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STUDIES ON AMMONIACAL LEACHING OF OXIDE ORES OF COPPER

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The results of a study on the aqueous ammoniacal leaching of an oxidized copper ore from the mines of M/s Hindustan Copper Limited at Malanjkhand, India are reported. Factors which influence copper recovery such as ammonia concentration, solid-liquid ratio, particle size and agitation have been studied at ambient temperature. Over 90% copper extraction could be achieved at 1.5 molar concentration of ammonia, 10% solids and at a stirring speed of 550 Min^{-1} . A kinetic study of the process indicated a mixed control reaction mechanism. The copper ammine solution obtained in the leaching step was subjected to precipitation by stripping of the ammonia at different temperatures and air flow rates. The kinetic treatment of the data obtained on precipitation process revealed that the decomposition reaction is controlled by chemical reaction control. The precipitated product analysed 75% Cu with a recovery of 80-85% copper.

INTRODUCTION

Metallic copper has long been known to dissolve in ammonia (1) and it was suggested (2) that the reaction could be utilized for recovering copper from ores. It has infact been used for tailings containing about 0.4% copper in its native state (3). A similar reaction has been used to recover cobalt (4) and Nickel (5) from certain ores after reduction to their elemental states. M/s Universal Minerals and Metals, Inc., also used this process on copper scrap (6) for copper recovery. Kinetic studies have been performed on copper dissolution with ammonium hydroxide solution and with very dilute solutions of cupric ammonium carbonate (7-11). Hewedi et al (12) has discussed in detail the role of ammonia-carbon dioxide-water system in non-ferrous extractive metallurgy. The thermo-

dynamic factors relevant to ammonia leaching reactions of copper sulphides have been discussed by Tozawa et al (13). Wilmshurst (14) described the development of ammonia leach process for a dolomitic copper ore to produce black cupric oxide.

The present investigation was undertaken to study the ammoniacal dissolution of oxide copper ore from Malanjkhand Copper Mine of M/s Hindustan Copper Limited, India. About 90% of this Malanjkhand ore occurs in a hydrothermally mineralized quartz reef that was emplaced in precambrian granites. The remaining 10% is in granite near the reef contact. In the primary ore zone, pyrite and chalcopyrite are the principal minerals. Chalcocite, covellite and bornite are placed in the zone of secondary enrichment and malachite, azurite, tenorite and

cuprite occur in the oxidized cap. The latter material, estimated about 5.5 million tonnes, is currently stockpiled (15). The present study deals with the utilization of this stockpiled material by adopting ammonia leach process. The product of this process is predominantly a tetrammine copper (II) which can be used in rayon making industry. Further, on evaporation this tetrammine copper (II) yields a very fine crystalline black cupric oxide, reclaiming 95% of ammonia.

MATERIALS AND METHODS

The copper oxide ore used in the present investigation was supplied by M/s Hindustan Copper Limited from their Malanjkhand Copper Project. The sample was crushed to 10 mesh and was further ground in a ball mill. The stock sample with the size distribution, shown in Table 1, was directly used in the leaching experiments. Table 2 shows the chemical analysis of the sample.

TABLE-1
Sieve analysis of the sample

S.No.	Particle size microns	Wt. %	% Copper
1	-210+150	10.66	1.14
2	-150+105	35.98	1.69
3	-105+75	17.21	1.62
4	-75+63	22.18	2.62
5	-63+53	10.8	2.98
6	-53	3.17	1.76

The microscopic examination of the material revealed that about 90% of the copper is present in the form of malachite and about 6% in the form of azurite and the rest as cuprite and tenorite. The analysis of the sample indicates that most of the

TABLE-2

Chemical analysis of the sample

Constituent	Percent
Copper	2.06
Iron	1.10
Silica	93.21
Calcium	0.10
Magnesium	0.076
Aluminium	Trace
Sulphur	0.09
L.O.I.	1.60
CO ₂	0.97

gangue is present in the form of silica.

The leaching experiments were carried out in a 500 ml twin necked glass reactor fitted with a mechanical stirrer, with provision to draw out samples during the course of the reaction. A small portion of the sample solution was periodically removed from the reactor at definite time intervals and analysed for copper using Atomic Absorption Spectrophotometer, Varian AA 575. After the experiment was over, the slurry was filtered to separate copper ammine solution and the residues were analysed to check up copper and ammonia contents.

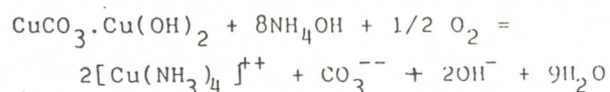
The decomposition studies were performed on the copper ammine stock solution obtained under optimum conditions of leaching. For this study a three necked glass reactor was used with provision for a thermometer, air inlet and outlet and a sampling device. The experiments were performed with a stock solution of 500 ml each time. Ammonia evolved at various time intervals was estimated by absorption in a definite volume of prestandardized hydrochloric acid and the excess HCl

was titrated against standard sodium hydroxide solution. Simultaneously, the amount of copper in solution was estimated by drawing samples and the amount of copper that was precipitated as black cupric oxide was calculated.

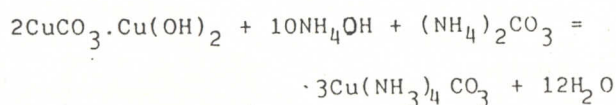
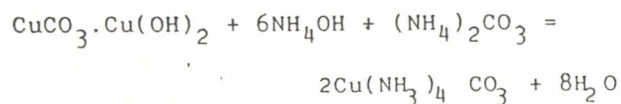
All the chemicals, viz. ammonia, hydrochloric acid, sodium hydroxide etc. used in the present investigation were of Analar grade reagents.

RESULTS AND DISCUSSION

The dissolution of copper in the form of $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ (Malachite) present in the ore in ammoniacal solutions can be represented by the following reactions.



Wendt (16) represented the dissolution of malachite and azurite in ammonia and ammonium carbonate solutions as follows :-



The rate of dissolution of copper from the oxide copper ore in ammonia solution was studied at different ammonia concentrations, stirring speeds, particle sizes and solid/liquid ratios at room temperature (30°C).

Fig. 1 represents the copper dissolution at three different ammonia concentrations. The experimental conditions were 10 g ore ($-75+63$ microns), pulp density 10% solids, stirring speed 550 min^{-1} and at 30°C . It is observed from the figure that the copper extrac-

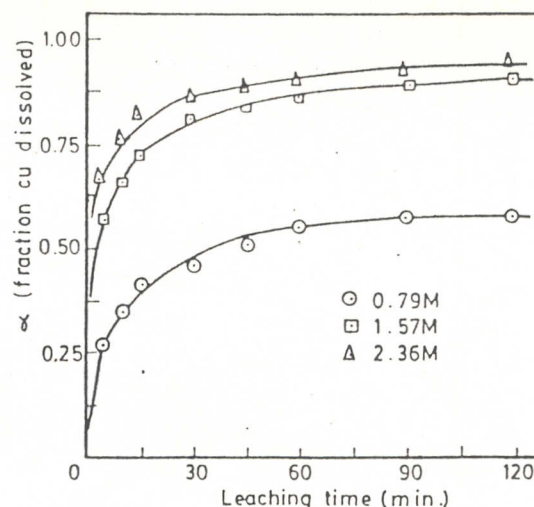


Fig. 1: Effect of ammonia concentration on Cu dissolution. Particle size: $-75+63$ microns. Solids: 10%. Stirring: 550 min^{-1}

tion increase appreciably with increase in ammonia concentration. The lower molar concentration to 1.57 M. Increase in the concentration of ammonia beyond 1.57 M caused only a slight improvement in copper recovery. The lower extraction of copper, observed at 0.79 M is explained by the presence of insufficient free ammonia to dissolve all copper as stable copper amines.

Further, from the results obtained above, it appears that for near complete dissolution of the copper from the ore, about 12 times of stoichiometric quantity (for tetrammine copper) of ammonia would be required. This is achieved with 1.57 M ammonia concentration with a copper recovery of over 90%.

The experimental data have been fitted into rate expressions for the chemical reaction model and the diffusion model. According to chemical reaction model, the plot of $1-(1-\alpha)^{1/3}$ against time should be linear, whereas according

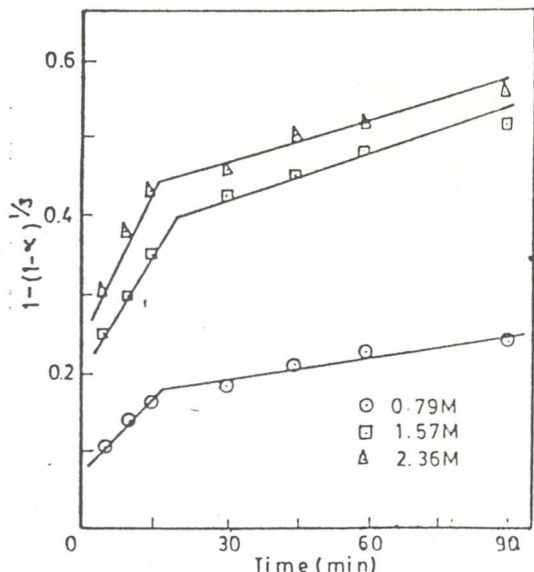


Fig. 2: $1-(1-x)^{1/3}$ Vs time plots at various ammonia concentrations.

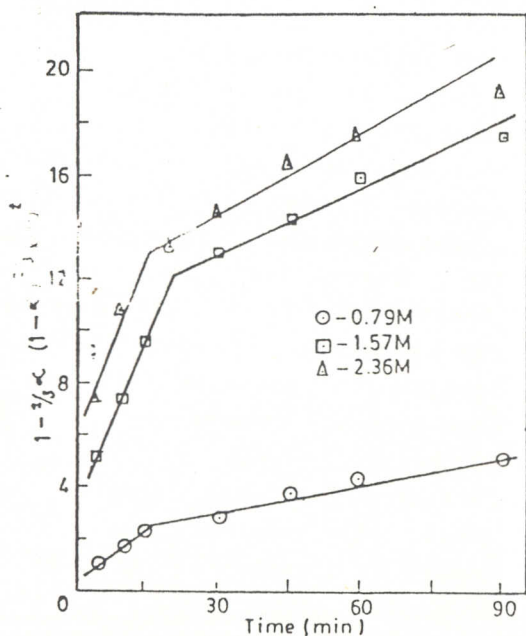


Fig. 3: $1-2/3\alpha - (1-x)^{2/3}$ Vs time plots at various ammonia concentrations.

to diffusion model, the plot of $1-2/3\alpha - (1-x)^{2/3}$ against time should be linear. Fig. 2 and 3 show the plots of $F(\alpha)$ versus time at different ammonia concentrations, indicating a mixed control reaction mechanism

in leaching of this oxide ore in ammoniacal solution.

The influence of stirring speed or agitation intensity, expressed in terms of rotating velocity, min^{-1} was studied in the range of $350-750 \text{ min}^{-1}$ with 60 minutes leaching time, 1.57 M ammonia concentration and 10% solids (-75+63 microns). It is well known that stirring is one of the most important factors affecting the leaching process. The results obtained, shown in Fig. 4, indicate that stirring speed has a pronounced effect on leaching rate. Copper dissolution is low at stirring speed of 350 min^{-1} which increased with an increase in stirring speed upto 550 min^{-1} and thereafter no significant change in copper extraction. Many researchers have proposed various models for leaching of particles for the purpose of quantitative description of leaching processes.

The influence of particle size on dissolution of copper is represented in fig.5, at 1.5 M ammonia concentra-

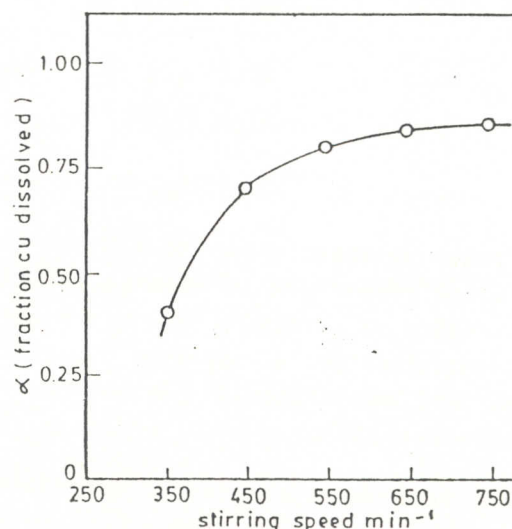


Fig. 4: Influence of stirring speed on leaching 1.5 M ammonia concentration, 10% solids. Particle size : -75+63 microns.

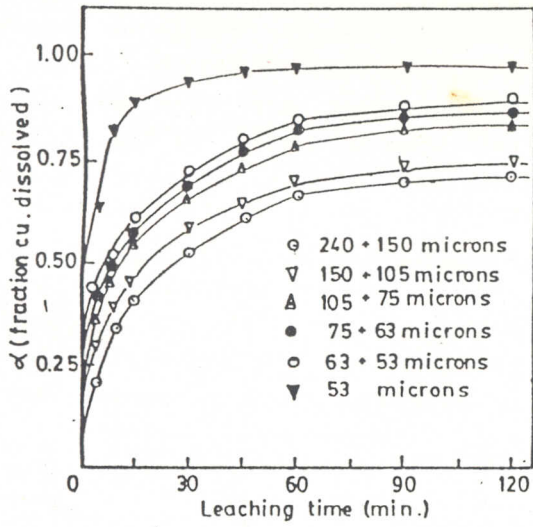


Fig. 5: Effect of particle size on leaching. Ammonia concentration 1.5 M. Stirring 550 min⁻¹

tion, 10% solids and at stirring of 550 min⁻¹. It could be seen from the fig. 5 that the rate of dissolution of copper increases with decrease in particle size. This is due to increased surface area solid per unit mass, in contact with the leaching agent, ammonia. The experimental data have been fitted into the rate expressions for the chemical reaction and diffusion

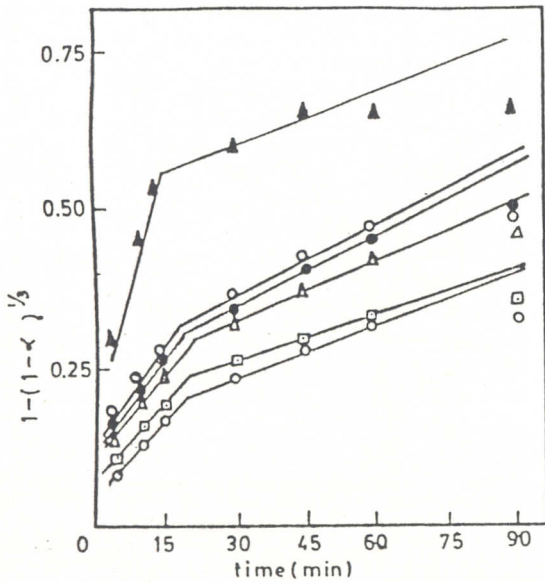


Fig. 6: $1-(1-x)^{1/3}$ Vs time at various particle sizes.

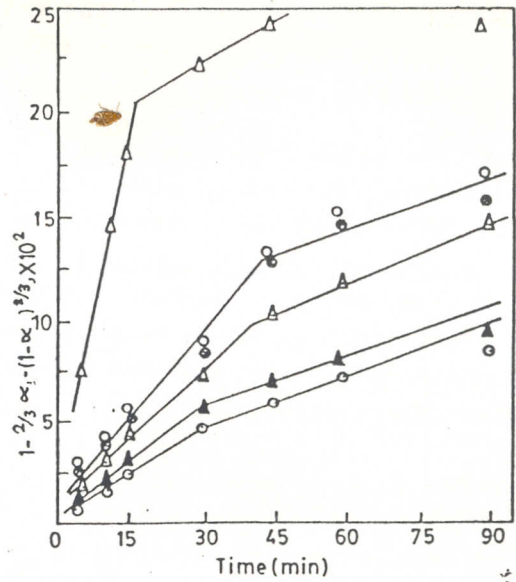


Fig. 7: $1-2/3 x - (1-x)^{2/3}$ Vs time at various particle sizes.

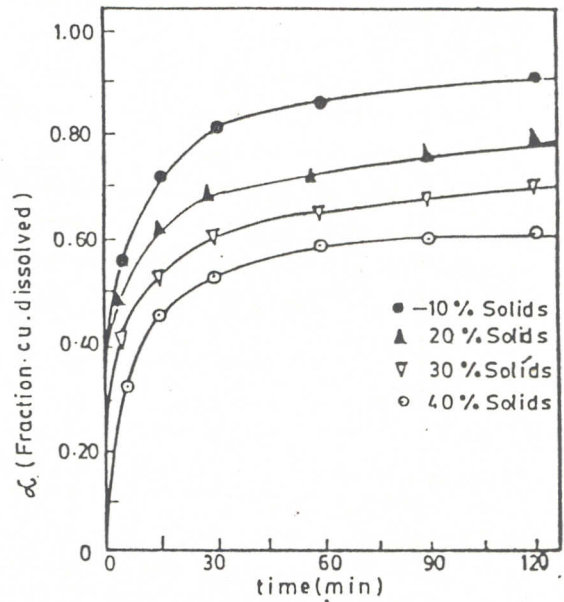


Fig. 8: Effect of solid/liquid ratio on copper dissolution. Particle size: 75 + 63 microns. Stirring 550 min.

models as already indicated. Fig. 6 and 7 show the plots of $F(\alpha)$ against time for various particle sizes, again indicate a mixed control reaction mechanism.

Fig. 8 shows the effect of solid/liquid ratio (% solids) on the rate of disso-

lution of copper from the ore at 1.5 M ammonia concentration. From the results it could be seen that the dissolution decreases with increase in pulp density.

From the above leaching data, it was found that the dissolution of copper from Malanjkhand oxide ore in the presence of atmospheric oxygen and at room temperature, depends mainly on the concentration of ammonia, and other parameters did not have any pronounced effect on the dissolution rate of copper.

Further studies were made on the precipitation of cupric oxide from leached copper ammine solutions. In the decomposition studies, the copper ammine solution from leaching step was stripped off its ammonia by heating in the presence of air as carrier. The evolved ammonia and extent of copper precipitation were measured at various temperatures and air flow rates. The mother liquor used in these studies contained 3 g/l of copper and about 3.2 g/l of ammonia. The chemical analysis of mother liquor is shown in Table 3.

TABLE 3
Chemical analysis of mother liquor used in decomposition studies

Constituent	Concentration
Copper	3.0341 g/l
Ammonia	3.2000 g/l
Zinc	14.2 ppm
Magnesium	3.5 ,,
Iron	1.98 ,,
Tin	0.89 ,,
Lead	0.65 ,,
Bismuth	0.70 ,,
Nickel	0.12 ,,

500 ml of ammine solution was taken each time and investigated for the rate of ammonia evolution and copper precipitation as black cupric oxide at different air flow rates keeping the temperature at 90°C (near boiling condition of the solution). Figs.9 & 10 show the effect of air flow rates on the rate of evolution of ammonia and of copper precipitation from the mother liquor. It is observed that the air flow rate had negligible effect on both the rates of ammonia evolution

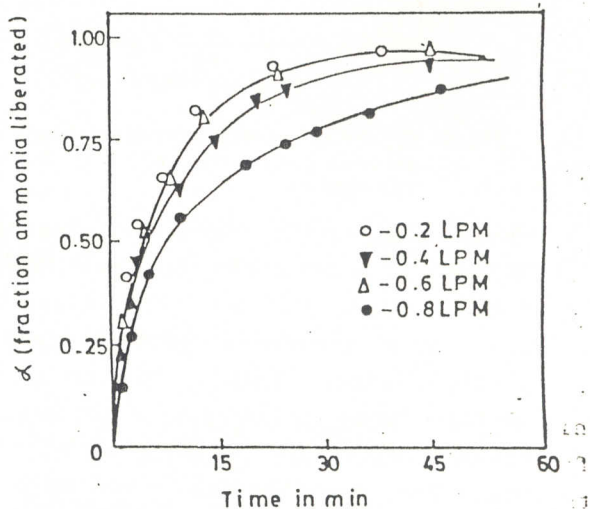


Fig. 9: Effect of air flow rate on ammonia liberation at 90°C.

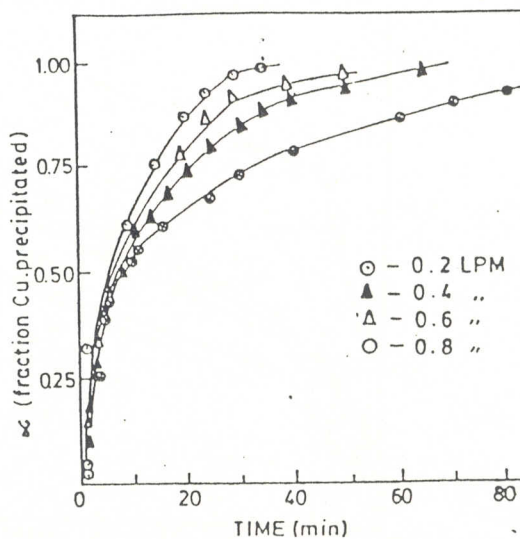


Fig. 10: Effect of air flow rate on copper precipitation at 90°C.

and copper precipitation. Further experiments were carried out at an air flow rate of 0.4 lpm.

The influence of temperature on the decomposition of copper ammine solution is shown in Figs. 11 and 12. Fig. 11 reveals that the rate of ammonia evolution increases with increase in temperature. At 90°C, more than 90% ammonia evolution was observed within 20 minutes, whilst at 60°C it took more than 140 minutes to evolve the same amount of ammonia. Further, it was generally observed that the rate of ammonia evolution was rapid at the initial stages of the decomposition process and it gradually decreased in the temperature range studied and this is due to the free ammonia present in the solution.

Fig. 12 shows the rate of copper precipitation as its black oxide at different temperatures at 0.4 lpm of air flow. The decomposition of copper

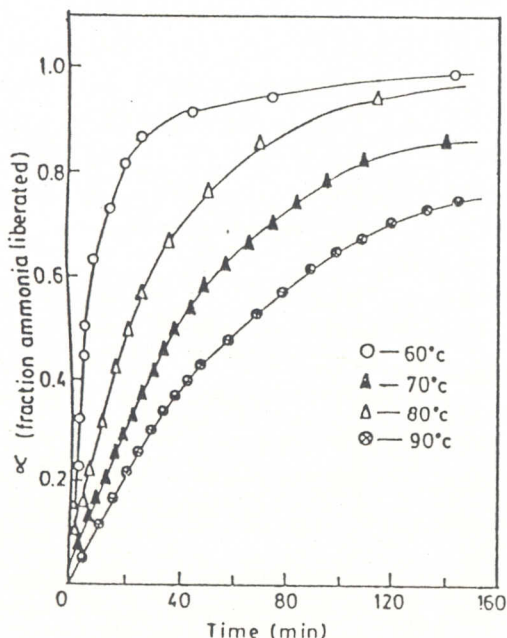


Fig. 11: Fraction of ammonia liberated vs time at different temperatures.

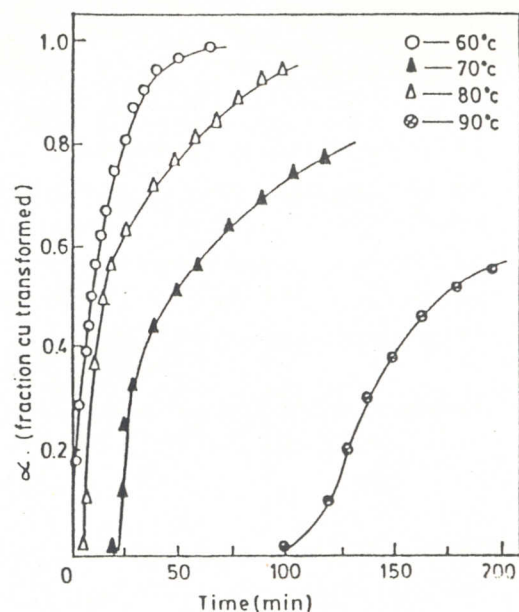


Fig. 12: Fraction of copper precipitated vs time at different temperatures.

amine solution started at 90°C with the formation of cupric oxide.

The rate of precipitation was fast, similar to ammonia evolution. More than 90% copper was precipitated as cupric oxide within 30 minutes of the decomposition process. At lower temperatures, the rate of copper precipitation was slow, i.e. the rate decreased with a decrease in temperature. Further as the temperature decreased, the time taken for the initiation of precipitation increased as - for example at 80°C the copper precipitation started after 7 minutes. At this instant the ammonia remaining in solution was just sufficient to hold the copper as $\text{Cu}(\text{NH}_3)_3^{++}$ complex. Similarly at 60°C the induction period for copper precipitation was about 115 minutes. At this point the ammonia remaining in solution was slightly above the quantity, sufficient to retain copper as $\text{Cu}(\text{NH}_3)_3^{++}$ complex. However, it is difficult to identify the species quan-

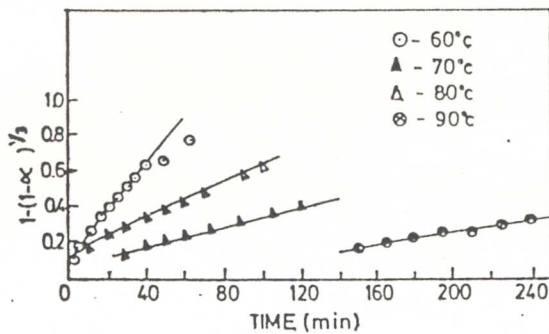


Fig. 13: $1-(1-x)^{1/3}$ vs time for copper precipitation.

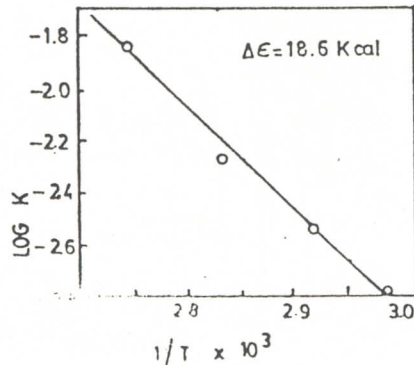


Fig. 14: $\log K$ vs $1/T$ plot for copper precipitation.

titatively in $\text{Cu-NH}_3\text{-H}_2\text{O}$ system at these temperatures, and further research is necessary for better understanding of this phenomenon.

The decomposition data were analysed in terms of (fraction transformed) to understand the kinetics of the process. Fig. 13 shows the plot of $1-(1-x)^{1/3}$ vs. time for copper precipitation at different temperatures. From the figure it is seen that $F(x)$ vs time plots are linear at all temperatures studied, indicating a chemical reaction control. The corresponding arrhenius plot, i.e. $\log K$ (slope values from figure 13) vs $1/T$ is shown in figure 14. Figs. 15 and 16 show the similar plots for ammonia evolution confirming the chemical control mecha-

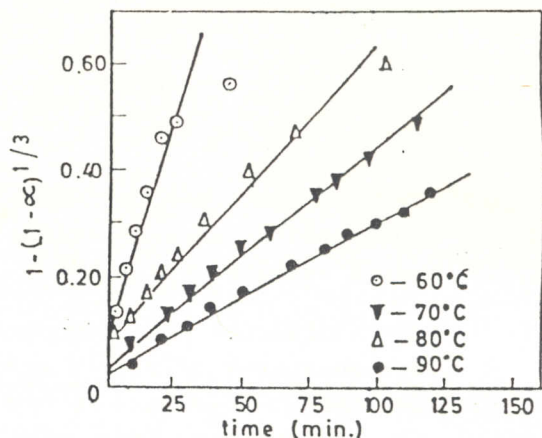


Fig. 15: $1-(1-x)^{1/3}$ vs time plot for ammonia liberation.

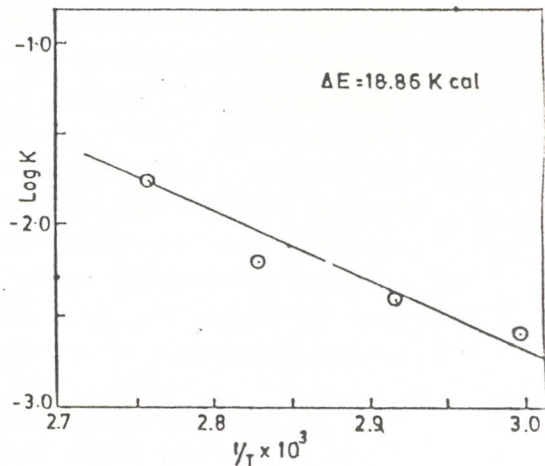


Fig. 16: $\log K$ vs $1/T$ plot for ammonia liberation.

nism of the decomposition process of copper ammine solution. The activation energy of 18.6 Kcal/mol has been obtained for the decomposition of copper ammine solution supporting the chemical control reaction mode.

The final product, i.e. black cuprous oxide obtained from the decomposition step is a very fine crystalline cuprous oxide powder and analysed 75% copper. The overall recovery of copper was about 80-85%. The recovery of ammonia was always above 95%.

CONCLUSIONS

Malanjkhand Copper oxide ore is suitable for the selective leaching of its copper by ammonia leaching-precipitation process. The process yields fine copper oxide powder of 93-95% purity, and the stripped ammonia can be recycled in the process. The kinetic studies reveal that the leaching step has a mixed reaction control mechanism, whereas the precipitation step follows a chemical reaction control mechanism with an activation energy of 18.6 Kcal/mol.

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