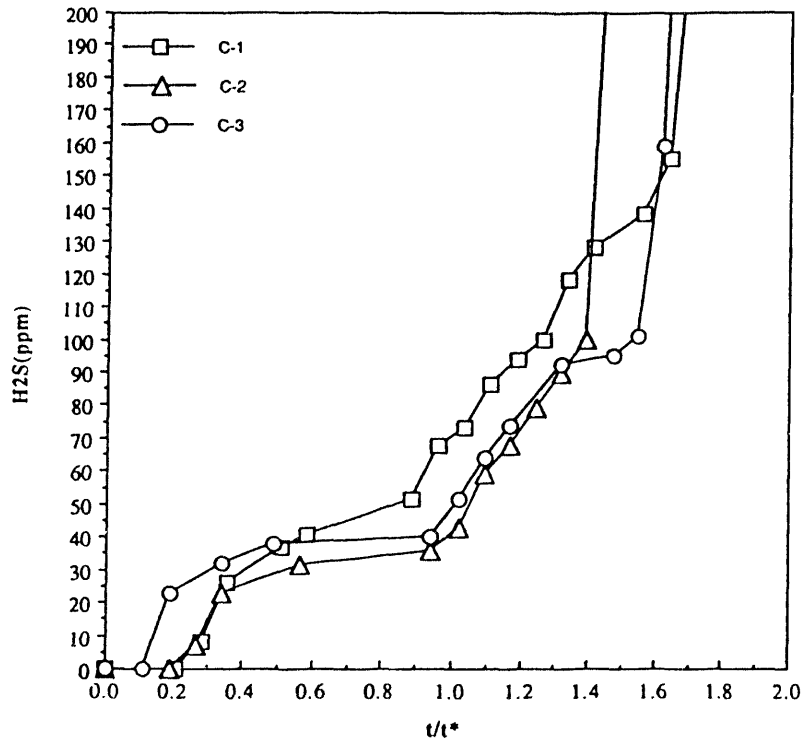


Figure 28. H₂S BREAKTHROUGH PROFILES FOR Cu-2Ce AT 850°C

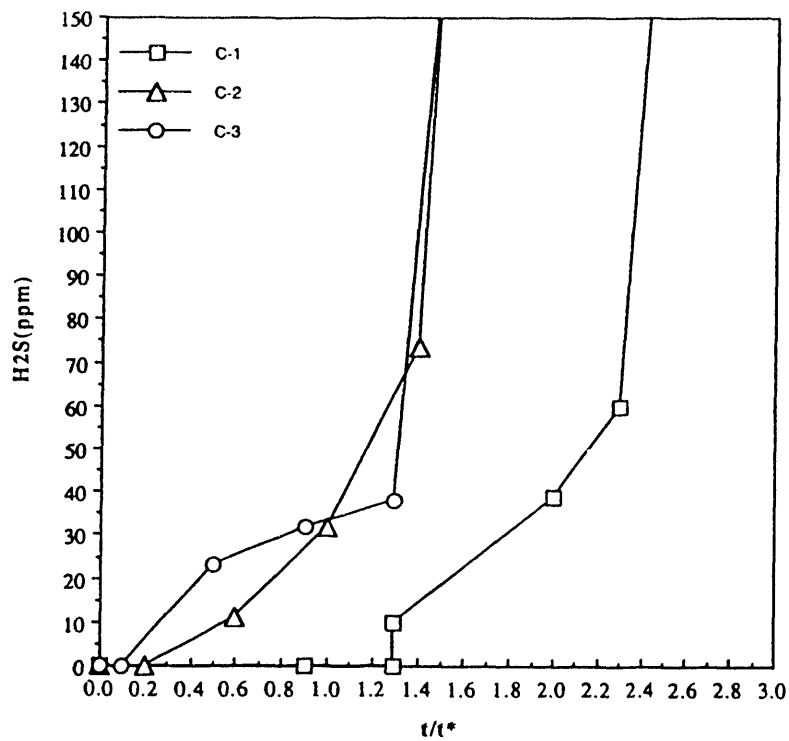


Figure 29. H₂S BREAKTHROUGH PROFILES FOR Cu-4Ce AT 850°C

PROJECT MANAGEMENT REPORT
June 1, 1993 through August 31, 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

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

COMMENTS

The project is on schedule.

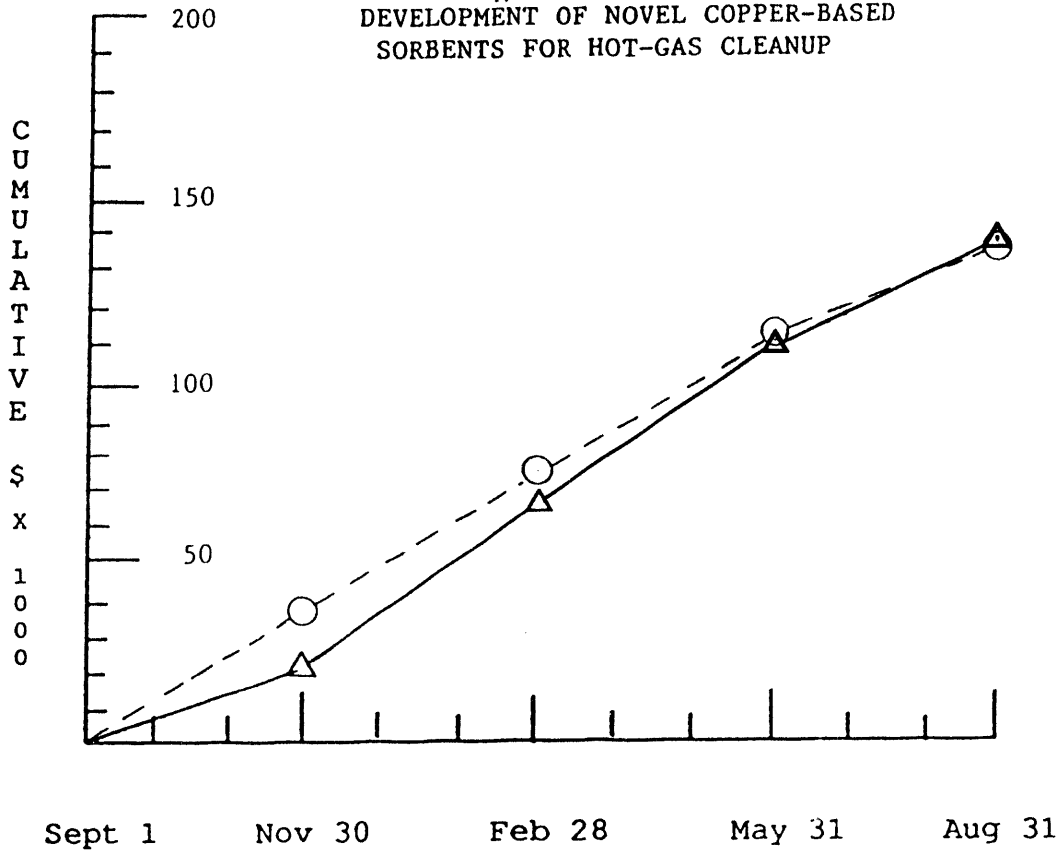
DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT-GAS CLEANUP

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	1316	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	18,516	0	3855		0	48,000	40,944	111,315
Sept. 1, 1992 to Aug. 31, 1993	Projected	21,609	0	4,000	1576	0	58,058	52,415	137,655
	Estimated	22,031	0	4386	1351	0	58055	52752	138,576

*Cumulative by Quarter

COSTS BY QUARTER
DEVELOPMENT OF NOVEL COPPER-BASED
SORBENTS FOR HOT-GAS CLEANUP



Months and Quarters

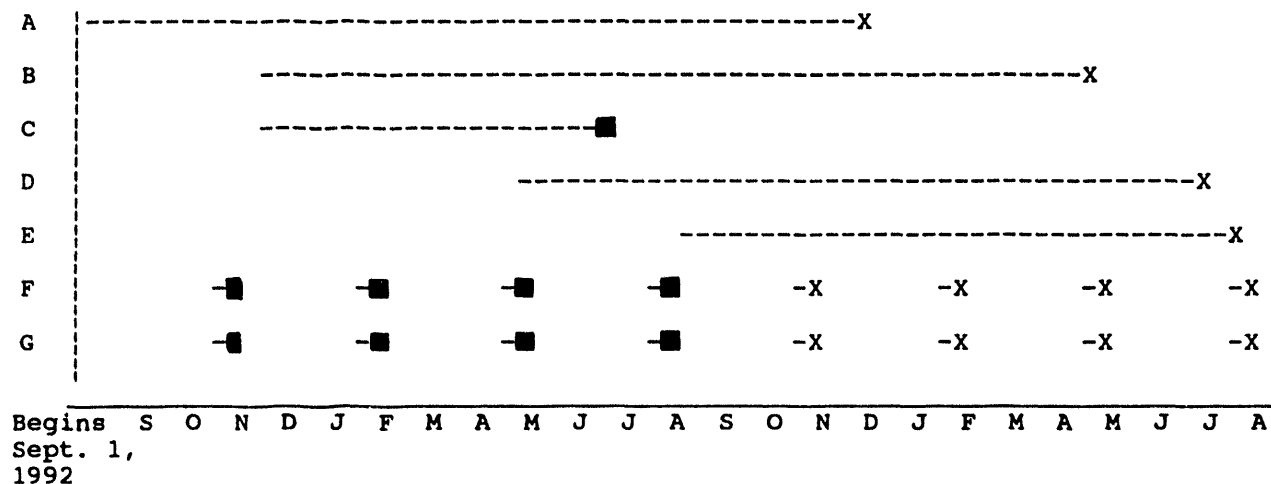
○ = Projected Expenditures \$ 137,655

△ = Estimated Actual Expenditures \$ 138,576

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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