CUPRIC CHLORIDE LEACHING OF SULPHIDIC COPPER ORES

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ABSTRACT

Cupric chloride leaching was carried out for the treatment of sulphidic massive copper rich ore sample taken from Küre-Turkey. Effects of cupric chloride concentration, leaching time, solid/liquid ratio, acid concentration, temperature and NaCl concentration on metal leaching recoveries were investigated. The optimum leaching conditions were found as Cu^{2+} concentration of 20 g/L, leaching time of 2 hours, HCl concentration of 20 g/L, temperature of 60°C, solid/liquid ratio of 1/10 and NaCl concentration of 200 g/L. At these conditions, 41% of Cu, 26% of Co, 89% of Ni, 98% of Pb, 76% of Zn and 69% of Ag were extracted.

INTRODUCTION

Precious metals, such as gold and silver, as well as cobalt and nickel are mostly associated with sulphidic minerals. Because of fine distribution of these minerals in the ores, they cannot be separated by physical separation techniques. There are five different types of sulfidic copper ore deposits located in Küre, Türkiye. These ores contain considerable amount of precious metals such as Au, Ag, Co, Ni and some rare metals in addition to the major metal (Cu, Pb, Zn) contents. The main copper mineral in all formations is chalcopyrite. However, there are considerable bornite occurrences in some zones. Since chalcopyrite is generally finely distributed in pyrite, a satisfactory liberation requires ultra fine grinding. In the previous studies, several separation techniques were used for the treatment of these complex ores [Project, 1994]. Researches were conducted on recovering the metallic values by the application of a process including sulphatizing roasting, acidic leaching and cyanidation. SO_2 gases produced during roasting are harmful to the environment. Since pyrometallurgical processes also require high temperature, they are more costly than hydrometallurgical processes. Therefore, from the economical and environmental viewpoints, hydrometallurgical processes are suitable for the treatment of complex ores. Several leaching agents such as ferric chloride, ferric sulphate, cupric chloride, sodium sulphate have been used for recovering these metals from their ores or concentrates. For this purpose, cupric chloride leaching was used in this study.

Cupric Chloride Leaching

Cupric chloride leaching of copper concentrates was first studied by Hoepfner in 1880 [Cases, 1980, Demarthe et al., 1978]. Cupric chloride has been used as a leachant for suphide concentrates and especially cupric chloride leaching of chalcopyrite, galena and sphalerite has been extensively studied [Correia et al., 1992, Demarthe et al., 1980, Wong et al., 1980].

Copper, lead and zinc are preferentially leached over pyrite by controlling Cu^{++}/Cu^{+} redox potential [Cases, 1980, Demarthe et al., 1978] and sulphides can be oxidized to elementary sulphur form. Leaching stage has been performed on either ore or Cu-Zn-Pb bulk concentrates with $CuCl_2$ solutions containing 200-300 g/L NaCl at 50-100°C. The leaching of ZnS, PbS, Ag_2S, $CuFeS_2$ are realised according to following reactions:

$$ZnS+2CuCl_2 \rightarrow ZnCl_2+2CuCl+S^0\downarrow \quad (1)$$

$$PbS+2CuCl_2 \rightarrow PbCl_2+2CuCl+ S^0\downarrow \quad (2)$$

$$Ag_2S+2CuCl_2 \rightarrow 2AgCl+2CuCl+ S^0\downarrow \quad (3)$$

$$CuFeS_2+3CuCl_2 \rightarrow 4CuCl + FeCl_2+ S^0\downarrow \quad (4)$$

Silver and copper are extracted with lower recoveries; lead and zinc are extracted with higher recoveries in the Minemet Recherche Cupric Chloride Leach Process.

Extraction procedures of Pb, Ag, Cu and Zn from leach solutions are as follows: Lead is extracted by reducing with hydrogen or cementing with iron or zinc. Silver is also recovered from solutions by cementing with iron or zinc. Copper extraction is made by solvent extraction with LIX 65N at suitable pH values.

Iron in the solution is removed by precipitation as a goethite form according to following reaction:

$$4CuCl+2FeCl_2+1/2O_2+H_2O \rightarrow 2FeOOH +CuCl_2 \quad (5)$$

Zinc extraction is performed by solvent extraction using D2ehpa as follows:

$$ZnCl_2+2RH \rightarrow R_2Zn+2HCl \quad (6)$$

$ZnSO_4$ is obtained from pregnant organic with sulphuric acid and then zinc is recovered by electrolysis [Demarthe et al., 1978].

EXPERIMENTAL

Sulphidic massive rich copper ore used in the cupric chloride leaching tests were obtained from Küre-Turkey. According to mineralogical examinations it was found that sulphidic massive rich copper ore mainly contains pyrite, chalcopyrite and bornite and also secondary minerals such as sphalerite, native gold, corallite, galena, tennantite, idaite, covellite, digenite, quartz and calcite [Project, 1994]. Chemical composition of this ore sample is given in Table I.

Table I. The chemical composition of ore sample.

ELEMENT	*CONTENT (%)*
Cu	7.95
Fe	23.24
Pb	2.13
Zn	0.341
Co	0.087
Ni	0.039
S	43.22
SiO_2	4.48
Ag (g/t)	17.0
Au (g/t)	0.9

Experiments were carried out using a standard glassware and a heater-stirrer. In the graphs, all points represent a single experiment meaning no sample solution was taken during the leaching; all experiments were performed separately. After each experiment, pulp was filtered and all metal analyses were made from leach cake using the atomic absorption spectrometer and X-Ray Fluorescence. No gold analysis was made, since it can not be leached by cupric chloride.

RESULT AND DISCUSSION

Effects of cupric chloride concentration, leaching time, solid/liquid ratio, acid concentration, temperature and NaCl concentration on metal leaching recoveries were investigated. These parameters and their values are listed in Table II.

Table II. Investigated parameters of leaching experiments.

Parameters	*Values*
Leaching Time	1, 2, 4, 6, 8 hours
$[Cu^{2+}]$ Concentration	10, 20, 30 g/L
HCl Concentration	10, 20, 30 g/L
Temperature	60, 80, 90°C
Solid/Liquid Ratio	1/3, 1/5, 1/10
NaCl Concentration	0, 100, 200 g/L

Effect of Leaching Time

In this part of the study, 10 g/L of cupric ion concentration, 10 g/L of HCl concentration, 60°C of temperature and 1/10 of solid/liquid ratio were kept constant and leaching time varied from 1 to 8 hours. Results are shown in Figure 1.

As it is seen from Figure 1, Pb, Ni and Ag leaching recoveries reached to the maximum at the end of one-hour leaching and levelled off after that point. At the end of one hour leaching, 98% Pb, 92.6% Ni, 15% Co and 34% Ag leaching recoveries were obtained. In the previous studies, it was found that copper started to precipitate as CuCl after 4 hours [Canbazoğlu, 1985]. Therefore, 2 hours leaching time was chosen as an optimum in this experimental study.

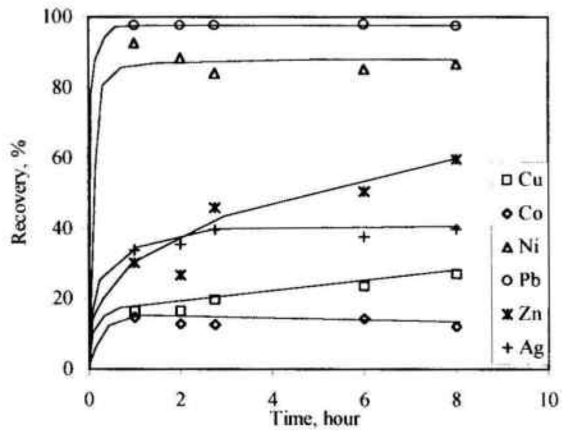

Figure 1. Effect of Leaching Time on Metal Leaching Recoveries.

Effect of Cupric Ion Concentration

Experimental conditions were: leaching time of 2 hours, 10 g/L of HCl concentration, 60°C of temperature and 1/10 of solid/liquid ratio and cupric ion concentration varied from 10 to 30 g/L. Results are shown in Figure 2.

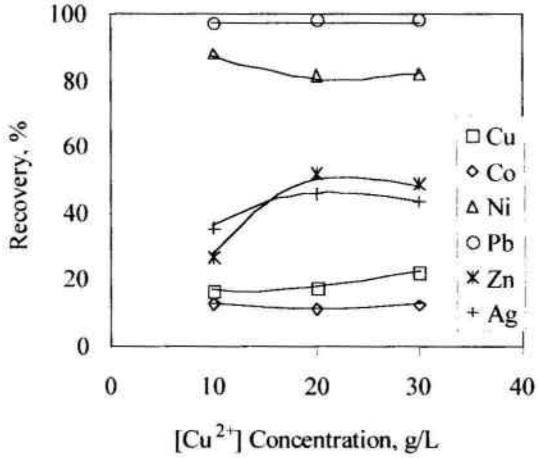

Figure 2. Effect of Cupric Ion Concentration on Metal Leaching Recoveries.

Ag and Zn leaching recoveries increased with increasing cupric ion concentration as seen from Figure 2. Increasing of cupric ion concentration did not affect Pb and Co leaching recoveries. Copper dissolution increased slowly with increasing Cu^{2+} concentration while Zn and Ag dissolution efficiencies increased remarkably. Increasing Cu^{2+} concentration had an increasing effect on the oxidation potential resulting in higher leaching rates. However, leaching rate is controlled by the diffusion of oxidizing ion in the phase layer formed between sulphur and Cu-Fe-S during leaching. Thus, dissolution will continue until diffusion layer thickness reaches to the level that prevents oxidizing ions diffusion. Therefore, parabolic character was observed on most of the dissolution curves [Scott and Dyson, 1976, Canbazoğlu, 1985]. According to the results presented here, 20 g/L of cupric ion concentration was chosen for the following tests.

Effect of HCl Concentration

During the tests, leaching time of 2 hours, 20 g/L of cupric ion concentration, 60°C of temperature and 1/10 of solid/liquid ratio were kept constant and HCl concentration changed between 10 and 30 g/L. Results are illustrated in Figure 3.

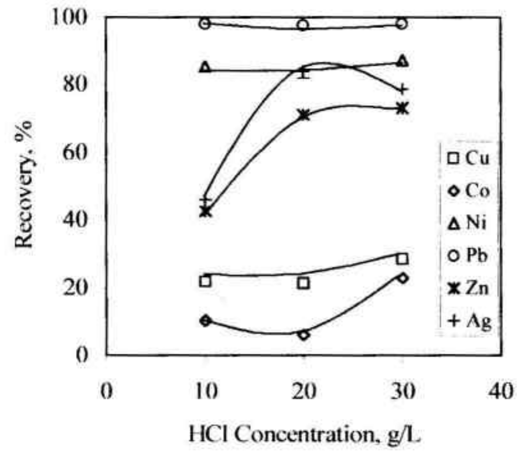

Figure 3. Effect of HCl Concentration on Metal Leaching Recoveries.

As shown in Figure 3, Pb and Ni leaching recoveries were not affected much by increasing acid concentration. Small changes on Cu and Co leaching recoveries were observed with increasing HCl concentration while there was a remarkable increase on Zn and Ag leaching recoveries. When all of these cases are considered, it was found that HCl concentration did not affect most of the metal leaching recoveries and 10 g/L of HCl concentration was chosen for the following tests. During the cupric chloride leaching process, hydrogen ions react with sphalerite and galena and then re-evaluated according to the following reaction. Therefore, hydrogen ion consumption is not in question [Canbazoğlu, 1985].

$$ZnS + 2H^{+} \rightarrow Zn^{++} + H_2S\uparrow \quad (7)$$

$$H_2S + 2Cu^{++} \rightarrow 2Cu^{+} + 2H^{+} + S^{0}\downarrow \quad (8)$$

$$ZnS + 2Cu^{++} \rightarrow Zn^{++} + 2Cu^{+} + S^{0}\downarrow \quad (9)$$

Effect of Temperature

Experiments were carried out at the following conditions:

Leaching Time	: 1,2, 4, 6 hours
[Cu^{2+}] Concentration	: 20 g/L
HCl Concentration	: 10 g/L
Solid/Liquid Ratio	: 1/10
Temperature	: 60, 80, 90°C

Results of the Cu, Co, Ni, Pb, Zn, Ag leaching recoveries versus time curves depending on temperature are illustrated in Figure 4, 5, 6, 7, 8 and 9, respectively.

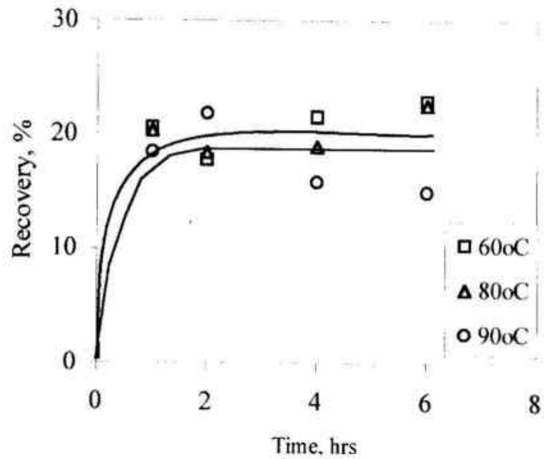

Figure 4. Effect of Temperature on Cu Leaching Recovery.

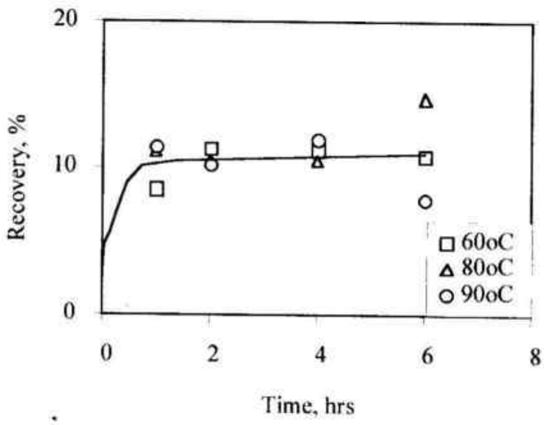

Figure 5. Effect of Temperature on Co Leaching Recovery.

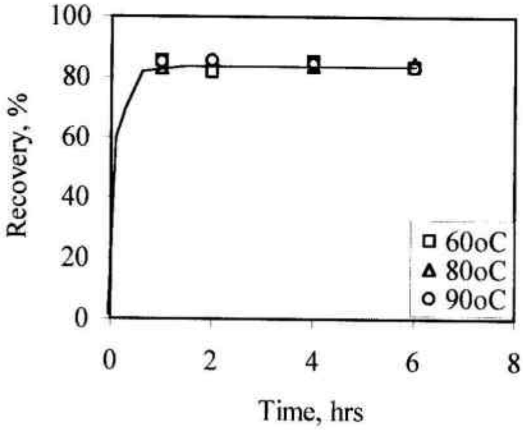

Figure 6. Effect of Temperature on Ni Leaching Recovery.

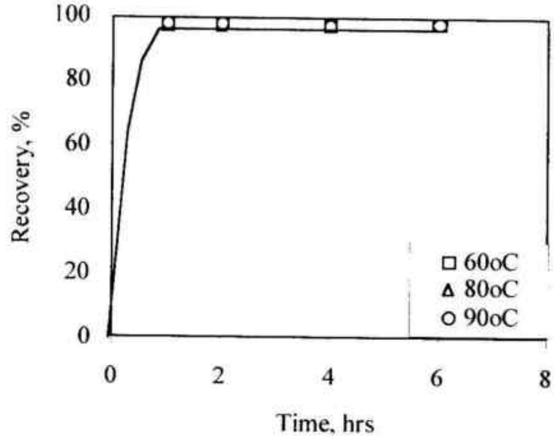

Figure 7. Effect of Temperature on Pb Leaching Recovery.

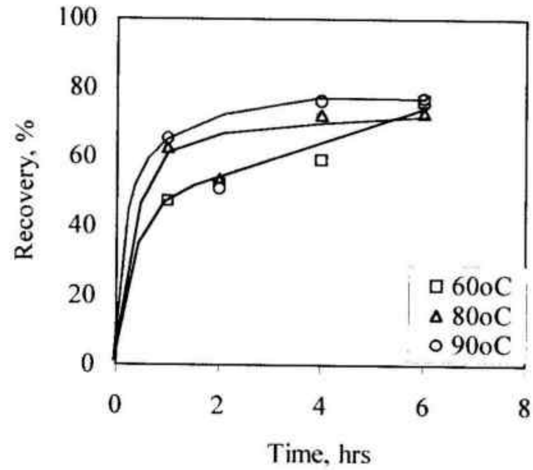

Figure 8. Effect of Temperature on Zn Leaching Recovery.

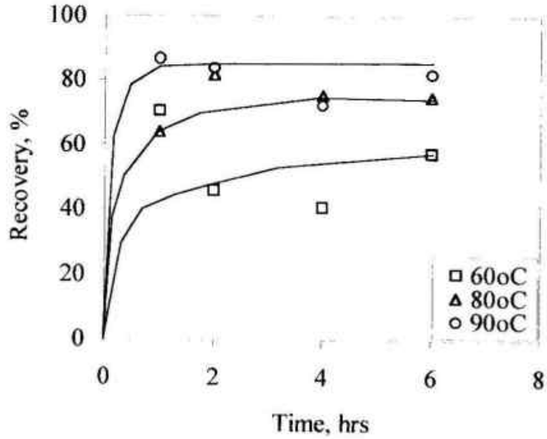

Figure 9. Effect of Temperature on Ag Leaching Recovery.

Figure 4, 5, 6, 7 and 8 show that temperature has no significant effect on Co, Ni, Pb, and Zn leaching recoveries. In terms of Cu leaching recovery as shown Figure 4, results were scattered and in longer runs, 60°C gave the best results. On the other hand, the increase in temperature has a positive effect on Ag recovery, as seen in Figure 9 Ag leaching recovery has reached up to 86.77% under the conditions of 1 hour leaching time and 90°C temperature.

Effect of Solid/Liquid Ratio

In order to examine the solid/liquid ratio on metal leaching recoveries, experiments were performed under the following conditions.

Leaching Time	: 2 hours
$[Cu^{2+}]$ Concentration	: 20 g/L
HCl Concentration	: 10 g/L
Temperature	: 60°C

Solid/liquid ratios were chosen as 1/10, 1/5, 1/3. Results are shown in Figure 10.

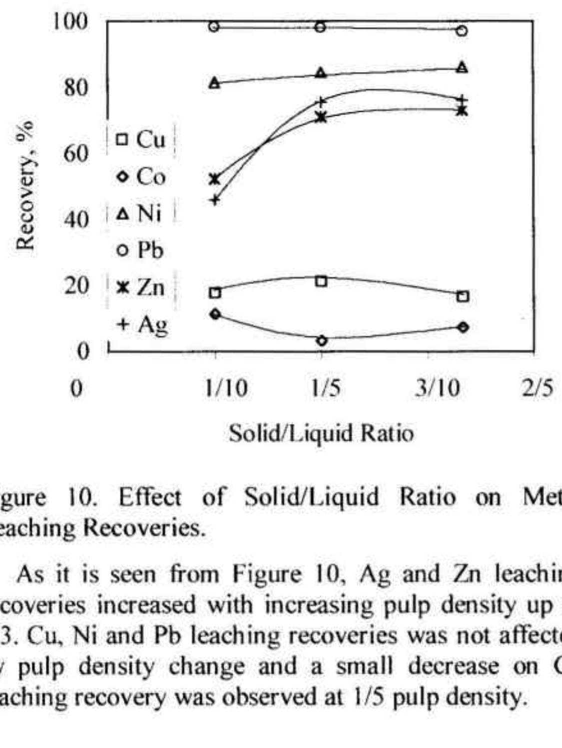

Figure 10. Effect of Solid/Liquid Ratio on Metal Leaching Recoveries.

As it is seen from Figure 10, Ag and Zn leaching recoveries increased with increasing pulp density up to 1/3. Cu, Ni and Pb leaching recoveries was not affected by pulp density change and a small decrease on Co leaching recovery was observed at 1/5 pulp density.

Effect of NaCl Ions

In order to examine the effect of chloride ions, NaCl was added during leaching and the experimental conditions were:

Leaching Time	: 2 hours
$[Cu^{2+}]$ Concentration	: 20 g/L
HCl Concentration	: 10 g/L
Temperature	: 60°C
Solid/liquid Ratio	: 1/10
NaCl Concentration	: 0-200 g/L

Metal leaching recovery versus NaCl concentration curves are shown in Figure 11. It was observed that the NaCl addition catalysed the reactions and increased all metal leaching recoveries, except Pb.

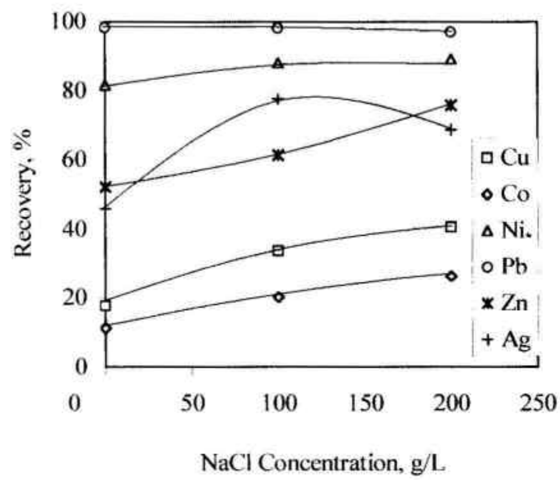

Figure 11. The Effect of NaCl Concentration to Metal Recovery.

200 g/L NaCl addition increased Cu recovery from 17.73% to 40.6%, which is the highest value obtained, Co leaching recovery increased from 10-12% up to 26% while 100 g/L NaCl addition increased Ag recovery from 46% to 78% but 200 g/L NaCl had negative effect on Ag recovery. Precipitation of Ag in AgCl form could be the reason for the decrease of Ag leaching recovery at high NaCl concentrations.

In all experiments, it was shown that Pb could easily be leached compared to other metals without being affected by the applied parameters. According to the earlier studies on the complex Cu-Pb-Zn concentrates, galena was suplhatized during the drying of samples at the temperatures between 100-150°C [Çakır, 1976]. Therefore, Pb could be dissolved in the solutions without even cupric ion and NaCl additions. Changes in the temperature and HCl concentration did not show any effect on Pb dissolution as the sulphates dissolve easily. Nickel also behaved like Pb during the leaching, probably for the same reason. Cu, Zn and Co acted similarly in all leaching conditions related to their mineralogical structure since some dissemination of chalcopyrite in sphalerite was observed.

CONCLUSIONS

As a result of this study, it was shown that it was possible to leach of sulphidic massive rich copper ores successfully using cupric chloride media. A catalyst such as NaCl has a positive effect on leaching recoveries.

The optimum leaching conditions were found as in Cu^{2+} concentration of 20 g/L, leaching time of 2 hours, HCl concentration of 20 g/L, temperature of 60°C, solid/liquid ratio of 1/10 and NaCl concentration of 200 g/L. Under these conditions, 41% of Cu, 26% of Co, 89% of Ni, 98% of Pb, 76% of Zn and 69% of Ag are extracted.

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