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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 was to evaluate several novel copper-based binary oxides for their suitability as regenerable sorbents for hot gas cleanup application in the temperature range of 650° to 850°C.

To achieve this objective, several novel binary oxides of copper were systematically evaluated and ranked in terms of their high-temperature stability against reduction to metal, sulfidation reactivity, and regenerability. The sorbents studied included oxides of chromium, cerium, aluminum, magnesium, manganese, titanium, iron, and silicon.

The results of initial testing indicated that mixed binary oxides of copper with chromium (CuCr_2O_4) and cerium ($\text{CuO}\cdot\text{CeO}_2$) were the most promising sorbents for such high temperature gas cleanup applications. These two sorbents were further evaluated in cyclic sulfidation/regeneration tests in 10-15 cycles to determine the effect of operating conditions on their performance.

The results of this investigation indicate that the two selected sorbents, copper-chromium and copper-cerium, are capable of removing H_2S from the hot fuel gas to very low levels (<10 ppmv) at temperatures as high as 850°C with good sorbent regenerability in cyclic process. These sorbents should be further studied to achieve optimum sorbent composition for hot gas cleanup application.

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EXECUTIVE SUMMARY

The objective of this investigation was to evaluate several novel copper-based binary oxides for their suitability as regenerable sorbents for hot gas cleanup application in the temperature range of 650° to 850°C. Such high temperatures will be required for the new generation of gas turbines in Integrated Gasification Combined Cycle (IGCC) Systems.

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 coal gasification-combined cycle (IGCC) power generation (using gas turbines) and gasifier/fuel cell power plants. The implementation of hot coal gas desulfurization heavily relies 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 sorbents. Not surprisingly, only a few metal oxides can meet these stringent requirements.

This investigation was directed towards evaluation of regenerable and novel copper-based sorbents for hot gas cleanup to identify the most promising sorbents for further development.

Several novel binary oxides of copper were systematically examined and ranked in terms of their sulfidation equilibrium, reduction stability, sulfidation reactivity, and regenerability in the temperature range of 650° to 800°C. The sorbents studied in this program included oxides of chromium, cerium, aluminum, magnesium, manganese, titanium, iron, and silicon. Based on available literature data on thermodynamic equilibria of the sorbents in reduction and sulfidation, coupled with the available information on the physical/structural properties of the oxides, several sorbents were selected and prepared for initial evaluation which included reduction stability tests in the Thermogravimetric Analyzer (TGA) unit at up to 1000°C and sulfidation screening tests in the packed bed microreactor at 650° to 850°C. From the results of these tests, binary oxides of copper with chromium (CuCr₂O₄) and cerium (CuO·CeO₂) were selected for further testing.

Detailed sulfidation/regeneration tests were conducted with the two selected sorbents in packed-bed as well as fluidized-bed at temperatures of 650° to 850°C. Parametric study included determination of the effects of gas composition, space velocity, sulfidation and regeneration temperatures, on sorbent performance in cyclic sulfidation/regeneration tests in 10-15 cycles.

The results of this investigation indicate that the two selected sorbents, copper-chromium and copper-cerium, are capable of removing H₂S from the hot fuel gas to very low levels (<10 ppmv) at temperatures as high as 850°C with good sorbent regenerability in cycling process. These sorbents should be further studied to achieve optimum sorbent composition for hot gas cleanup application.

OBJECTIVE

The overall objective of this investigation was to evaluate several novel copper-based sorbents for their suitability for hot gas cleanup application in the temperature range of 650° to 850°C.

The program goals are specifically directed toward the Gas Cleanup, Research Priority 6.1A: Removal of Sulfur-Containing Gases From the Hot Overhead Effluent Obtained by Gasification of High-Sulfur Illinois Coal. The program is targeted toward the determination of structural stability, sulfidation reactivity, regenerability, durability, and attrition resistance characteristics of the novel copper-based sorbents.

The specific objectives of this project were to:

1. Prepare and characterize specific compounds of copper oxide with each of the oxides of Mg, Ti, Al, Cr, Si, Fe, and Mn;
2. Determine the reduction stability of the binary oxides in H_2-N_2 and $H_2-H_2O-N_2$ gas mixtures to be carried out at temperatures of 650° to 1000°C;
3. Carry out sulfidation screening tests with the stable CuO -phases identified in (2) using $H_2-H_2S-N_2$ and $H_2-H_2S-H_2O-N_2$ gas mixtures and temperatures of 650° to 850°C.
4. Carry out detailed sulfidation tests with two selected sorbents using fuel gas mixtures and temperatures of 650°C and 850°C (regeneration using 6% O_2+N_2 at 750°C) with intermittent solids analysis by BET, XRD, etc.
5. Carry out up to fifteen sulfidation-regeneration cycles with selected sorbent compositions and determine sorbent regenerability and structural stability in cyclic operation using $H_2-H_2S-H_2O-N_2$ mixtures as well as simulated coal gasifier exit gas.
6. Carry out sulfidation/regeneration tests in an ambient-pressure fluidized-bed reactor using the most promising sorbents in the temperature range of 650° to 850°C for sulfidation and 750°C for regeneration with an $H_2S-H_2-H_2S-H_2O-N_2$ mixture for sulfidation and air- N_2 mixture for regeneration.
7. Compare the sulfidation reactivity of the most "promising" sorbents identified in this program with one commercial sorbent and one sorbent previously developed by U.S. DOE (such as zinc titanate) under similar operating conditions.
8. Carry out attrition tests with the copper-based sorbents to determine their suitability for moving-bed or fluidized-bed application.

INTRODUCTION AND BACKGROUND

Integrated Gasification Combined-Cycle (IGCC) Power Plants and Fuel Cell Power Generation Technologies are among the leading contenders for coal conversion. Development of technology for coal gas desulfurization to sufficiently low levels at temperatures of 650° to 850°C is now recognized as crucial to the 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 heavily relies 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. COS, CS₂ and other organic sulfur compounds, present in gasifier fuel gas streams, also need to be removed regeneratively and efficiently by the sorbents. Structural stability and good mechanical strength are additional desired features of the sorbents.

In recent years it has been shown that certain mixed oxides have superior properties compared to single oxides for hot gas cleanup.⁽¹⁻³⁾ A compound of zinc and iron oxides, zinc ferrite (ZnFe₂O₄), developed by DOE/METC has reached the pilot-stage of testing for desulfurization of low-Btu gases.⁽⁴⁾ The H₂S removal efficiency of ZnFe₂O₄ is similar to ZnO because zinc ferrite is converted into a mixture of ZnO and Fe₃O₄ when exposed to the reducing gas. Similarly, the rate of zinc loss (via ZnO reduction) is the same in both ZnFe₂O₄ and ZnO. Therefore, the application of zinc ferrite is limited to temperatures below 600°C.

Titanium dioxide has been examined as a potentially better alternative to iron oxide additives in terms of the higher stability of the titanates over the ferrite compounds of zinc, and their not too different sulfidation equilibria.^(5,6) With zinc titanates, the sulfidation temperature was shown to extend to 700°C, and sintering of ZnO was greatly reduced. Because zinc titanate also showed better attrition resistance than zinc ferrite in preliminary pilot tests at General Electric and better regenerability and mechanical stability in the highly reducing Texaco gasifier-exit gas composition, further development of the zinc titanates is underway.

However, at sulfidation temperatures above ~750°C, zinc titanates will also suffer zinc losses. Such high temperatures will be required for the new generation gas turbines (with inlet temperatures exceeding 1400°F). If gas cleanup can be performed at matching conditions, then higher power plant cycle efficiency gains will be realized. For these applications the metal oxide sorbents should have low vapor pressures in all their oxidation states (including the metallic state).

Copper oxide-based sorbents have been examined to a lesser extent than zinc oxide sorbents for high-temperature gas desulfurization. Mixed oxides of copper, iron and aluminum in bulk (unsupported) form were developed earlier and were found suitable for desulfurization of gases from fluidized-bed gasifiers at temperatures up to 800°C.⁽⁷⁾ Work with another type of copper compound, copper manganates, has been carried out by ElectroChem.⁽⁸⁾ Instability problems in the presence of water vapor have been reported for the

CuMn_2O_4 phase, which has high sulfur capacity at high temperature. Other copper-based mixed oxide sorbents have not been tested for their suitability for hot gas cleanup. Systematic evaluation of novel copper-based sorbents is very important because of their potential for hot gas cleanup application at higher temperatures.

This research program has focused on the evaluation of regenerable and novel copper-based sorbents for hot gas cleanup to identify the most promising sorbent for further development.

EXPERIMENTAL PROCEDURE

Thermodynamic Evaluation

Using available phase diagrams and thermodynamic data from the literature⁽⁹⁻¹⁵⁾, several of the binary oxides were evaluated in terms of their reduction stability and sulfidation equilibria.

The thermodynamic equilibria data were used as a guideline for selection of copper-based binary oxides sorbents. However, because reduction and sulfidation properties also depend on the kinetics and structural information, these factors were also considered in selecting the candidate sorbents. The thermodynamic evaluation includes binary oxides of copper with aluminum (CuAlO_2), chromium (CuCrO_2 and CuCr_2O_4), and magnesium (Cu_3MgO_4). The sulfidation and reduction equilibria constants of these compounds were compared with corresponding values of copper oxides (both cupric Cu^{+2} and cuprous Cu^{+1}).

Sorbents Selection and Preparation

Based on the thermodynamic equilibria as well as available physical and chemical property data, several copper-based binary oxides were chosen to combine with copper for the initial evaluation of copper-based desulfurization sorbents. The oxides chosen for initial evaluation included copper magnesium (Cu_3MgO_4 , CuMg_2O_3 , and 2CuMgO_3), copper chromium (CuCrO_2 and CuCr_2O_4), copper manganese (CuMnO_2), copper aluminum (CuAl_2O_4), and copper titanium (Cu_3TiO_4). Copper ferrite and copper silicon were not prepared in this project. The experimental data from other published work on Cu-Fe was used for comparison in this project. Because literature data on reduction-sulfidation of a highly dispersed copper silicon had indicated that complete reduction to copper metal proceeds sulfidation, this binary oxide was not prepared in this project. Binary oxides of copper with cerium ($\text{CuO}\cdot\text{CeO}_2$) were added to the list and prepared during the second year of the program. It should be emphasized that the formulas given above correspond to stable phases, that may not have comprised totally the material formed at various temperatures; so it is perhaps more appropriate to designate the solids by the atomic ratio of copper-to-other metal component, e.g. $3\text{Cu}:\text{Mg}$.

All solids used in the reduction experiments described below were prepared according to the amorphous citrate method.⁽¹⁶⁾ An aqueous solution of the metal nitrates was slowly added into an aqueous citric acid solution. An equimolar citric acid to total metals ratio was used. The resulting complex

solution was concentrated in a rotary evaporator under vacuum at 70°C, and then dried in a vacuum oven at 70-80°C overnight. The dried solid foam was pyrolyzed and calcined in flowing air at 500°C for 30 minutes in a muffle furnace.

Reduction Stability Tests

Reduction experiments were performed in a Cahn System 113-X thermogravimetric analyzer (TGA) unit equipped with a Cahn 2000 electrobalance, a Micricon temperature controller, and a Bascom Turner data acquisition system. The TGA measured the weight loss as a function of time and temperature required for reduction of copper oxide to metals.

The reactant gas containing 10% H₂-90% N₂ was introduced into the apparatus through a side arm. Gas flow rates were set by passing H₂ and N₂ gases through mass flow controllers. A gas flow rate of 485 sccm was used in the experiments. A thin layer of sample (~6 mg and 90-125 μm size particles) was placed on a quartz pan suspended by a quartz hangdown wire. The sample was pretreated in N₂ (~450 sccm) by raising the temperature to 473 K at a rate of 10 K/min, and holding it at 473 K for ten minutes. Hydrogen was then introduced into the system followed by an immediate temperature ramping at a constant heating rate of 5 K/min up to 1123 K.

These tests were conducted with all binary oxide sorbents (except copper cerium that was prepared later) to determine the best candidate sorbents for the next evaluation step.

Sulfidation/Regeneration Tests

The sulfidation screening tests were carried out in the 1 cm-ID, packed-bed, quartz micro-reactor unit at MIT at ambient pressure in the temperature range of 650° to 850°C. Sulfidation of sorbents was carried out in 10% H₂, 20% H₂O, 5000 ppm H₂S, balance N₂ gas mixture at a sulfidation temperature of 650°C and 850°C, with a space velocity of 2000 hr⁻¹. Regeneration was conducted with a 6% O₂-94% N₂ gas mixture at 750°C with a space velocity of 2000 hr⁻¹. Sorbents used in these tests were granular form -20+35 mesh (400-800 μm size) particles and included copper chromium oxides that showed the bed reduction stability, copper magnesium because of the high stability of Cu₃MgO₄, copper manganese because of its potentially high sulfur capacity (manganese participate in sulfidation), and copper cerium.

Detailed sulfidation/regeneration tests were carried out with copper chromium, copper cerium, and copper magnesium sorbents over three to four cycles at 650° and 850°C in the microreactor. Fresh and reacted sorbent samples were analyzed by X-ray diffraction (XRD) for crystalline phase identification and BET-N₂ desorption for surface area measurement.

Copper chromite (CuCr₂O₄) and copper cerium (Cu-Ce-O) were selected for further evaluation based on the results of sulfidation tests and XRD analyses as well as BET measurements.

Cyclic sulfidation regeneration tests were conducted over ten cycles with copper chromite and over nine cycles with copper cerium sorbents.

These packed-bed tests were conducted in the quartz microreactor at ambient pressure at 850°C with different feed gases containing approximately 5000 ppm H₂S, and H₂, H₂O, CO and CO₂ at various concentration levels. The space velocity was approximately 2000 hr⁻¹ (STP) in all tests. Regeneration was typically run at 750°C to 850°C with a gas containing 30% air and 70% nitrogen. The effects of gas composition on the performance of these sorbents were determined.

The regenerability of copper cerium at 650, 750 and 850°C was also determined over fifteen cycles.

Fluidized-Bed Sulfidation Tests

The fluidized bed sulfidation/regeneration tests were conducted in the 2.5-cm-diameter quartz reactor at IGT at 650°C and 850°C during sulfidation, and 650°C and 750°C during regeneration. The reactant gas during sulfidation contained 5000 ppm H₂S, 20% H₂, 10% H₂O, and 69.5% nitrogen while the regeneration gas contained 3% oxygen and 97% nitrogen. The space velocity in the fluidized bed tests were approximately 6500 hr⁻¹ (STP). The sorbents used in these tests included copper chromite, copper cerium, and zinc titanate (0.8 ZnO/TiO₂).

Comparison of Hot Gas Desulfurization Sorbents

A series of packed-bed sulfidation/regeneration tests were conducted in the 2.5-cm-diameter quartz packed bed reactor at IGT under identical operating conditions to compare the performance of copper chromite and copper cerium with a zinc titanate sorbent produced by United Catalyst as well as a commercial copper chromite dehydrogenation catalyst. These tests were conducted at 850°C with the reactant gas containing 20% hydrogen, 10% steam, 4800 ppmv H₂S and balance nitrogen. The space velocity was 5000 hr⁻¹ and the packed bed height was 1 cm. Because of the difference in the density of these materials, the bed weight ranged from 1.72 gm (Cu-Ce) to 6.6 g (Zn-Ti).

Attrition Tests

The purpose of these tests was to measure the attrition resistance of the copper-based sorbents to determine if these sorbents can be used in a fluidized-bed hot-gas cleanup reactor. In an attrition test of this type, the sorbent is exposed to a high velocity air jet for specified periods of time, and the change in the particle size distribution is measured.

An attrition test apparatus was used to measure the attrition resistance properties of the copper-based sorbents. The unit design is based on one described by Anderson and Pratt.⁽¹⁷⁾ The unit consists of a 2.54 cm ID by 152 cm tall glass tube with a single 0.38-mm orifice gas inlet. During an attrition test with a 50 cc to 80 cc sorbent bed volume, the air flow is adjusted to 7 slpm (at room temperature) to generate sonic velocity through

the orifice, thus creating a strong shearing effect to provide measurable attrition between sorbent particles.

The attrition tests in this program were conducted with two copper-chromite and a zinc titanate sorbent, all of which were manufactured by United Catalyst, Inc. (UCI). In addition, lignite, char and alumina were also tested in this apparatus to cover a wide range of attrition resistant materials. A measure of the (relative) attrition resistance (A_R) for the solids is defined as

$$A_R = 100 \left[\frac{P}{F} - (X_f - X_i) \right]$$

where X_i is original fraction of fines ($d_p < 105 \mu m$) in the sorbent, and X_f is the fraction of fines after the attrition test, F is the initial weight of the sorbent, and P is the weight of the sorbent recovered.

The attrition resistance of the solids tested were determined in tests conducted for 1, 3, and 5 hours.

RESULTS AND DISCUSSION

Thermodynamic Evaluation

The hydrogen reduction and sulfidation equilibria of several copper-based sorbents (calculated from available literature data) are shown in Figures 1 and 2.

Hydrogen reduction equilibria of the compound phases $CuAl_2O_4$, $CuCr_2O_4$, Cu_3MgO_4 , $CuAlO_2$, and $CuCrO_2$ in comparison to the single copper oxides (CuO and Cu_2O) are shown in Figure 1 in terms of the reduction equilibrium constant as a function of temperature. The reduction reactions to metallic copper are listed on the same figure. Cupric compounds containing Cu^{+2} have reducibility similar (but lower) to CuO , while cuprous compounds have similar (but lower) reducibility to Cu_2O . In either set, the reduction stability of compound oxides is higher than that of the uncombined (CuO or Cu_2O) copper oxide.

Thermodynamic data for the Cu-Ti-O binary oxide system are not shown. Based on information found in the literature^(14,15), the only known compound of copper and titanium oxides has the stoichiometry $CuO \cdot Cu_2O \cdot TiO_2$ (or Cu_3TiO_4) and exists only in a narrow range of temperature (1220-1280 K). At lower temperatures, $CuO + TiO_2$ co-exist, perhaps along with a limited range of oxide solid solutions.

Ranking these solids in terms of equilibrium reduction stability, $CuCr_2O_4$ and Cu_3MgO_4 are the most stable phases. Among the cuprous compounds, $CuCrO_2$ is more stable than the corresponding aluminate, $CuAlO_2$. No cuprous magnesium compound was found in the literature. All cuprous oxide-based materials have higher reduction stability than the corresponding cupric oxide-based solids. In practical applications, intermediate cuprous compound phases may dominate during reduction-sulfidation, both because of their higher reduction stability as well as because of local inhomogeneities and/or kinetic limitations preventing complete reduction to metal copper.

Figure 2 shows sulfidation equilibrium reaction constants as a function of temperature for the compounds shown in Figure 1 as well as for metal copper sulfidation, Reaction (8). The product is Cu_2S (cuprous sulfide), which is the stable form of copper sulfide at these temperatures. Compounds based on the oxides CuO or Cu_2O will always have intermediate sulfidation equilibria between CuO (best) and Cu (worst). This is clearly shown in Figure 2. Between cupric and cuprous compounds, the former (Cu^{+2}) have better sulfidation equilibria than the latter. Among the various cupric and cuprous compounds, the aluminates lie closest to the single oxides of copper, while the chromites have inferior sulfidation equilibria. Cu_3MgO_4 is a better choice at 1100 and 1200 K. Again, it should be emphasized that complete evaluation of these compounds with respect to their combined reduction/sulfidation properties cannot be made on the basis of thermodynamics alone. Kinetics and structural information in reduction and sulfidation is needed to complement equilibrium considerations in properly evaluating the potential of these sorbents for hot coal-gas cleanup.

Sorbents Selection, Preparation, and Characterization

Based on the thermodynamic equilibria and available structural property data, several binary oxide sorbents were prepared for testing in this project. The surface areas of the sorbents were determined by BET- N_2 desorption and are given in Table 1. The surface areas of the sorbents decrease with increasing calcination temperature. These surface areas are high enough to meet the requirements of bulk sorbent sulfidation at high temperatures.

Table 1. SURFACE AREAS OF THE SORBENTS

<u>Sorbent</u>	<u>Calcination Temp., K</u>	<u>Surface Area, m^2/g</u>
Cu-2Cr-O	773	14.9
Cu-2Cr-O	1123	3.5
Cu-Cr-O	1123	0.3
Cu-Ce-O	1123	10.2
3Cu-Mg-O	923	7.7
2Cu-Mg-O	773	18.1
Cu-Mg-O	923	9.3
Cu-Mg-O	1123	1.7
Cu-2Mg-O	923	31
Cu-2Mg-O	1123	4.3
3Cu-Ti-O	773	6.7
3Cu-Ti-O	923	3.1
3Cu-Ti-O	1123	1.5
Cu-2Al-O	773	278
Cu-2Al-O	1073	31

X-Ray Diffraction (XRD) analyses were performed on several fresh sorbents. The XRD diffractogram of unreacted sorbent Cu-2Cr-O is shown in Figure 3. The Cu-2Cr-O sorbent consists of one phase, cupric chromite, CuCr_2O_4 . On the other hand, 3Cu-Mg-O, as suspected from the earlier TGA and microreactor

tests, consists of two phases, namely CuO and MgO. This indicates that a calcination temperature higher than 850°C should have been used to produce the high-stability phase Cu_3MgO_4 . X-ray diffraction analysis of fresh Cu-Mn-O sorbent indicates that a single crystalline phase $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ dominates the diffraction.

Reduction Stability Tests

Figure 4 shows the temperature-programmed reduction (TPR) data obtained with a number of CuO-based solids. The vertical axis shows the percent of unreduced sorbent remaining at each temperature; this is given here by the ratio $Y = (W - W_f)/(W_i - W_f)$, where W_i and W_f are, respectively, the maximum and minimum solid weight recorded before and after all copper-bound oxygen was lost. The reactor temperature is also presented on the vertical axis as $T = Y \times 1000 \text{ K}$.

The solids Cu-2Cr-O and Cu-2Al-O prepared at high calcination temperature and with a metal ratio adequate for compound formation, i.e., CuCr_2O_4 and CuAl_2O_4 , respectively, show the highest reduction stability in these TPR experiments. The solid Cu-Cr-O has an initial rapid weight loss (probably corresponding to reduction of free CuO) followed by a slowly reducing weight. The solid Cu-Ti-O, although containing a ratio of 3/1 of Cu/Ti, corresponding to Cu_3TiO_4 , is reduced very fast; apparently the phase Cu_3TiO_4 was not stable at the calcination temperature of 850°C (1560°F), and free CuO + TiO_2 comprised the sorbent. The copper-magnesium oxide sorbents tested in the reduction stability tests included 3Cu-Mg-O, 2Cu-2Mg-O, and Cu-2Mg-O sorbents. All these sorbents indicated a rather fast reducing phase. The copper-manganese oxide sorbents also indicated a fast reducing phase in the reduction stability tests.

Sulfidation-Regeneration Tests

Copper-Chromium Oxide Sorbents: For sulfidation at 650°C (923 K), the Cu-2Cr-O sorbent was tested over three cycles. H_2S breakthrough times given as t/t^* in Figure 5 are 1.1 and 1.2 for the 2nd and 3rd sulfidation cycle, respectively. t^* is the theoretical breakthrough time calculated by assuming copper oxide as the only active phase sulfided by H_2S to Cu_2S . During the sulfidation process, the exit H_2S concentration was in the range of 0 to 40 ppm before breakthrough. Based on the results of Figure 5, sulfidation of copper in the Cu-2Cr-O sorbent was completed by the breakthrough time and the Cu-2Cr-O sorbent exhibited stable cyclic sulfidation-regeneration performance.

For the H_2S removal at 850°C (1123 K), the Cu-2Cr-O sorbent was tested over four cycles. For fresh Cu-2Cr-O sorbent (Figure 5), a low exit H_2S concentration (<10 ppm) was observed until t/t^* reached a value of 0.75, and then the H_2S concentration increased gradually to 150 ppm (equilibrium concentration with copper metal, as discussed below), followed by a fast breakthrough to the inlet H_2S value. For the 2nd sulfidation, low exit H_2S concentration (<10 ppm) was observed until t/t^* reached a value of 0.40, after which it increased gradually to 150 ppm at $t/t^* = 0.85$, followed by a sharp breakthrough to the inlet H_2S value. The results indicate that the H_2S removal efficiency exceeds that of metallic copper for a considerable fraction of the theoretical saturation time, t^* . The regenerability of this sorbent is

satisfactory; however, regeneration with air-N₂ had to be followed with N₂-purge at 850°C to completely remove the SO₂ from the sorbent.

For the Cu-Cr-O sorbent, a low exit H₂S (<10 ppm) was observed until $t/t^* = 0.35$, which stayed at 150 ppm until $t/t^* = 1.6$ followed by a sharp breakthrough to the inlet H₂S value. The cyclic sulfidation-regeneration performance is stable as indicated by the similar H₂S breakthrough profiles for the 2nd and 4th sulfidations.

Copper-Magnesium Oxide Sorbents: For H₂S removal at 650°C (923 K), the performance of 3Cu-Mg-O sorbent was tested. The H₂S breakthrough times are at $t/t^* = 1.25$ and 0.85 for 1st and 2nd sulfidation cycles, respectively. At the beginning of the sulfidation process, the exit H₂S concentration was below 10 ppm until $t/t^* = 0.15$. The H₂S concentration then increased and stabilized at 50 ppm (equilibrium value with copper metal at 923 K) until $t/t^* = 1.25$, followed by a sharp breakthrough toward the inlet H₂S value. Higher H₂S values observed in the initial part of the second cycle may be due to MgSO₄ decomposition (incomplete regeneration of sorbent).

For the H₂S removal at 850°C (1123 K), the performance of Cu-2Mg-O sorbent was studied. The H₂S breakthrough time was at $t/t^* = 1.6$ for all three cycles. After introduction of H₂S, the exit H₂S concentration increased gradually to 150 ppm at $t/t^* = 1.6$, followed by a sharp breakthrough toward the inlet H₂S value. The reproducibility of the data indicates clearly that Cu-2Mg-O is a stable sorbent for H₂S removal at 850°C (1123 K). However, the H₂S removal efficiency of this material is similar to copper metal.

Copper-Manganese Oxide Sorbents: The Cu-Mn-O sorbent was tested for H₂S removal at 650°C (923 K). The H₂S breakthrough time was at $t/t^* = 3.7$ (for t^* based on Cu₂S formation) for the 2nd and 3rd cycles, although t/t^* was not accurate for the 1st cycle due to gas leakage. At the beginning of each cycle, the exit H₂S concentration was low (<10 ppm) until $t/t^* = 0.5$. However it increased to and stayed at 50 ppm until $t/t^* = 3.7$ followed by a sharp breakthrough toward the inlet H₂S value. Apparently, manganese oxide participated in the sulfidation. The sulfidation conversion of this Cu-Mn-O sorbent would be 92 percent if the final product is assumed to be CuMnS₂.

Sulfidation tests were also conducted with copper manganese (Cu-Mn-O) sorbent at 850°C (1123 K). The sulfur capacity of this sorbent remains high at 850°C (similar to the sulfur capacity at 650°C), however its H₂S-removal efficiency is only 90% prior to breakthrough. The results of these tests also suggest that manganese oxide participates in the sulfidation. The values of sorbent conversion presented are for t/t^* based on formation of only Cu₂S in the product.

Copper-Cerium Oxide Sorbents: During the second year of this program, a copper-cerium oxide sorbent was synthesized by the amorphous citrate technique, and tested in reductive sulfidation in the packed-bed microreactor at P = 1 atm. The H₂S removal efficiency of this sorbent was 99.9% in three

cycles of sulfidation at 650°C with intermittent regeneration at 750°C (Figure 6). The performance of the Cu-Ce-O sorbent was slightly better than the best sorbent tried to date in sulfidation, namely Cu-2Cr-O.

Figure 6 shows the performance of Cu-Ce-O sorbent in 4 cycles of sulfidation at 850°C. This material shows 100% H₂S removal efficiency for $t/t^* \leq 0.5$ and excellent regenerability. However, after the first regeneration, severe (40-50%) shrinkage of the bed volume was observed. Regeneration of Cu-Ce-O sorbent at 750°C was fast and complete. Therefore, this sorbent, along with the copper chromite Cu-2Cr-O sorbent were selected for further detailed evaluation.

The surface areas of the reacted sorbents were determined by BET-N₂ desorption and the results are presented in Table 2.

Table 2. SPECIFIC SURFACE AREA OF SORBENTS

Sorbent	BET-Surface Area (m ² /g)
Cu-Cr-O, 850°C-calcined	0.3
850°C, C-4 sulfidation	0.2
Cu-2Cr-O, 850°C-calcined	3.5
850°C, C-2 sulfidation and partial regeneration	0.5 (1.0)
Cu-Ce-O, 850°C-calcined	10.2
850°C, C-4 sulfidation	2.2
850°C, C-4 regeneration	2.3
3Cu-Mg-O, 650°C-calcined	7.7
650°C, C-2 sulfidation	5.0
Cu-2Mg-O, 850°C-calcined	4.3
850°C, C-3 sulfidation	0.9

Detailed Sulfidation/Regeneration Tests: These tests were carried out with the copper-chromite over 10 cycles and with copper-cerium over nine cycles. The H₂S breakthrough curves for the ten sulfidation/regeneration cycles using the Cu-2Cr-O sorbent in the 1-cm ID, packed-bed microreactor at MIT are shown in Figure 7. The sorbent (-20+35 mesh) was diluted with 50 vol % low surface area (Alcoa-T64) α -Al₂O₃ particles (-20+35 mesh). The total volume of the sorbent and α -Al₂O₃ in the reactor was 6 ml.

For all of the tests there is a plateau in all the breakthrough curves corresponding to the equilibrium of metallic copper sulfidation (to Cu₂S). The first breakthrough of H₂S (<25 ppm) always occurred at 0.24 to 0.4 normalized sorbent conversion and a second breakthrough occurred at about normalized conversion of 1.2 to 1.7. The feed gas composition in this series of tests is given in Table 3. Comparison of cycles No. 6, 7, and 8 indicate that the prebreakthrough H₂S level increases from 130 ppm to 300 ppm as the hydrogen content of the fuel gas increases from 10 to 40%. The steam content

of the fuel gas in these three runs was about 20%. Similar results were obtained at low steam-containing (10%) fuel gas (cycles 2, 3, and 5).

Table 3. SULFIDATION TEST CONDITIONS WITH Cu-2Cr-O SORBENT AT 850°C

Cycle No.	Space Velocity, hr ⁻¹	Gas Composition*, vol. %				
		H ₂	H ₂ O	H ₂ S	CO	CO ₂
1	2000	40.5	10.8	0.5	--	--
2	2000	39.5	12.0	0.5	--	--
3	2000	20	11.5	0.5	--	--
5	2000	10.5	10.5	0.5	--	--
6	2000	20	20	0.5	--	--
7	2000	39.5	20	0.5	--	--
8	2090	10.1	21.5	0.5	--	--
9	2020	10.4	20.8	0.5	24.8	5.9
10	2020	10.4	20.8	0.5	24.8	5.9

* Balance (to 100%) is N₂ gas.

Comparison of results obtained in cycles 3 and 6 indicate that the steam content of the fuel gas in the range tested (10-20%) does not have any effect on the sorbent performance. Addition of CO and CO₂ to the fuel gas appears to result in an increase in the H₂S prebreakthrough concentration from 130 to 180 ppmv (cycles No. 8, 9, and 10).

The surface area of the sulfided (after 10 cycles) and regenerated (after 10 cycles) Cu-2Cr-O sorbent was 3.2 and 2.0 m²/g, respectively. Insignificant bed shrinkage took place during these cycles.

The H₂S breakthrough curves for the nine sulfidation/regeneration cycles conducted using the Cu-Ce-O sorbent in the packed-bed microreactor are shown in Figure 7. As in the Cu-2Cr-O tests, there is a plateau in all the curves with two H₂S breakthrough levels. The feed gas compositions in each cycle in this series of tests are given in Table 4.

Table 4. SULFIDATION TEST CONDITIONS WITH Cu-Ce-O SORBENT AT 850°C

Cycle No.	Space Velocity, hr ⁻¹	Gas Composition*, vol. %				
		H ₂	H ₂ O	H ₂ S	CO	CO ₂
1	2030	40	13	0.5	--	--
2	2212	37	21	0.5	--	--
3	2000	40	12	0.5	--	--
4	2029	12	24	0.5	--	--
5	2012	20	12	0.5	--	--
6	2000	40	12	0.5	--	--
7	2000	20	21	0.5	--	--
8	2024	12	21	0.5	25	6
9	2047	12	22	0.5	25	6

* Balance (to 100%) is N₂ gas.

Comparison of cycles No. 2, 4, and 7 as well as 1, 5, and 6 indicate that the prebreakthrough H_2S level (with Cu-Ce-O sorbent) increases with increasing H_2 concentration which is similar to the trend observed with the Cu-2Cr-O sorbent. The effect of H_2O is not significant (compare cycles 5 and 7) within the range of H_2O concentration tested (10-20%) which is also similar to the Cu-2Cr-O tests. The effect of CO and CC_2 addition can be realized by comparing cycles 4 with 8 and 9. As in the Cu-2Cr-O tests, when CO and CO_2 are added to the feed gas, the second breakthrough H_2S level increased by about 50 ppm.

The surface area and particle size distributions of the fresh and reacted Cu-Ce-O sorbent are shown in Table 5. Although there was a reduction in both the sorbent surface area and porosity (bed volume), sorbent reactivity was not adversely affected. Analysis of particle size distribution of the fresh and spent sorbents (after 9 cycles) indicates significant reduction in the sorbent particle size. This may be due to either attrition or chemical degradation in the cycling process.

Table 5. SELECTED Cu-Ce-O SORBENT PHYSICAL PROPERTIES

Surface Area:	Before C-1, 1000°C-calcined	2.0 m ² /g
	After C-1 regeneration	1.5 m ² /g
	After C-9 sulfidation	0.8 m ² /g

Bed Volume Shrinkage: Fresh and After C-6 Sulfidation

Particle Size Analysis:	<u>Fresh</u>	
	-20+35	56.6% (wt)
	-35+60	39.8%
	<60	3.6%
	<u>After C-9 Sulfidation</u>	
	-20+35	35.6% (wt)
	-35+60	38.1%
	-60+80	9.4%
	<80	16.9%

The sulfided copper chromite sorbent (after 10th cycle) and the sulfided copper cerium sorbent (after 9th cycle) were analyzed by XRD. The results indicate that in the case of copper chromite the oxide phases were identified as Cr_2O_3 and $CuCrO_4$, but no CuO was found. This indicates that copper oxide was completely converted to copper sulfide while Cr_2O_3 did not participate in sulfidation. Phases of $Cu_{1.8}S$, $Cu_{7.2}S_4$, Cu_7S_4 and Cu_9S_5 were also identified. These results are consistent with the H_2S breakthrough at times t/t^* over one observed in sulfidation experiments.

In contrast, both CuO and CeO_2 in the copper cerium sorbent were sulfided during sulfidation tests. The results indicate the existence of CeS_2 rather than Cu_2S (see Figure 2), which explains the t/t^* value of 2, 3, or even higher, where t^* was calculated for the Cu_2S stoichiometrically (see Figure 7).

Sorbent Regenerability Tests

Cyclic sulfidation/regeneration tests of $\text{CuO}\cdot\text{CeO}_2$ calcined at 910°C were conducted at regeneration temperature of 650°C , 750°C and 850°C . Complete regenerations were easily achieved at all three temperatures. Figure 8 shows the times required for regeneration at the three different temperatures. As expected, the higher the regeneration temperature, the faster the regeneration. Complete regeneration was achieved in about 48 minutes at 650°C , while it took only 24 minutes at 850°C .

Elemental sulfur was produced during the regeneration of $\text{CuO}\cdot\text{CeO}_2$ sorbent. More sulfur was observed at 750°C , the total amounting to about 10% of H_2S input for each cycle. The amount of sulfur for the other two temperatures was 2.9% and 3.8% of the H_2S input at 650°C and 850°C , respectively. The results are shown in Table 6.

Table 6. SULFUR BALANCE IN CYCLIC SULFIDATION*/
REGENERATION OF Cu-Ce-O SORBENT

Temp., $^\circ\text{C}$	S Input (as H_2S), mg	S Output				Total Sulfur %
		Elemental S		SO_2		
		mg	%	mg	%	
650	114	3.3	2.9	69	60	63
750	123	12.5	10.1	94	76	86
850	113	4.3	3.8	101	89	93

* All sulfidation tests were performed at 850°C .

Sulfur mass balances of about 86% and 93% were calculated for regeneration at 750°C and 850°C , respectively. For regeneration at 650°C , it can be seen that the amount of sulfur dioxide measured by GC was only about 60% of the H_2S input. This was probably due to the fact that the maximum peak was missed during GC sampling.

Comparison of the H_2S breakthrough curves in the sulfidation tests conducted at 850°C following sorbent regeneration at different temperatures indicates that 750°C is the best regeneration temperature, especially if the gas composition can be optimized at this temperature to increase the elemental sulfur production to or above the level considered marketable.

Bed Shrinkage: The $\text{CuO}\cdot\text{CeO}_2$ sorbent bed shrinkage is related to the calcination temperature used in sorbent preparation. For the sorbent calcined at 910°C , the shrinkage was about 32% after 7 cycles, and 50% after 15 cycles (see Table 7). It was about the same for sorbent calcined at 850°C . However, the shrinkage was much less for the sorbent calcined at 1000°C , which was about 18% after 6 cycles (see Table 5).

The particle size distribution of the fresh and used $\text{CuO}\cdot\text{CeO}_2$ calcined at 910°C is shown in Table 8. Shrinkage was accompanied by sorbent attrition. While calcination temperature affects the structural properties of the

sorbent, it also affects the dispersion of the active phase, formation of oxide solid solutions, etc. These are reflected in the sulfidation kinetics, sulfur capacity, and H₂S removal efficiency of the sorbent. Figure 9 shows the effect of calcination temperature on the H₂S breakthrough profiles

Table 7. SURFACE AREA AND BED SHRINKAGE OF
SORBENT Cu-Ce-O CALCINED AT 910°C

Surface Area:	Before C-1, 910°C-calcined	5 m ² /g
	After C-15 regeneration	1.3 m ² /g
	After C-16 sulfidation	1.7 m ² /g

	Sorbent Bed Height, cm	Shrinkage, %
Initial	7.0	0
After C-3	6.5	7.1
After C-5	5.5	21.4
After C-7	4.7	32.9
After C-9	3.9	44.3
After C-12	3.6	48.6
After C-15	3.5	50

Table 8. PARTICLE SIZE (MESH) OF SORBENT
Cu-Ce-O CALCINED AT 910°C

Fresh:	-20+35	100% (wt %)
After C-15 sulfidation:	-20+35	53.9%
	-35+60	10.3%
	-60	35.8%

observed with the CuO·CeO₂ sorbent in the tests conducted at 850°C with the same feed gas composition. The sorbent calcined at 910°C shows the highest overall H₂S removal efficiency (up to high conversion) even at higher space velocity, 3900 h⁻¹ (STP), than the other two samples (2300 h⁻¹, 1000°C; 2100 h⁻¹, 850°C).

Comparison of Hot Gas Desulfurization Sorbents

Sulfidation/regeneration tests were further conducted in the larger 2.5-cm-diameter quartz reactor at IGT with the two selected sorbents (developed in this program), commercial copper chromite sorbents (UCI G-13 and G-89), and

the zinc titanate sorbent (L-3014, Zn/Ti = 0.8). The chemical analyses of these sorbents are given in Table 9. The copper sorbents (G-13 and G-89) are commercial hydrogenation catalysts while L-3014 zinc titanate sorbent was produced by United Catalyst Inc. for DOE as a hot gas desulfurization sorbent.

Table 9. CHEMICAL COMPOSITION OF THE SORBENTS TESTED

<u>Sorbent</u>	<u>Cu</u>	<u>Cr</u>	<u>Zn</u>	<u>Ti</u>	<u>Mn</u>	<u>Ce</u>
G-13 (UCI Commercial)	40	25	--	--	--	--
G-89 (UCI Commercial)	39	37	--	--	3	--
L-3014 (UCI/DOE)	--	--	35	32	--	--
Copper Chromite	27	45	--	--	--	--
Copper Cerium	27	--	--	--	--	59

The tests with all these sorbents were conducted under identical gas composition, space velocity and temperature in both fluidized-bed and packed-bed modes of operation. Because of significant differences in the sorbent densities and capacities, in order to compare the sorbents, the bed height (bed volume) was the same in all these runs and H₂S breakthrough curves are reported in terms of H₂S concentration versus sulfur loading in the sorbents.

Fluidized-Bed Tests: These tests were conducted at 650°C with all sorbents and at 850°C with the two sorbents developed in this program. The reactant gas contained 0.5% H₂S, 10% H₂O, 20% H₂, and 69.5% N₂. The fluidized-bed height was about 5 cm. All these sorbents were regenerated at 750°C with a gas mixture containing 6% O₂ and 94% nitrogen. The results of these tests are shown in Figures 10 and 11.

The G-13 sorbent reduced the H₂S level to less than 10 ppm at a sulfur loading of 40 g S/kg sorbent for three cycles which is very acceptable for fluidized-bed operation. The faster breakthrough time for the third cycle may have been caused by incomplete regeneration after the second sulfidation test. There is some question, however, as to whether the sorbent bed was completely fluidized in the tests using the G-13 sorbent. The G-89 sorbent was able to reduce the H₂S level below 50 ppm at a sulfur loading of 10-25 g S/kg sorbent. The L-3014 zinc titanate sorbent reduced the reactor exit gas H₂S concentration to less than 50 ppm up at sulfur loading of 40 g S/kg sorbent. These results are typical for this type of sorbent under these operating conditions.

The copper chromite sorbent, developed in this program, reduced the H₂S to below 5 and 50 ppmv at sulfur loadings of 10 to 25 g S/kg sorbent in tests conducted at 650°C. The sulfur loading for the corresponding levels of H₂S essentially doubled when the sulfidation temperature was increased to 850°C. The results obtained for the copper cerium were similar to those obtained with copper chromite at 850°C (i.e. 5-50 ppm at 20-50 g S/kg sorbent).

Packed-Bed Tests: The performance of these sorbents at 850°C were also determined in packed-bed tests conducted under similar conditions. The results of these tests, shown in Figure 12, indicate that all of these sorbents can reduce the H₂S content of the feed gas to below 5 ppm followed by a sharp breakthrough. The sulfur loadings at breakthrough for the G-13, copper chromite, copper cerium and zinc titanate were 10, 13, 18 and 60, respectively. Although zinc titanate showed higher sulfur capacity at this temperature, this sorbent is not expected to be suitable for such high temperature applications because of zinc volatilization.

Attrition Tests

To cover a wide range of attrition resistant materials, two copper chromium-based sorbents (UCI G-13 and G-89), UCI ZnTiO₃, alumina, and a lignite char were tested in the attrition test apparatus at IGT. Figure 13 shows that the ZnTiO₃ sorbent is highly attrition resistant (over 95%) even after five hours of testing, followed closely by the alumina and then the UCI G-13 and G-89 sorbents. The lignite char showed lower attrition resistance and was not tested further.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made for this study:

Based on literature data, in terms of reduction stability equilibrium, CuCr₂O₄ and Cu₃MgO₄ are the most stable cupric (Cu⁺²) phases, while among cuprous (Cu⁺¹) compounds, CuCrO₂ is the most stable phase. Between cupric and cuprous compounds, cupric (Cu⁺²) has better sulfidation equilibrium than cuprous (Cu⁺¹) compounds. Among various copper-based sorbents, the aluminates lie closest to single oxides of copper.

Based on the initial experiments conducted in this study, the novel copper-based sorbents are ranked as follows:

- Reduction Stability: Cu-Cr-O
- H₂S Removal Efficiency: Cu-Ce-O
Cu-2Cr-O
- Sulfur Capacity: Cu-Mn-O
- Still Uncertain: 3Cu-Mg-O (high stability phase
Cu₃MgO₄ has not been prepared)
- Dropped from the list:
 - based on experiment Cu-Ti-O
 - based on literature Cu-Al-O⁽⁷⁾
Cu-Fe-O⁽⁷⁾
Cu-Si-O⁽¹⁸⁾

The copper chromite and copper cerium binary oxides were selected for further testing. Comparison of the results of various tests conducted with these two sorbents indicate that both sorbents are capable of removing H₂S to below 10 ppm and are suitable for operation at 850°C. Both these sorbents can be completely regenerated at 750°C with 30% air, 70% nitrogen in a short period. The copper chromite has higher physical strength than copper cerium. Its bulk density is about four times higher than copper cerium, both prepared at 850°C-calcination temperature. Sorbent shrinkage was not observed in copper chromite while for copper cerium the bed shrinkage was about 50% after 10 cycles.

The theoretical capacity of the copper cerium is much higher than that of copper chromite, mainly because of cerium participation in the sulfidation process.

Additional work is needed to achieve overall sorbent optimization. This includes determination of the structural effect of CeO₂ and Cr₂O₃ addition in CuO, as well as effects on the sulfidation kinetics, stability, and regenerability of these sorbents. Also, more detailed regeneration studies are needed to optimize the regeneration off-gas composition.

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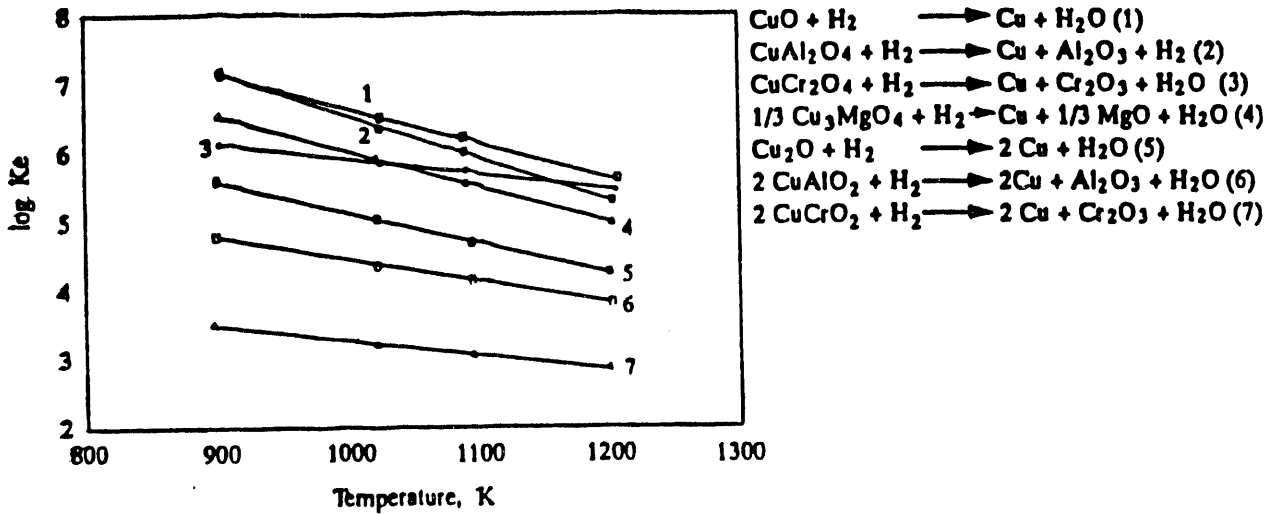


Figure 1. EQUILIBRIUM CONSTANTS FOR REDUCTION OF COPPER-BASED SORBENTS IN HYDROGEN

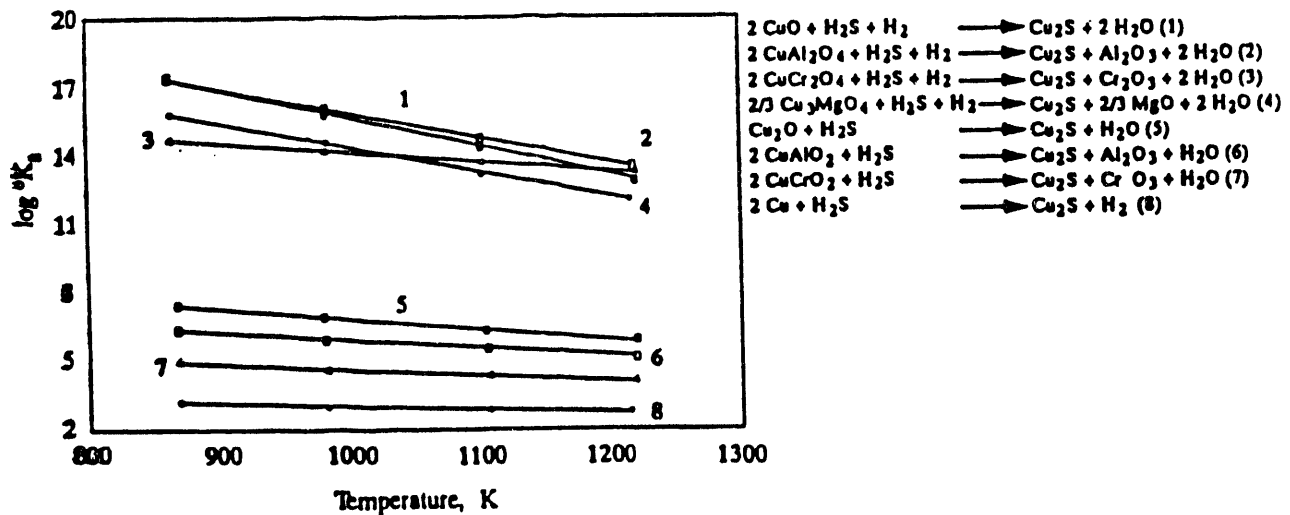


Figure 2. EQUILIBRIUM CONSTANTS FOR SULFIDATION OF COPPER-BASED SORBENTS

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 PUF 11-34, 424

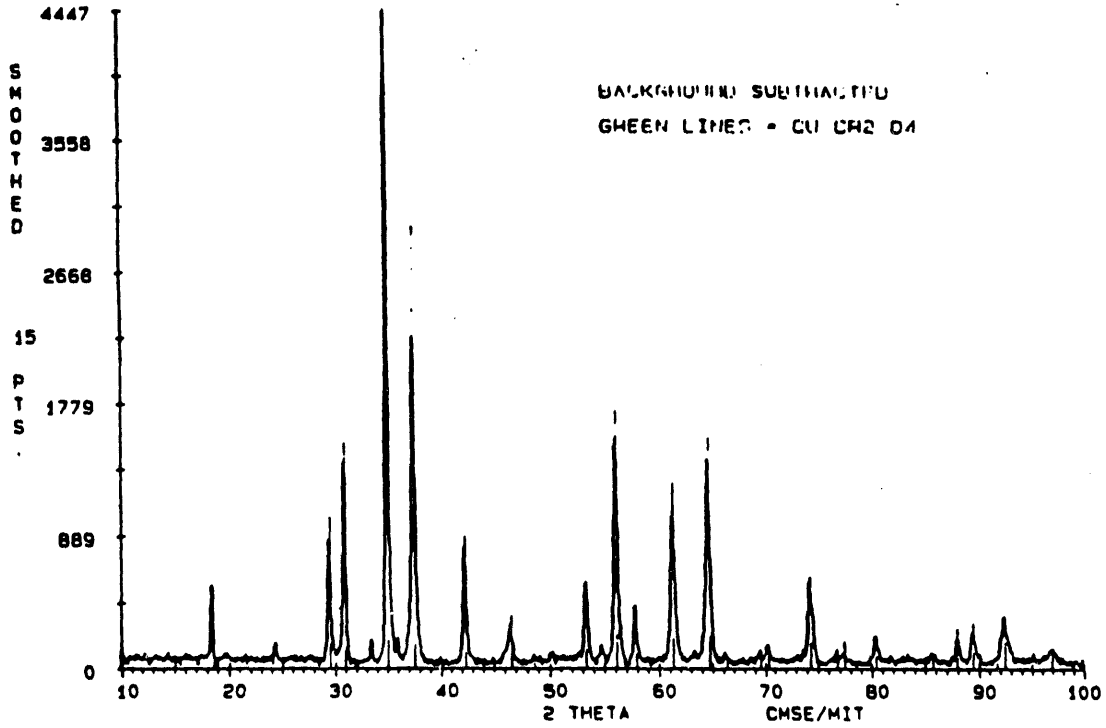


Figure 3. X-RAY DIFFRACTOGRAM OF SORBENT Cu-2Cr-O, CALCINED AT 850°C

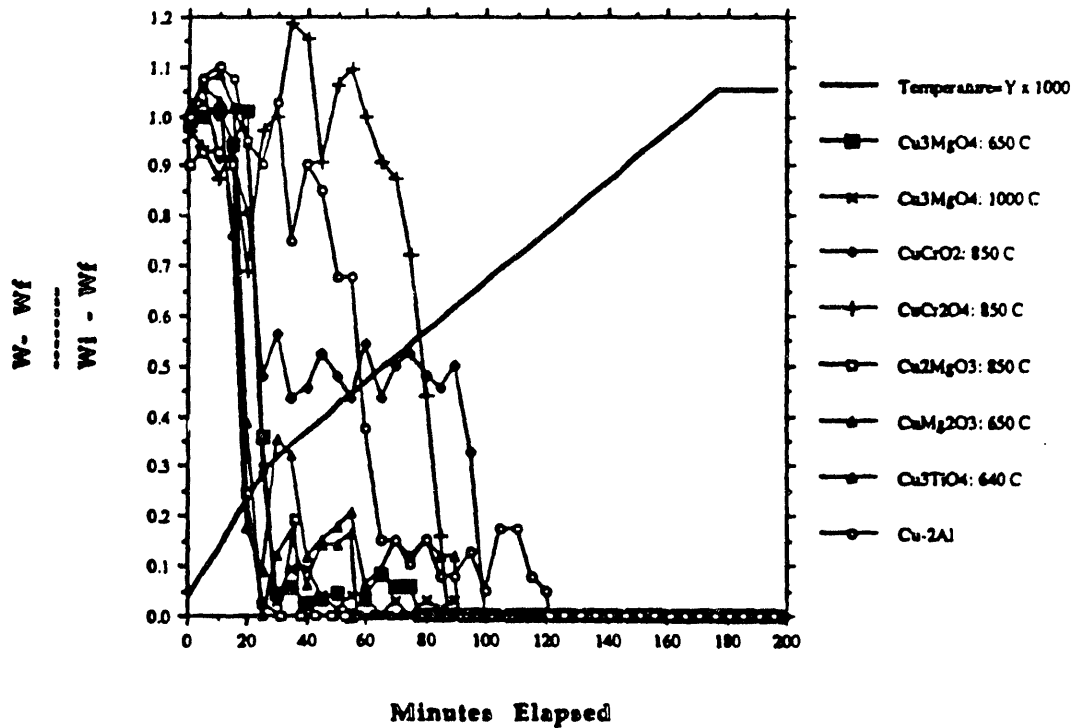


Figure 4. REDUCTION PATTERNS OF CuO-BASED SORBENTS

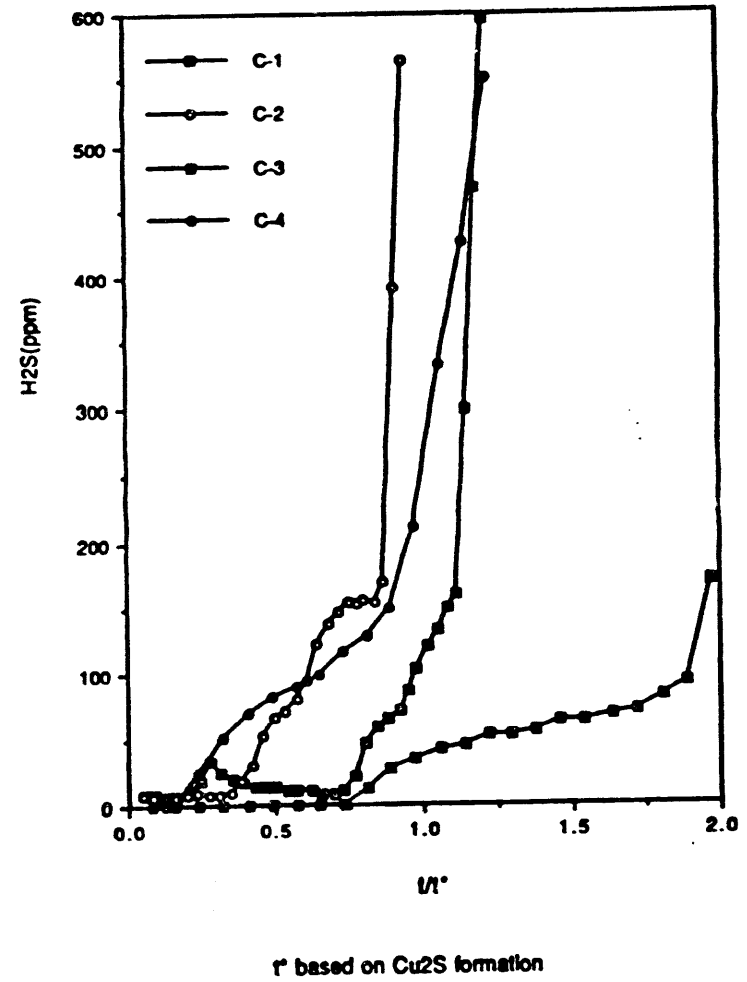
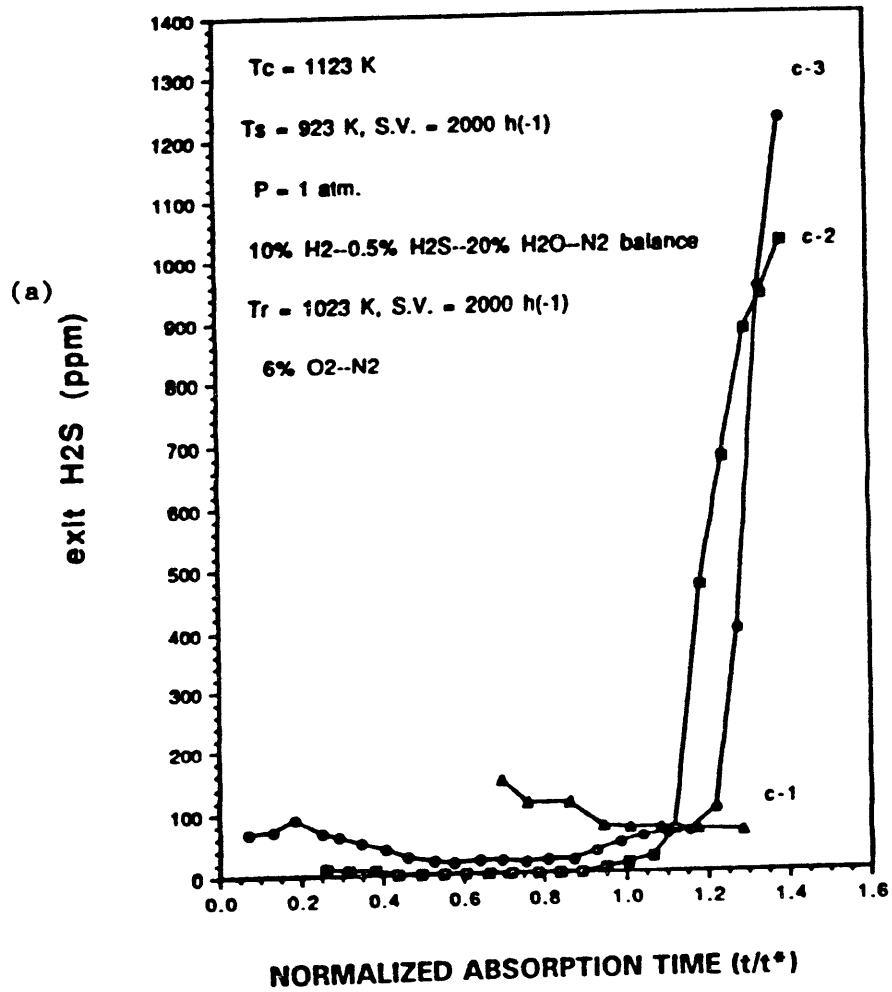
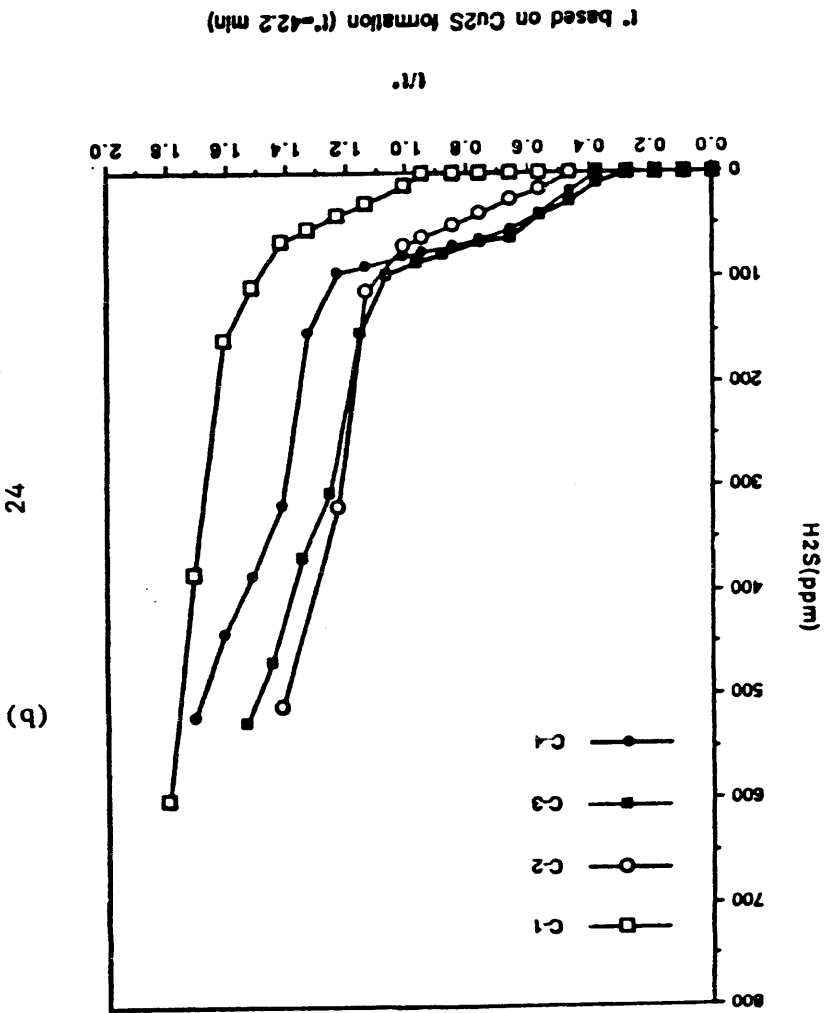
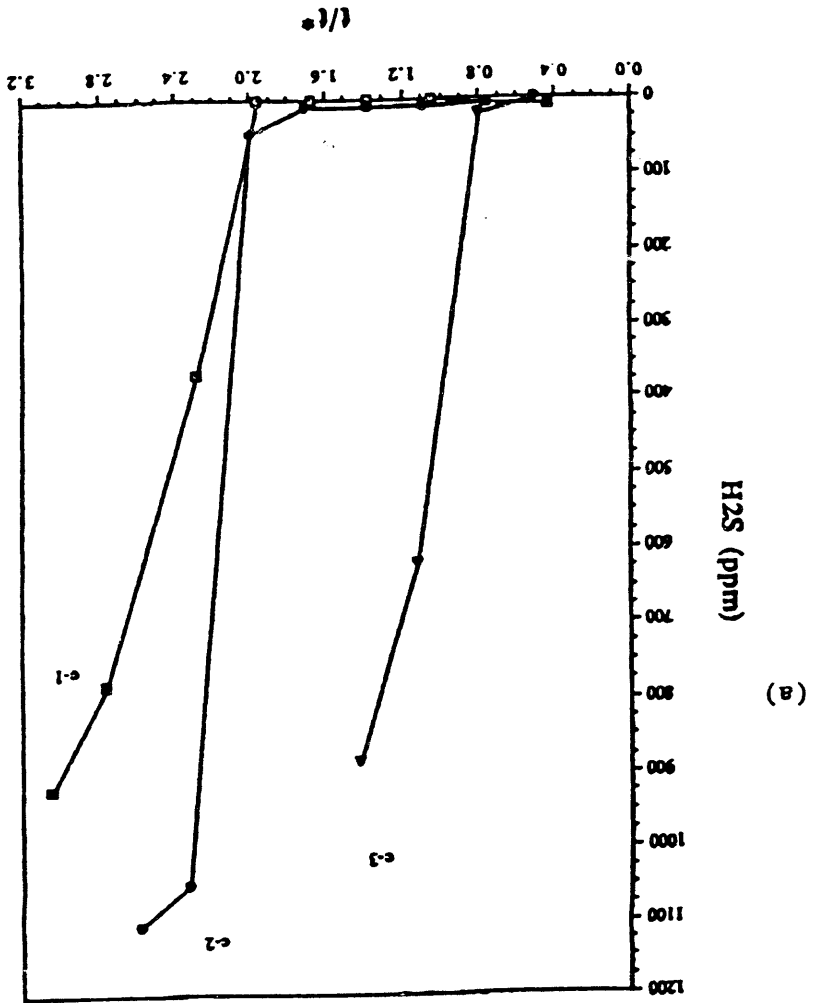


Figure 5. CYCLIC SULFIDATION OF Cu-2Cr-O SORBENT
 a) 650°C, b) 850°C

Figure 6. CYCLIC SULFIDATION OF Cu-Ce-O SORBENT
 a) 650°C, b) 850°C



t based on Cu₂S formation (t=42.2 min)

24

(b)

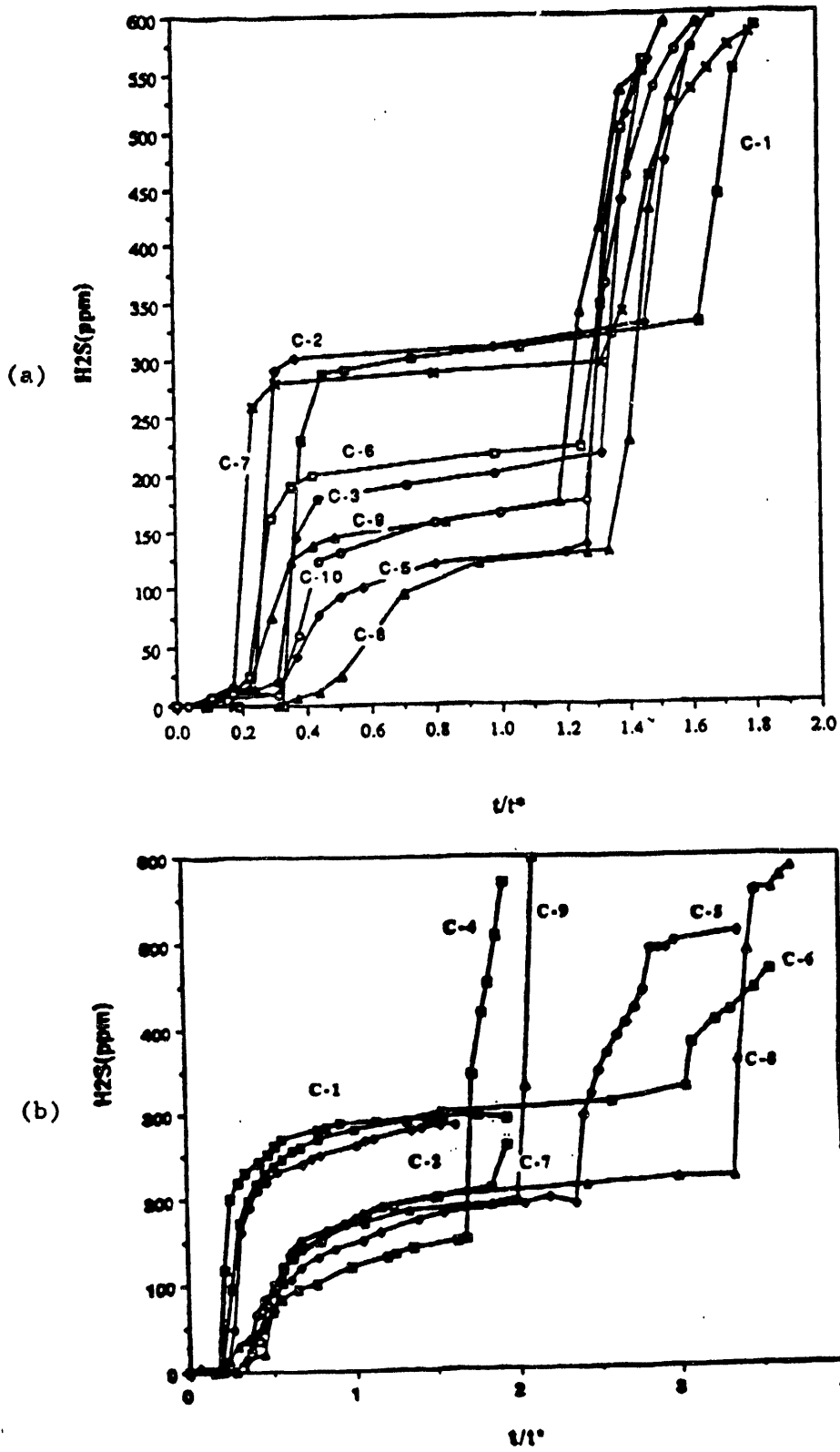


Figure 7. H₂S BREAKTHROUGH PROFILES OF SELECTED SORBENTS AT 850°C
 a) Cu-2Cr-O, b) Cu-Ce-O

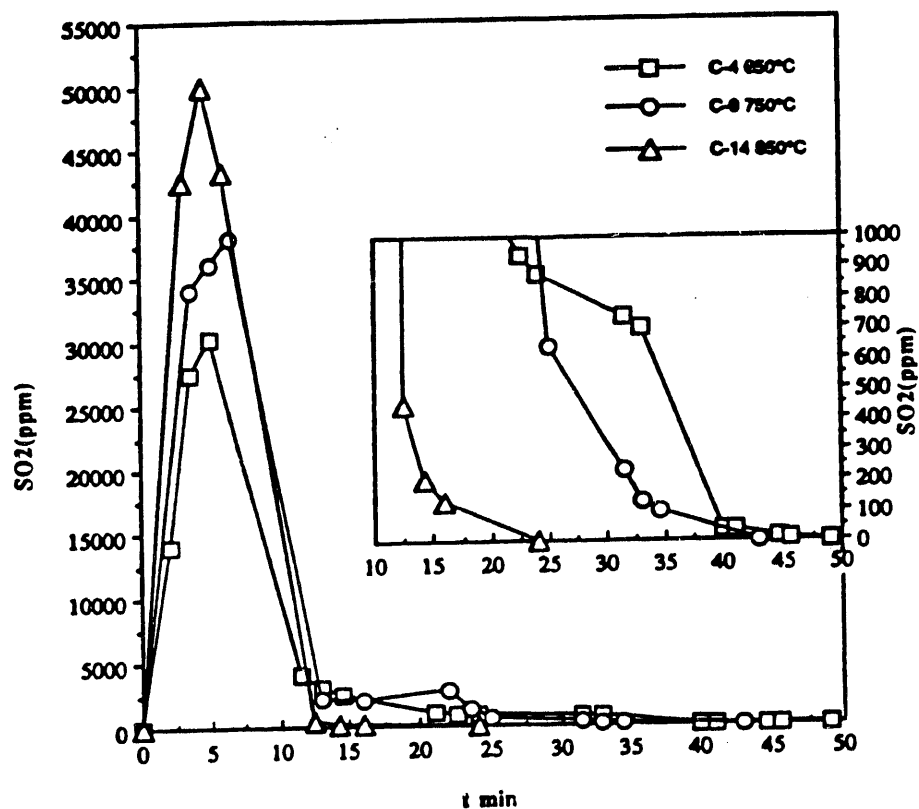


Figure 8. CYCLIC REGENERATION OF Cu-Ce-O SORBENT AT DIFFERENT TEMPERATURES

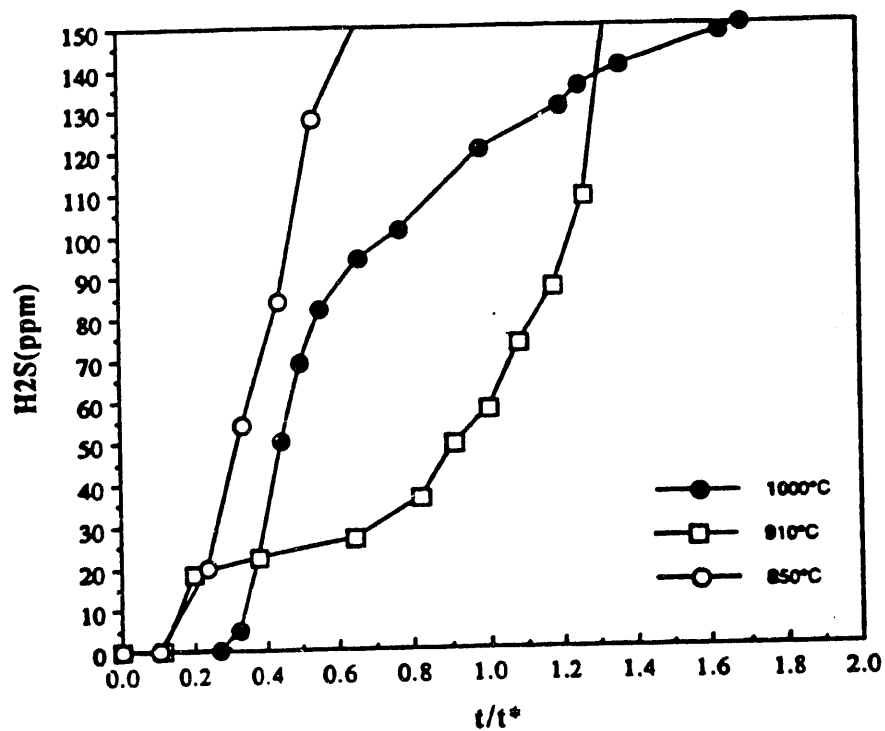


Figure 9. SULFIDATION OF Cu-Ce-O SORBENT AT 850°C AS A FUNCTION OF CALCINATION TEMPERATURE

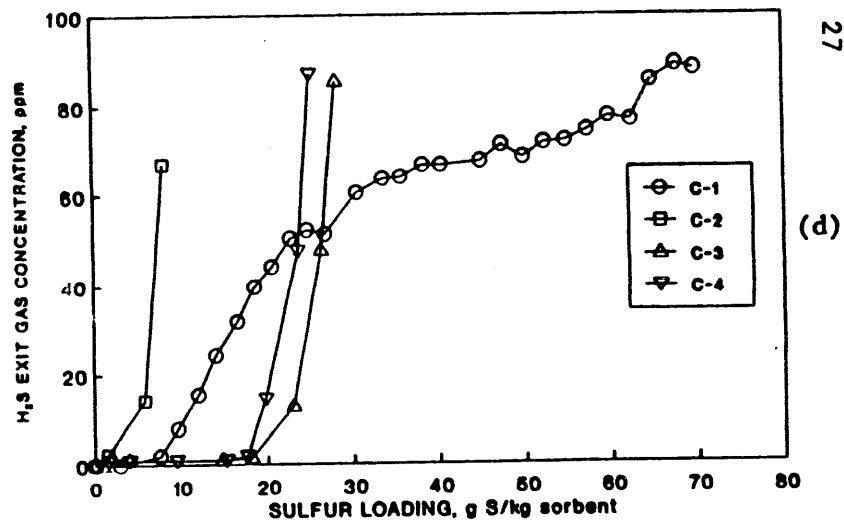
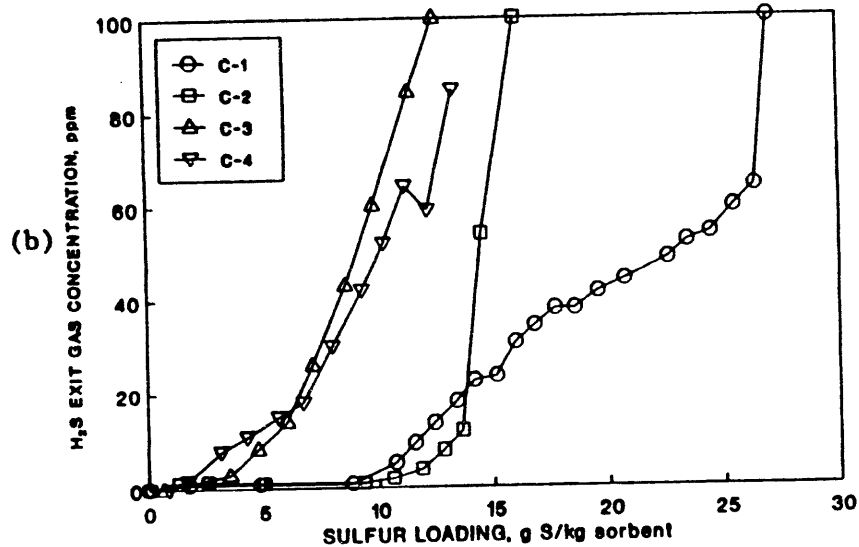
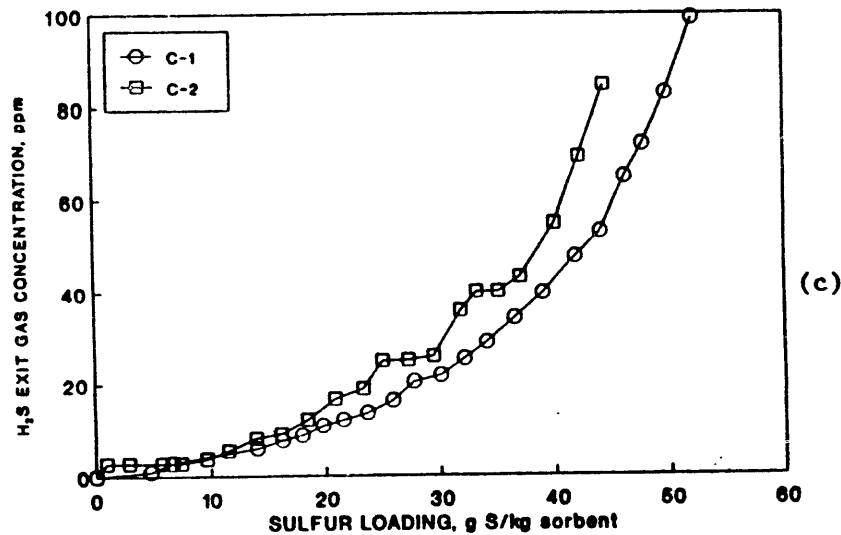
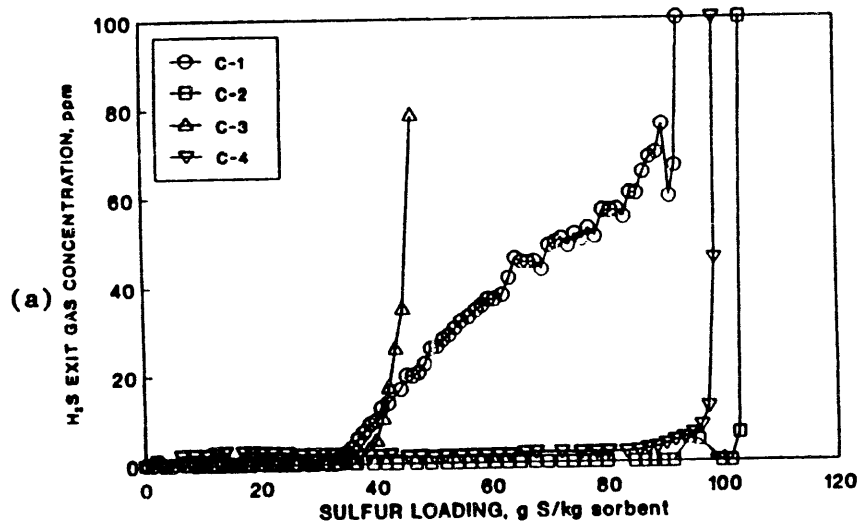


Figure 10. H₂S BREAKTHROUGH CURVES FOR VARIOUS SORBENTS IN FLUIDIZED BED AT 650°C
 a) G-13 (UCI) b) G-89 (UCI) c) Zinc Titanate (UCI)
 d) Copper Chromite (this study)

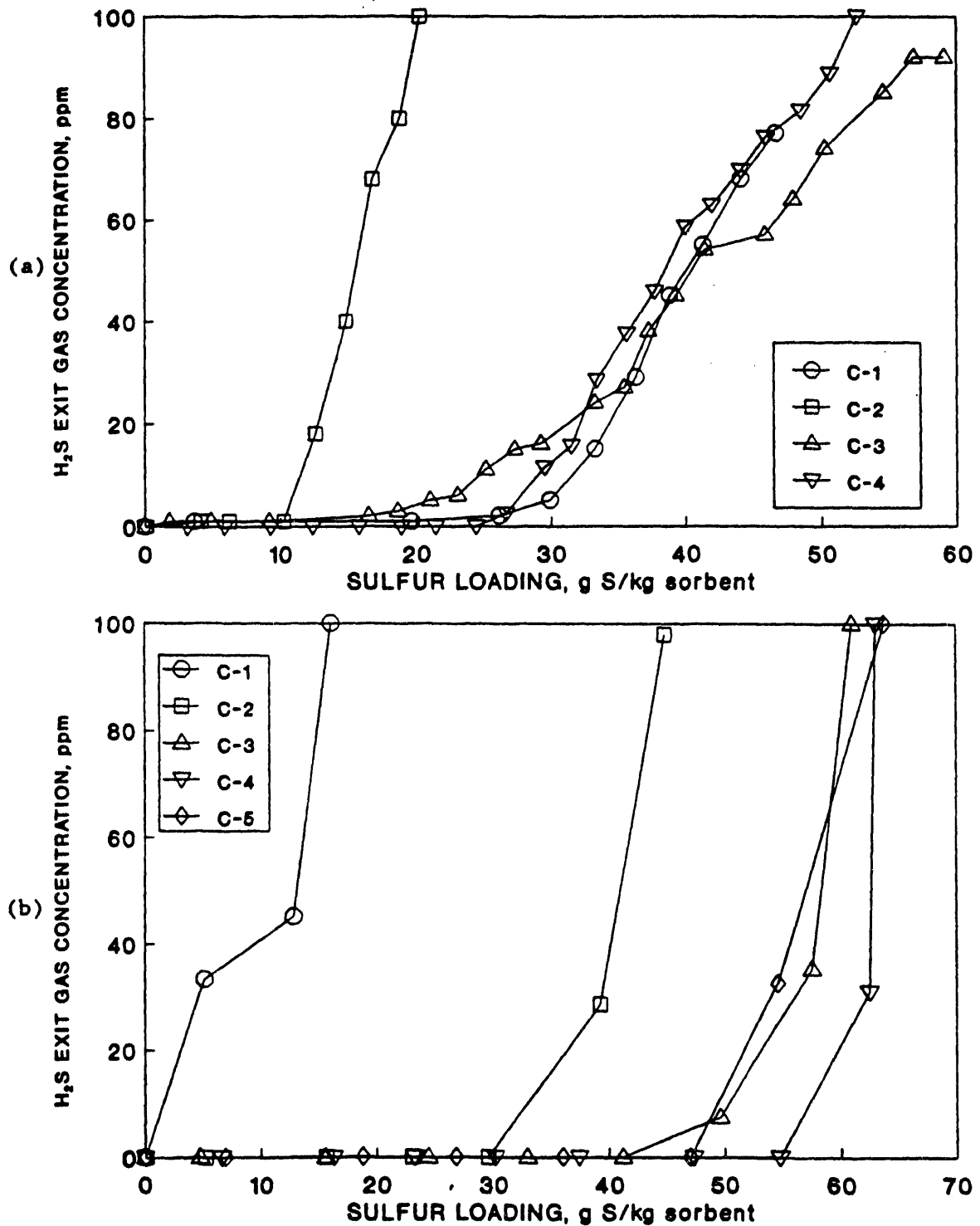


Figure 11. H₂S BREAKTHROUGH CURVES FOR THE SELECTED SORBENTS IN FLUIDIZED BED AT 850°C
 a) Copper Chromite b) Copper Cerium

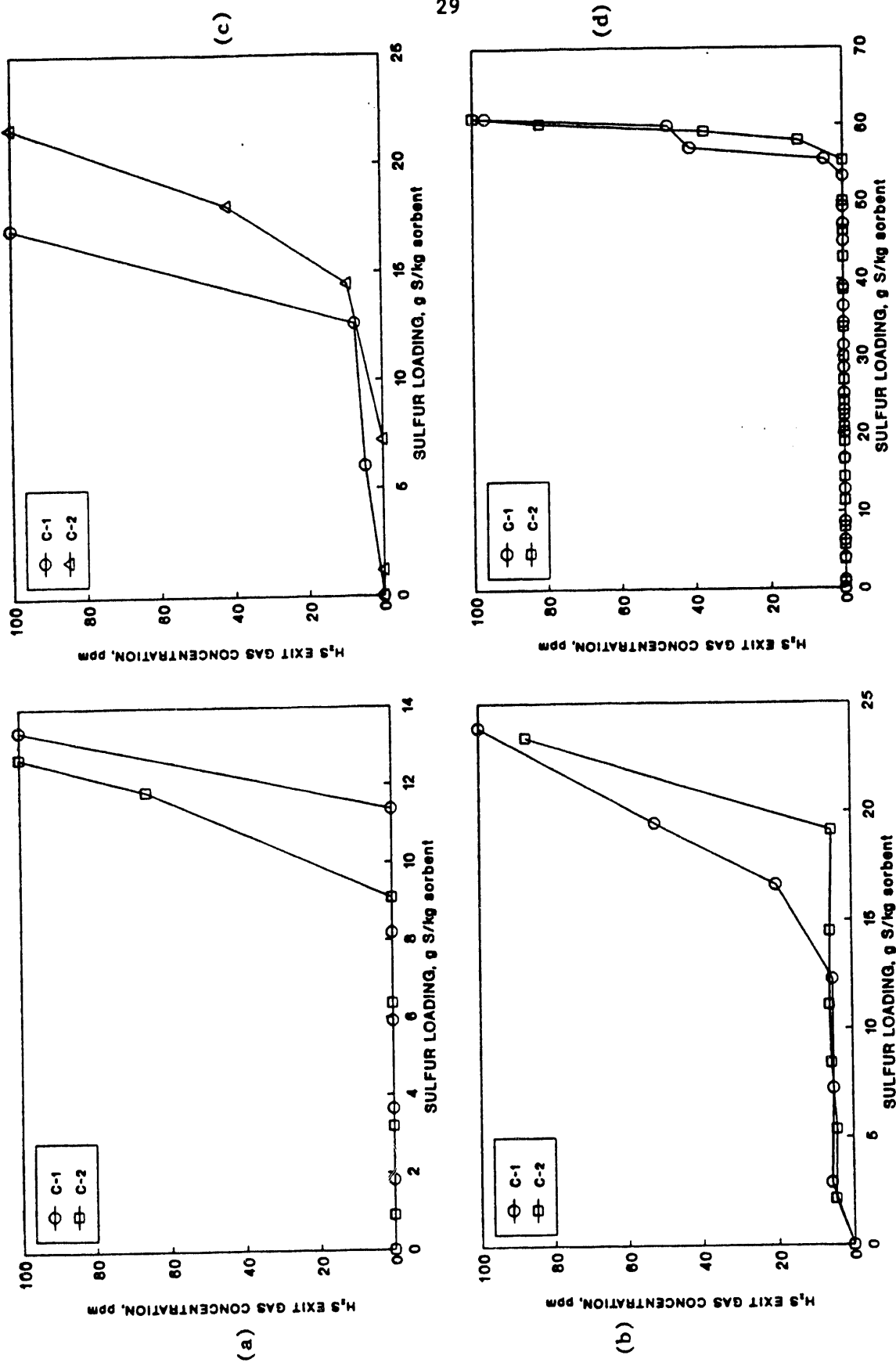


Figure 12. H₂S BREAKTHROUGH FOR VARIOUS SORBENTS IN PACKED BED AT 850°C

a) G-13, b) Copper Chromite, c) Copper Cerium, d) Zinc Titanate

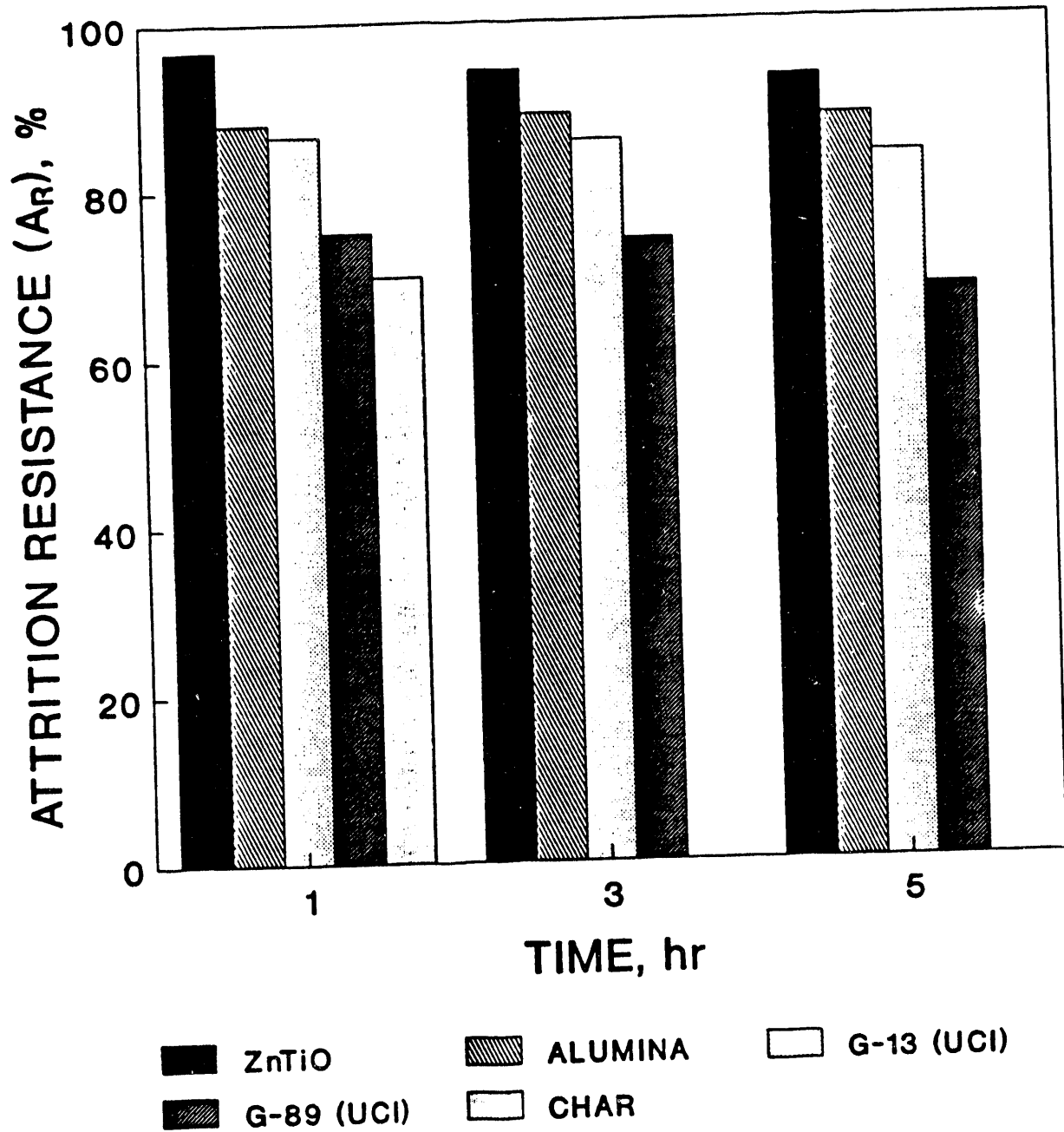


Figure 13. ATTRITION RESISTANCE OF VARIOUS SOLIDS

PROJECT MANAGEMENT REPORT

September 1, 1991 through August 31, 1992

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

Principal Investigator: Javad Abbasian, Institute of Gas Technology

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

Other Investigators: Andy H. Hill, Institute of Gas Technology
James R. Wangerow, Institute of Gas Technology
Luhong Bo, Massachusetts Institute of Technology
Chandra Patel, Massachusetts Institute of Technology

COMMENTS

The project was completed on schedule and all objectives of the project were achieved.

Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1991 to Nov. 30, 1991	Projected	5,740	625	1,269		13,700	13,160	34,224
	Estimated	2,500	--	600		13,000	7,374	23,474
Sept. 1, 1991 to Feb. 29, 1992	Projected	10,940	1,250	1,269		27,400	26,054	66,913
	Estimated	12,638	1,065	600		25,000	28,439	67,742
Sept. 1, 1991 to May 31, 1992	Projected	16,410	2,200	1,269		41,100	39,015	99,994
	Estimated	17,620	1,200	1,691		38,000	41,629	98,940
Sept. 1, 1991 to Aug. 31, 1992	Projected	18,232	2,500	3,318		55,140	45,750	124,940
	Estimated	19,150	1,935	1,826		55,140	46,977	125,028

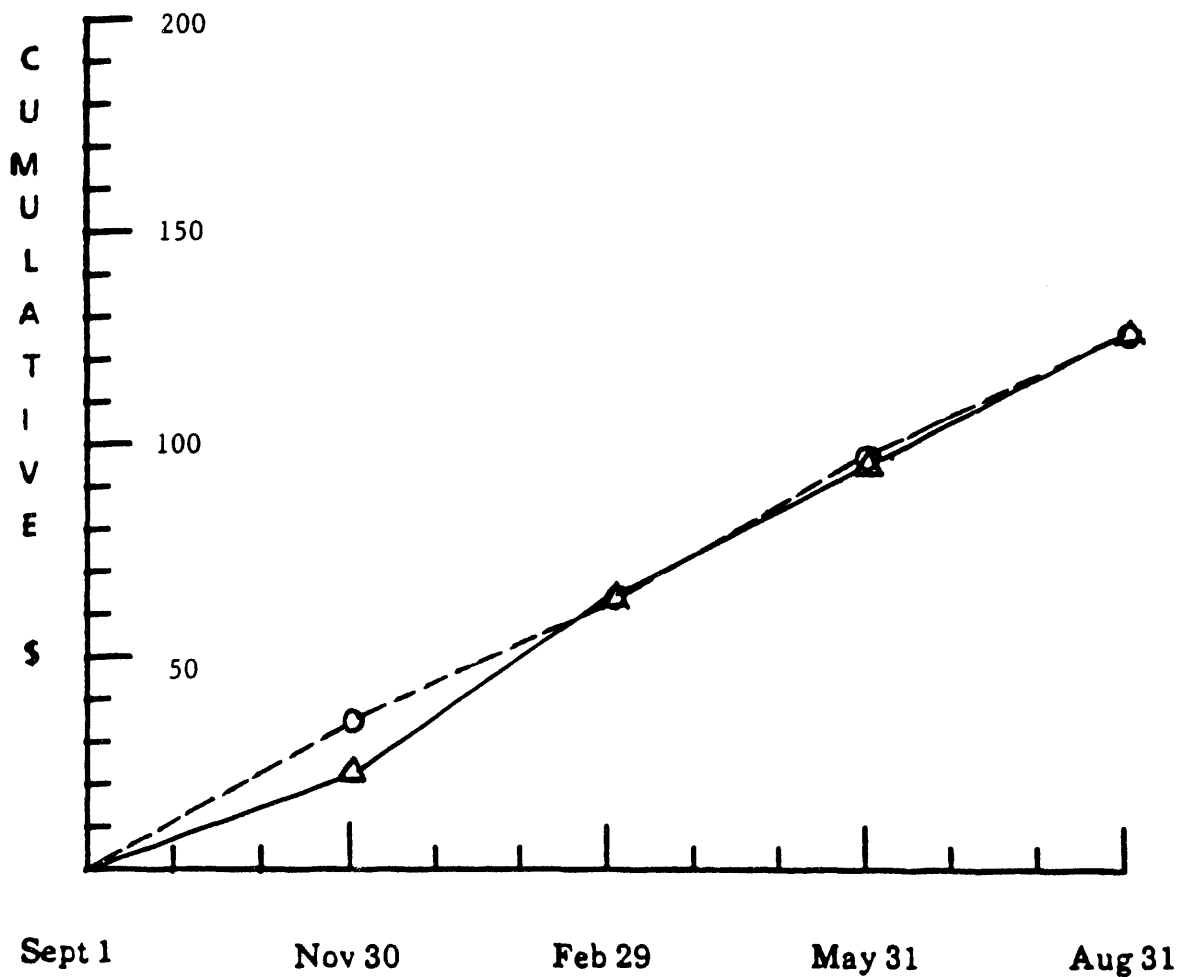
*Cumulative by quarter

DEVELOPMENT OF NOVEL COPPER BASED SORBENTS FOR HOT GAS CLEANUP

COSTS BY QUARTER

(Place Your Project Title Here)

DEVELOPMENT OF NOVEL COPPER BASED SORBENTS FOR HOT GAS CLEANUP



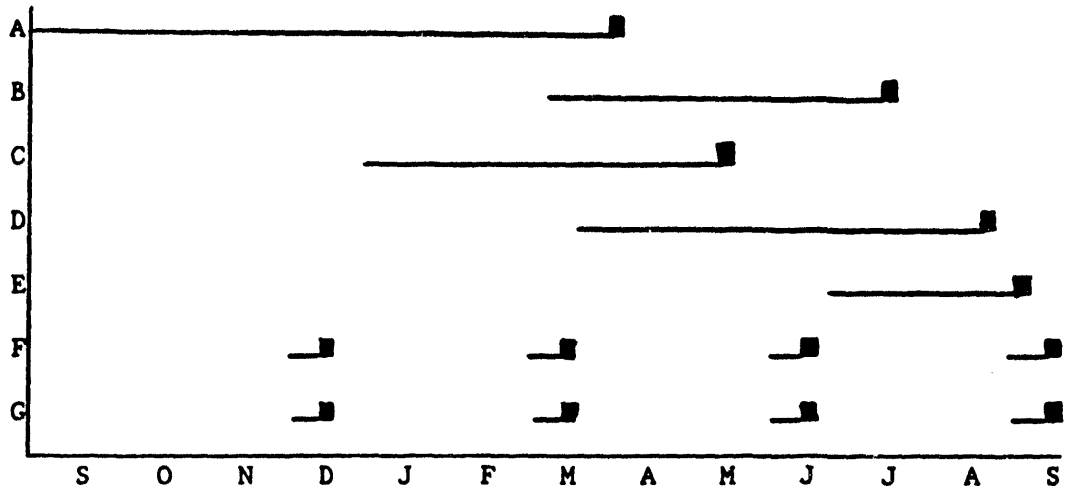
Months and Quarters

○ = Projected Expenditures 124,940

△ = Estimated Actual Expenditures 125,028

Total CRSC Award \$ 124,940

DEVELOPMENT OF NOVEL COPPER-BASED SORBENTS FOR HOT GAS CLEANUP



Begins
September 1, 1992

- A. Detailed Sulfidation Tests with Selected Sorbents
- B. Regenerability and Cycling Tests (MIT)
- C. Ambient Pressure Fluidized-Bed Tests
- D. Comparison of Novel Sorbent With "Other" Sorbents
- E. Attrition Tests
- F. Preparation of Technical Reports
- G. Preparation of Project Management Reports

SCHEDULE OF PROJECT MILESTONES