FINAL TECHNICAL REPORT
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Project Title: Coal Gas Desulfurization by Hot Copper Sorbents
ICCI Project Number: 86-87/3.2A-2
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ABSTRACT

This research project investigates the feasibility of desulfurizing product
gases obtained during the processing of Illinois coal. Examples of such pro-
duct gases are coke-oven gas, gas from low-temperature charring, and gases
obtained from coal gasification. The method employs copper-based solid
sorbent and operates at elevated temperatures and pressures. Much of the
reaction chemistry involved is based on copper smelting technology. The
technique is thermally more efficient than existing low-temperature pro-
cesses such as amine scrubbing and Claus and Beavon processes, and it avoids
the solubility problem associated with carbonyl sulfide. The experimental
technique employed is thermogravimetric in nature. Various copper sorbents
are being examined in both the desulfurization and regeneration modes; the
most promising sorbent system found will then be tested over multiple desul-
furization/regeneration cycles to determine its useful life. The primary
variables being studied experimentally are reaction temperatures and pres-
sures. Secondary variables are product gas and regeneration gas composi-
tions. Successful desulfurization experiments were performed during the
summer in the TGA, at pressures as high as 100 psig and temperatures be-
tween 800 and 900°C. These experiments indicate that both pure CuO and
$CuO:Fe_2O_3$ (2/1 Cu/Fe) experience an increase in desulfurization rates at
elevated pressures. Interestingly, the reduction reaction for both sorbents is
relatively insensitive to increased pressure. Regeneration of both sorbents in
5% O_2, 95% N_2 at 850°C and one atmosphere, followed by repeated desul-
furization runs, indicates $CuO:Fe_2O_3$ is a much better sorbent than CuO
alone.

EXECUTIVE SUMMARY

The intent of the proposed research was to investigate the potential of a new process for removing sulfur from gases produced during the utilization of high-sulfur Illinois coal. Oxides of metals such as iron, manganese, and copper form stable sulfides at high temperatures in highly reducing atmospheres. Thus, by controlled exposure to one or more of these oxides, gases from coke ovens, low-temperature charring reactors, and other similar processes can be desulfurized prior to subsequent combustion in a powerhouse, or before being fed to a combined-cycle system. Copper appears to be particularly well suited for the latter approach due to its very high affinity for sulfur. It should theoretically produce cleaned coal gases with the lowest concentration of sulfur.

A thermogravimetric technique was employed, initially concentrating on the copper oxide system. Using simulated coal gases for reliability and flexibility of operation, kinetic rate constants were determined at elevated temperatures and pressures for both the desulfurization and regeneration reactions. The most promising sorbent formulation was tested over multiple desulfurization/regeneration cycles to determine its useful life.

INTRODUCTION AND BACKGROUND

The reaction of hydrogen sulfide with copper oxide is believed to proceed as follows:

$$Cu_2O + H_2S \rightarrow Cu_2S + H_2O. \tag{1}$$

As with most metal oxides, the reaction is first order with respect to hydrogen sulfide, and obeys Arrhenius' law. High-temperature kinetic data have been reported in the literature (Jalan 1984).

The reaction of carbonyl sulfide with copper oxide is believed to proceed in a similar fashion:

$$Cu_2O + COS \rightarrow CU_2S + CO_2. \tag{2}$$

However, a decomposition reaction is also possible for the carbonyl sulfide:

$$COS \rightleftharpoons CO + \tfrac{1}{2} S_2. \tag{3}$$
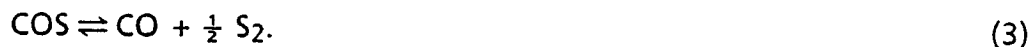
The presence of carbon monoxide at levels usually found in coal product gases is sufficient to suppress the decomposition at temperatures up to as high as 800°C, and at concentrations up to 0.3% carbonyl sulfide. This is precisely why it must be dealt with in the desulfurization of coal gases.

The regeneration reaction is essentially the same chemical reaction employed in the roasting process during copper smelting, which is:

$$2\,Cu_2S + 4\,O_2 \rightleftharpoons CU_2O + CuO \cdot CuSO_4 + SO_2. \tag{4}$$
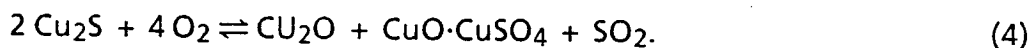
It should be noted that, depending on the temperature and partial pressures of oxygen and sulfur dioxide, a complicated equilibrium exists between all the copper compounds possible in these circumstances (Biswas and Davenport 1980). The range of possible compounds is: Cu, CuO, Cu_2O, CuS, Cu_2S, $CuO \cdot CuSO_4$, and $CuSO_4$.

Depending on the processing conditions employed, the formation of any particular compound can be promoted to the point where essentially none of the others are present. The presence of alloying agents, especially iron, can also be employed to predictably alter the equilibrium relationship at a given temperature. This is precisely why copper makes such an attractive desulfurizing sorbent. The only clear competitor (economically and chemically) to copper is zinc, and its rather low melting point (419°C, versus 1083°C for copper) causes severe operating problems at elevated temperatures in a reducing atmosphere.

Another bonus associated with the use of copper-based sorbents is that a large body of information already exists concerning the chemistry of copper and sulfur, in the area of the extraction metallurgy of copper. Copper is present in the earth's crust mainly in the form of sulfide minerals such as chalcopyrite ($CuFeS_2$), barnite (Cu_5FeS_4), and chalcocite (Cu_2S) (Biswas and Davenport 1980). The desulfurization of coal gases by copper sorbents and (especially) the subsequent regeneration process involve many of the same

chemical reactions that take place in copper smelting. This fact will be of considerable help in selecting actual sorbents and in defining acceptable operating conditions.

Because many of the processes which manufacture coal product gases operate at elevated pressures as well as temperatures, it is felt necessary by this researcher to extend the data-gathering ability of this apparatus to pressures up to 100 psig. Pressures of this magnitude may have a favorable impact on reaction rates and may reduce the size of the apparatus needed for commercial coal gas desulfurization.

EXPERIMENTAL PROCEDURES

The experimental apparatus employs a thermogravimetric technique which has previously been used at this institution in studies of the high-temperature desulfurization of coal gases using calcium-based systems. Difficulties associated with handling hydrogen sulfide, carbonyl sulfide, and simulated coal gases at high temperatures have been solved, at least at the research level.

A transducing cell with microscale accessory is used to measure the weight change of a sorbent sample which is suspended from the microscale by a quartz basket at the end of a quartz fiber. The sample basket is centered within a reaction tube that is maintained at the desired temperature by a combustion tube furnace and associated temperature controller. The transducer-microscale is housed in a metal box located above the reaction tube. The two are separated by a transition tube. Inside the transition tube, baffles restrict the flow of reaction gases from entering the transducer-microscale housing, yet allow precise measurement of sorbent weight changes. A nitrogen flow rate of one-half liter per minute supplied to the housing maintains the microscale in a non-corrosive, stable environment.

During the desulfurization and regeneration reactions, the weight of the sorbent will change due to the conversion of copper oxide to copper sulfide, and vice versa. Measuring the change in weight of samples as a function of time allows a determination of the apparent rate constants of the particular reaction. The rate is a function of the amount of unreacted sample, the reaction temperature, and the feed gas composition.

In order to make sure the measured change in weight is due only to the reaction being studied, the rest of the system must be made as non-reactive as possible to side reactions. For this reason, a quartz basket and hanger are employed to suspend the sample, and the reactor is lined with quartz.

RESULTS AND DISCUSSION

The experimental apparatus employed in this research is illustrated in Figure 1. It is capable of reaching pressures as high as 100 psig, and maintaining them ± 1 psi. This is accomplished by feeding reactant gases directly from high-pressure cylinders, through regulators set at the desired pressure, to the TGA apparatus. A solenoid valve controlled by a pressure switch on the nitrogen purge line permits gases to exit the TGA reactor vessel. This is not the system originally designed to pressurize the TGA. That system employed a low-displacement compressor capable of reaching 200 psig. Unfortunately, the compressor failed every time a corrosive gas such as hydrogen sulfide or
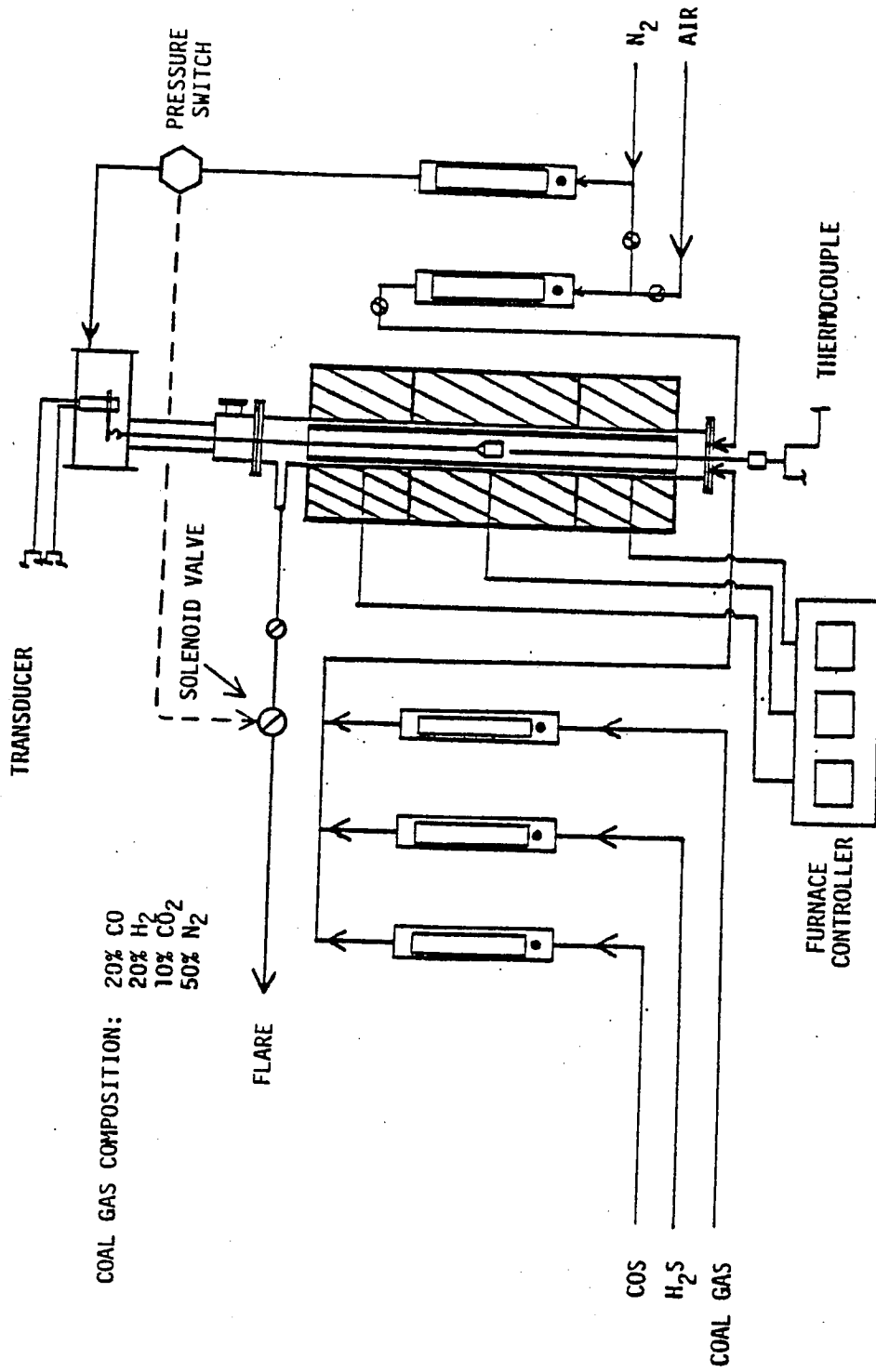
EXPERIMENTAL APPARATUS

PRESSURE SWITCH

THERMOCOUPLE

N_2

AIR

TRANSDUCER

SOLENOID VALVE

COAL GAS COMPOSITION: 20% CO
20% H_2
10% CO_2
50% N_2

FLARE

FURNACE CONTROLLER

COS

H_2S

COAL GAS

Figure 1. Experimental apparatus.

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hydrogen chloride was used. The mode of failure was scoring of the stainless steel cylinder walls and resultant loss of teflon piston rings. Coating the cylinder walls with gold by vapor deposition only extended the pump's life (at 100 psig) from approximately 90 minutes to 2 hours.

The modified, or direct-flow, pressurization system functions quite well for simulated coal gas (50% N_2, 10% CO_2, 20% CO, and 20% H_2) at pressures up to 100 psig and H_2S contaminations as high as 3%. It is not capable, however, of handling contaminants such as COS or HCl at pressures above 10 or 15 psig. At higher pressures, the precision gas regulators (MG Industries, North Branch, NJ; 300 series constructed of 316 stainless steel) either began controlling erratically, or failed entirely due to loss of diaphragms. For future work, a compressor designed specifically for this application is being constructed. The original pressure control system will then be refitted.

The data obtained with the present TGA is illustrated in Figures 2, 3, 4, and 5. Figures 2 and 3 illustrate typical weight-loss curves for reduction of pure CuO and $CuO:Fe_2O_3$ (Cu/Fe atomic ratio of 2/1). The reduction reaction is much more rapid than the sulfidation reaction; thus, a weight loss always occurs initially during a coal gas desulfurization experiment. In light of this fact, no H_2S is admitted into the TGA reactor until the reduction reaction is completed. The reason these curves are presented is precisely because they are typical of all reduction reactions observed with CuO and $CuO:Fe_2O_3$. Ultimate weight loss does not appear to depend on either temperature (800 or 900°C) or pressure (ambient or 100 psig) for pure CuO. Over 11 different experiments, the initial weight loss was 14.9% ± 0.1%. Stoichiometrically, this corresponds to a composition of 50 mol percent Cu_2O and 50 mol percent copper metal. This has been confirmed by x-ray diffraction.

A similar situation appears to exist for the $CuO:Fe_2O_3$ sorbent, although not enough data exist yet to generalize. The ultimate weight loss for this material averages 17%. The shape of this curve is also different. Two distinctly separate slopes exist. The first is almost certainly associated with the reduction of CuO, and the second with reduction of Fe_2O_3.

Figures 4 and 5 illustrate the effect of pressure on sulfidation of reduced CuO and reduced $CuO:Fe_2O_3$ (2/1 Cu/Fe). For both systems, increased pressure ultimately yields increased rates of sulfidation. However, for times less than 4 hours, the effect is not as pronounced, especially for the $CuO:Fe_2O_3$ sorbent.

The appearance of sulfided CuO is dramatically different than sulfided $CuO:Fe_2O_3$. The former sorbent completely loses its granular identity (+ 60 -35 mesh) upon sulfidation, forming large sulfide crystals. $CuO:Fe_2O_3$, on the other hand, retains its granular identity (-200 mesh), becoming only slightly sintered. Upon regeneration in 5% O_2/95% N_2 at 850°C, the $CuO:Fe_2O_3$ behaves almost identically to its initial TGA run. The CuO sorbent is much less reactive after similar regeneration conditions. Evidently pure CuO is not an easily regenerable sorbent for the desulfurization of coal gas.

The $CuO:Fe_2O_3$ sorbent was prepared following a procedure outlined by Marcilly et al. (1970). The method used was as follows:
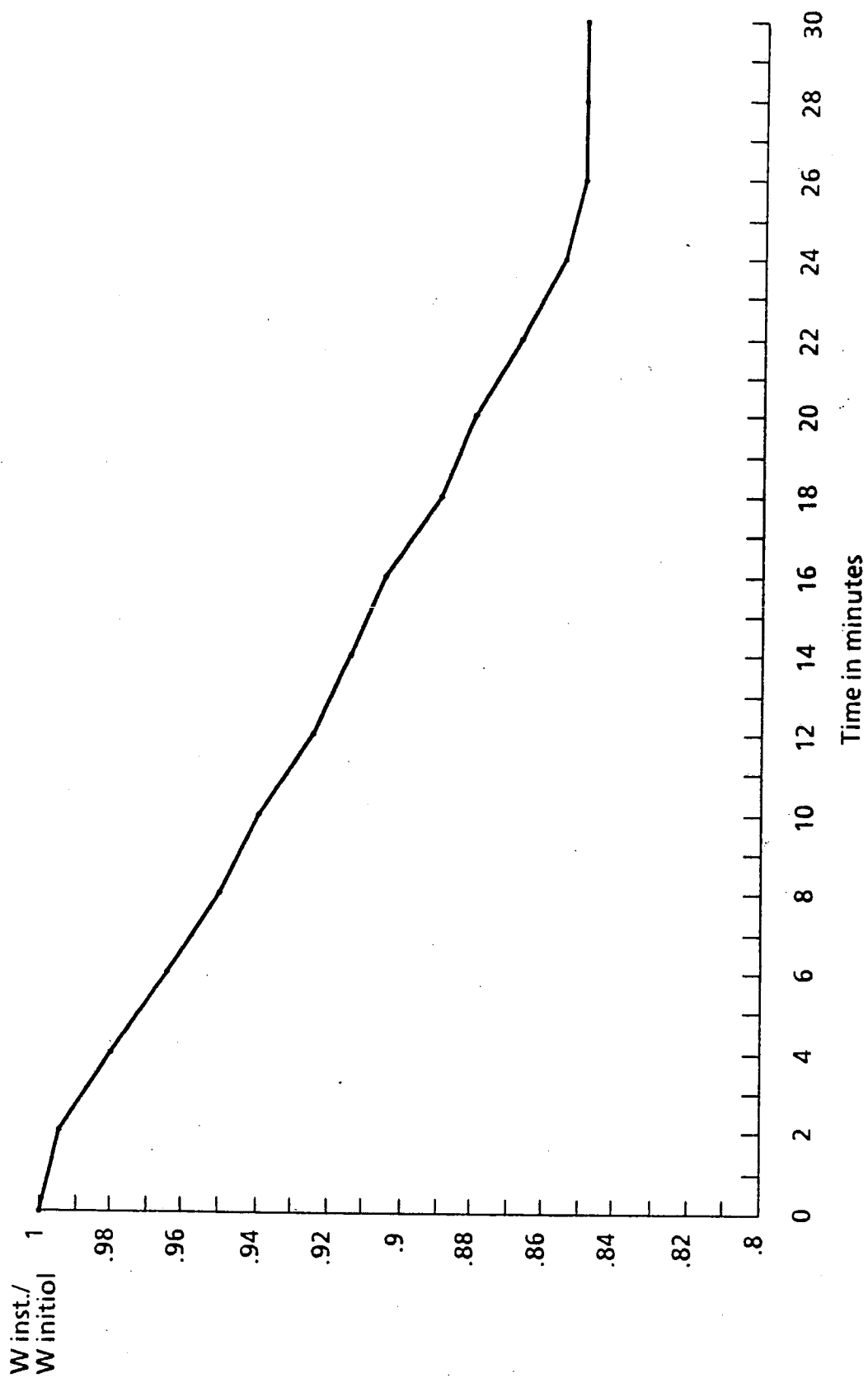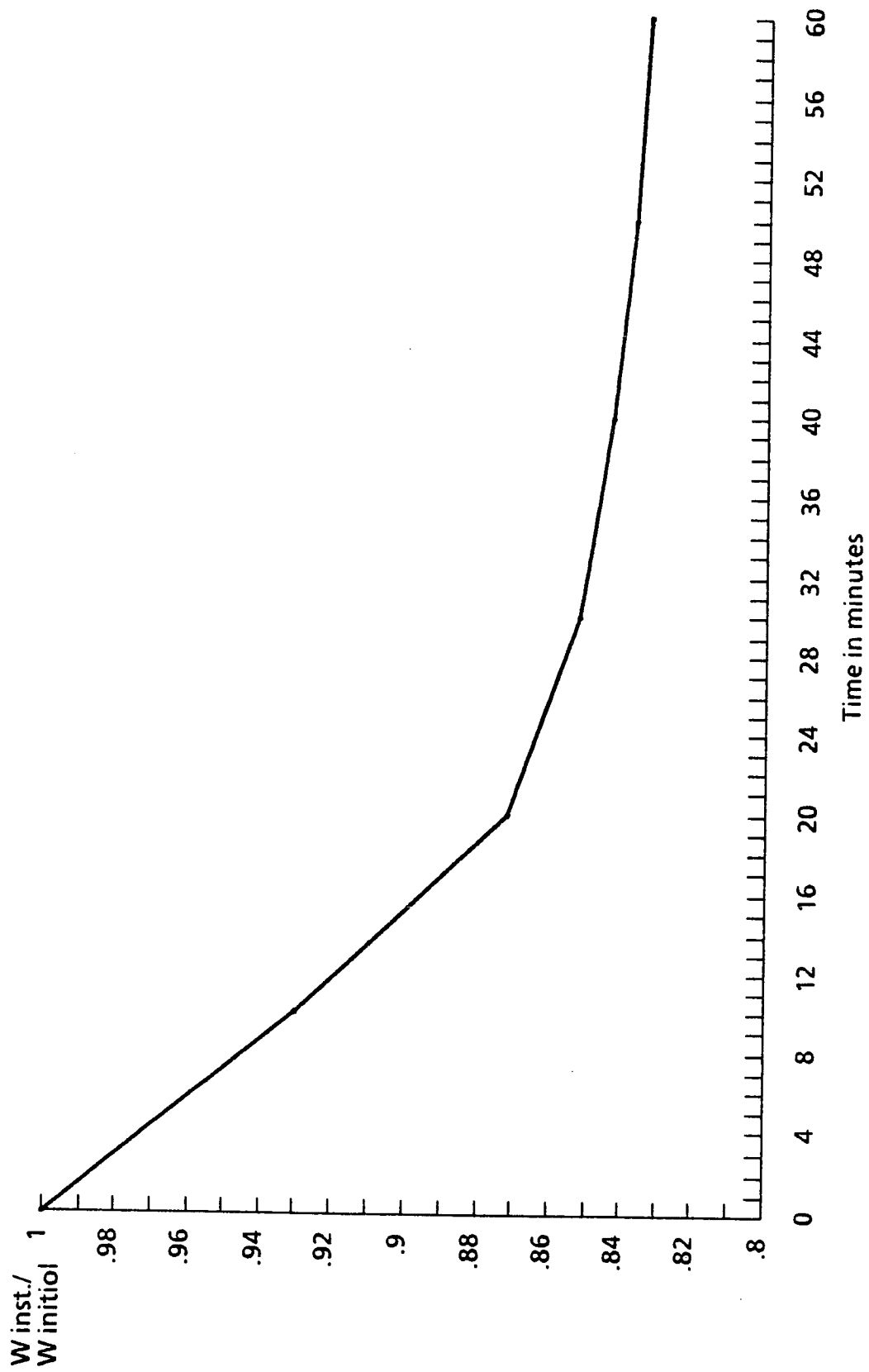
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Figure 2. Reduction of CuO, 900°C, 100 psig.

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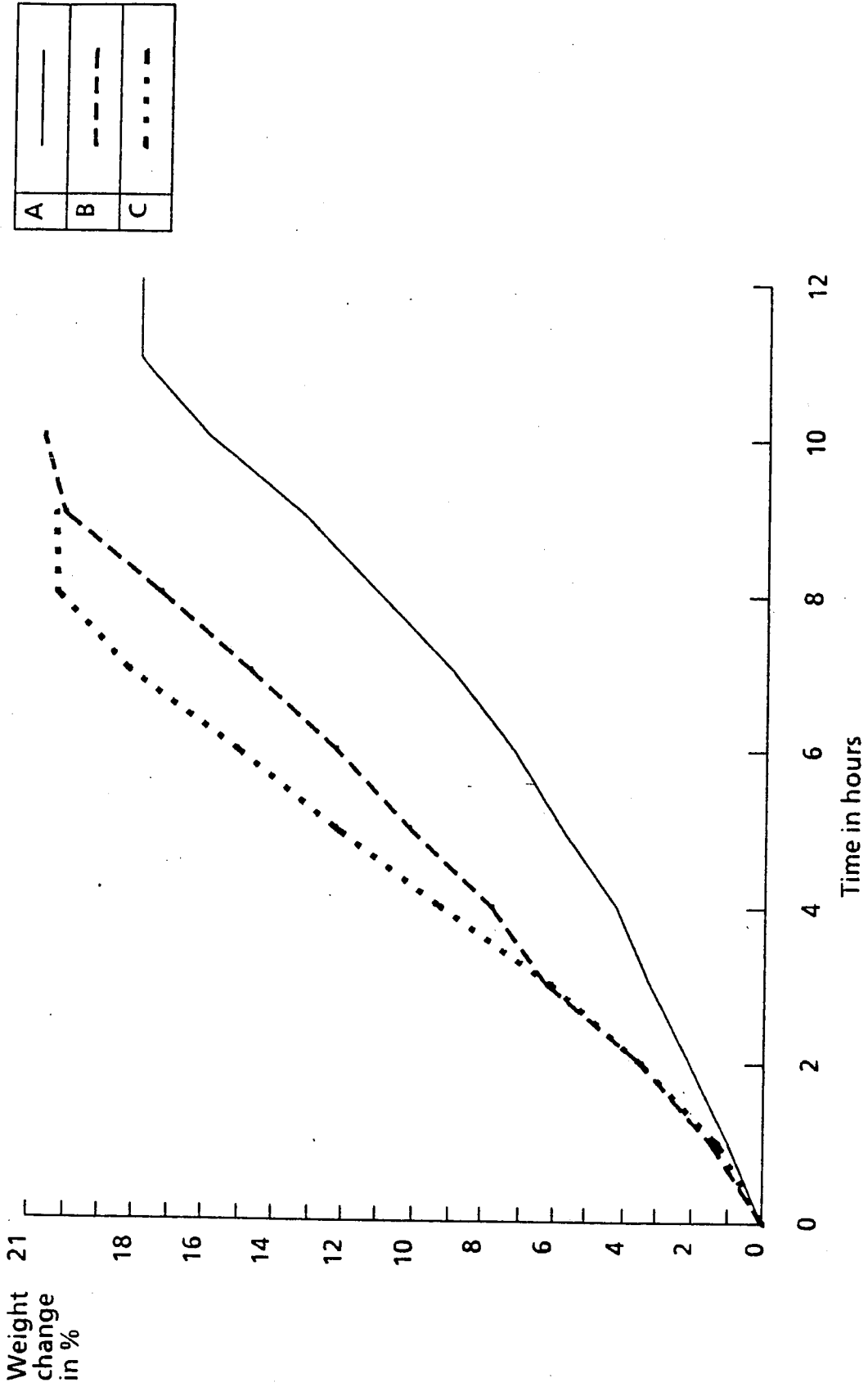Figure 3.   Reduction of CuO:Fe$_2$O$_3$, 800°C, 100 psig.

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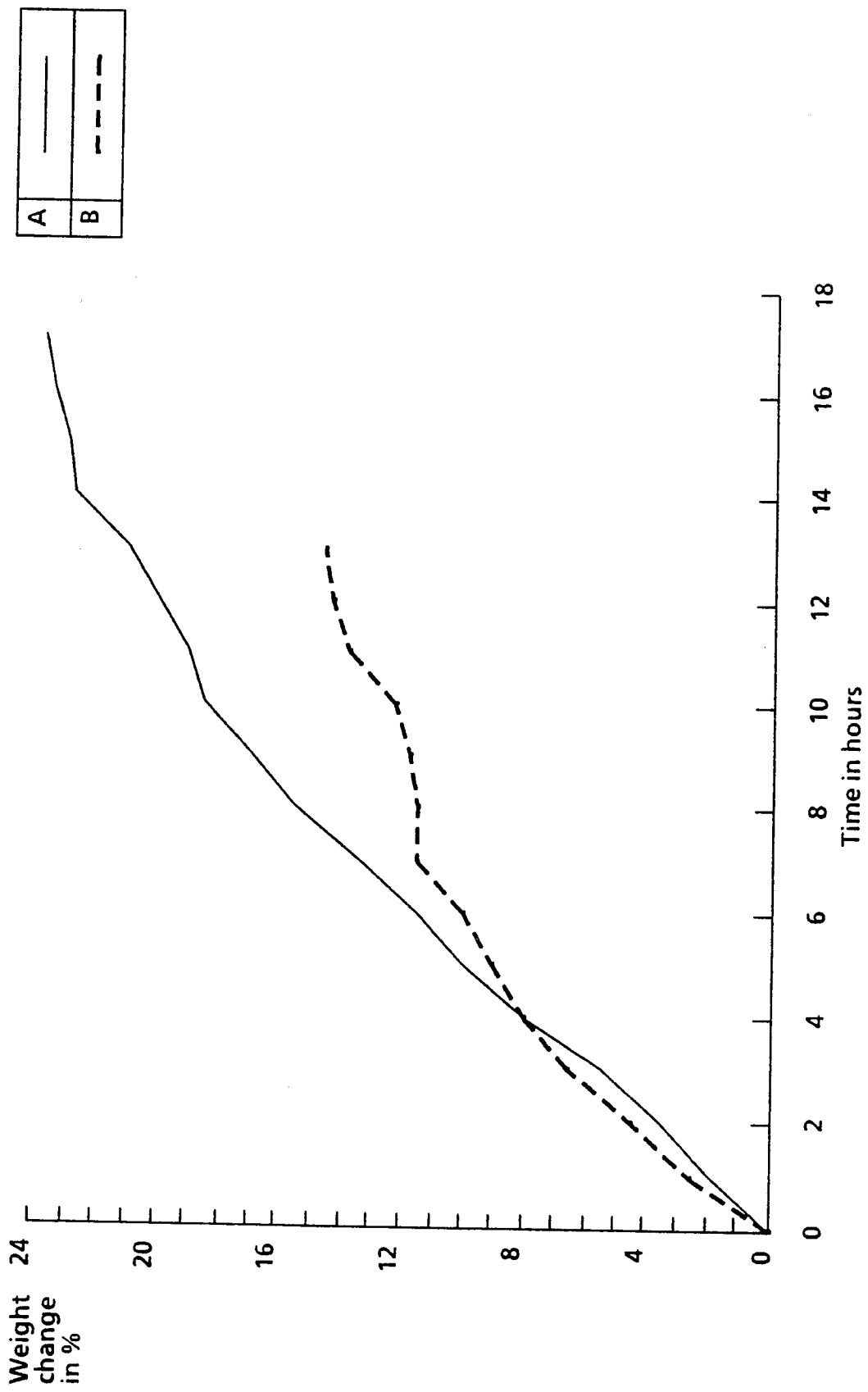
Figure 4. Sulfidation of CuO, 900°C and 1 % H_2S. A = 1 atm; B = 50 psig; C = 100 psig.

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Figure 5.   Sulfidation of CuO:Fe$_2$O$_3$ (2/1 Cu/Fe) 800°C abd 2% H$_2$S. A = 100 psig; B = 1 atm.

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1. A concentrated solution of the salts [~5N] was prepared. The salts used in this case were Cupric Nitrate and Ferric Nitrate in the ratio which varied from 2:1 to 4:1.

2. A 5M solution of polyfunctional acid, citric acid in this case, was also prepared. The volumetric ratios were selected such that for every gram ion of a metal ion there was one gram mole of the polyfunctional acid.

3. The mixture was dehydrated in a vacuum dryer at 70°C and 20 mm of Hg. This was continued until the solution became very viscous.

4. The temperature was raised to 90°C and the drying continued for 24 hours.

5. The dried "foamy" salt was then pyrolysed at 500°C for 3 hours.

It was noted that during drying the salt solution splashed out of the beaker and plugged the vacuum outlet port. The use of watchglass above the beaker proved futile. It was also noticed that during pyrolysis the dried salt foamed out of the beaker, causing a loss of metal sorbents. For one experiment an excess of citric acid (1.5 times the stoichiometric amount) was taken, and it yielded a hard mass instead of the usual highly dispersed mixed oxide.

CONCLUSIONS

Increased pressure has little effect on the reduction reactions that take place in CuO and CuO:Fe_2O_3 sorbents.

Increased pressure raises appreciably the rate of sulfidation of both CuO and CuO:Fe_2O_3.

Regeneration of CuO in 5% O_2/95% N_2 does not appear feasible; whereas CuO:Fe_2O_3 regenerates easily and undergoes similar reaction kinetics during a second sulfidation.

The pressure control system on the TGA should be refitted with a boost pump.

REFERENCES

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Marcilly, C., P. Courty, and B. Delmon. 1970. Preparation of highly dispersed mixed oxides and oxide solid solutions by pyrolysis of amorphous organic precursors. Journal of the American Ceramics Society 53(1):56.