

## A COMPARATIVE STUDY ON FERRIC CHLORIDE AND FERRIC SULPHATE LEACHING OF A SULPHIDIC COPPER ORE FROM TURKEY

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### ABSTRACT

Massive rich copper ore containing 7.95 % Cu, 2.13 % Pb, 0.341 % Zn, 0.087 % Co, 0.039 % Ni, 0.9 (g/t) Au, 17 (g/t) Ag subjected to this experimental study was taken from Küre-Türkiye. Effects of leaching time, ferric ion concentration, solid/liquid ratio, acid concentration and temperature on the metal dissolution efficiencies were investigated in both ferric chloride and ferric sulphate leaching processes. Optimum leaching conditions were determined and the results of these two processes have been compared. As a result of ferric chloride leaching experiments, carried out under the optimum leaching conditions, 76 % of Cu, 54.9 % of Co, 93.4 % of Ni, 100 % of Pb, and 91.37 % of Zn were leached. Under the optimum conditions of ferric sulphate leaching, 58.84 of Cu, 56.8 % of Co, 96 % of Ni, 97.2 % of Pb, 78.46 % of Zn leaching recoveries were obtained. According to these studies, ferric chloride leaching gave better results in terms of metal leaching recoveries. Silver can also be recovered in ferric chloride leaching while there is no silver dissolution in ferric sulphate leaching.

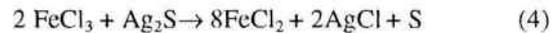
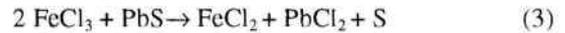
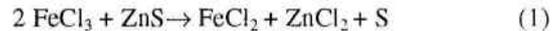
### INTRODUCTION

There are five different types of sulfidic copper ore deposits located in Küre, Türkiye. These ores contain considerable amount of precious metals (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 [Project-1994]. A blend of these ores, containing 1.7 % Cu on the average, is fed to the Küre Copper Flotation Concentrator whose annual capacity is 1.2 million tons of ore.

Earlier studies on these ores, focused on recovering other metallic values in addition to the major metals by the application of a process including sulphatizing roasting + acidic leaching + cyanidation [Arslan et al.-1995, Arslan et al.-1998]. SO<sub>2</sub> gases

produced during roasting are harmful to the environment. Therefore, direct application of hydrometallurgical processes is proposed for the treatment of these ores.

Ferric chloride leaching of chalcopyrite, sphalerite and galena concentrates has been extensively studied by various researchers [Dutrizac-1992, Jin et al.-1993, Havlik et al.-1995, Mulak et al.-1995]. The high chloride concentration leach medium is aimed at increasing the solubility of metal chlorides. A number of metallic sulfides such as Cu, Zn, Pb, Bi, Ag etc. are likely to pass into solution during the ferric chloride leaching process. These minerals react with ferric chloride and dissolve according to the following reactions:



There are several studies also conducted on the beneficiation of complex sulfidic ores taken from Black Sea region of Türkiye by applying ferric chloride leaching process [Çakır-1976, Cambazoğlu-1985, Arslan et al.-1996, Gürkan et al.-1998].

Ferric sulphate leaching has also been investigated by several researchers [Becstead et al.-1977, Jones et al.-1977, Iglesias and Carranza-1996]. Ferric sulphate dissolves some sulfide minerals according to the following reactions:



### EXPERIMENTAL AND MATERIAL

The ore sample, used in the experiments, was taken from Küre-massive rich copper ore deposit. Chemical analysis of the ore sample is given in Table I.

According to the mineralogical examinations it was found that [Project, 1994, Sirkeci et al., 1996] chalcopyrite (CuFeS<sub>2</sub>) and pyrite (FeS<sub>2</sub>) were the

dominant minerals, however, there are considerable bornite ( $\text{Cu}_5\text{FeS}_4$ ) occurrences in some zones. The other minerals observed were covellite ( $\text{CuS}$ ), sphalerite ( $\text{ZnS}$ ), native gold, galena ( $\text{PbS}$ ), tennantite ( $(\text{Cu,Fe,Zn,Ag})_{12}\text{As}_{14}\text{S}_{13}$ ), carolite ( $\text{CuCo}_2\text{S}_4$ ), bravoite ( $(\text{Ni,Fe})\text{S}_2$ ), quartz and calcite. Pyrite is generally seen as fractured grains and shows a complex structure in which substituted by chalcopyrite and bornite. Sphalerite inclusions were observed within chalcopyrite that formed along the cleavages of pyrite. Bornite usually occurs as finally disseminated grains within other minerals.

Table I. Chemical analysis of massive rich copper ore.

Element	% Content
Cu	7.95
Fe	23.24
Pb	2.13
Zn	0.341
Co	0.087
Ni	0.039
S	43.22
$\text{SiO}_2$	4.48
Ag(g/t)	17
Au(g/t)	0.9

In order to recover Cu, Zn, Pb, Co, Ni and Ag present in the ore, ferric chloride and ferric sulphate leaching experiments were performed with these samples ground under 106 microns. Experiments were carried out using standard glassware and a heater-stirrer. In the graphs, all points represent a single experiment, meaning no sample solution was taken during the leaching and all experiments were carried out separately. After each experiment, pulp was filtered and all metal analyses were made from leach cake. Effects of leaching time, ferric ion ( $\text{Fe}^{3+}$ ) concentration, HCl concentration, solid/liquid ratio and leaching temperature on the dissolution efficiencies of above mentioned metals were investigated in the leaching experiments.

## RESULTS AND DISCUSSION

Ferric chloride and ferric sulphate leaching experiments carried out almost at the same conditions for comparison. Leaching conditions and results are summarized in the following parts:

### Effect of leaching time:

Constant experimental conditions for ferric chloride leaching were  $\text{Fe}^{3+}$  ion concentration: 75 g/l,

HCl concentration: 20 g/l, S/L ratio: 1/10, temperature: 90°C and for ferric sulphate leaching;  $\text{Fe}^{3+}$  ion concentration: 30 g/l,  $\text{H}_2\text{SO}_4$  concentration: 10 g/l, S/L ratio: 1/10, temperature: 60°C. Parameters in both leaching experiments are not chosen the same since ferric chloride leaching tests require higher temperatures closed to the boiling point.

Leaching time varied between 1 and 8 hours. Effect of leaching time on ferric chloride and ferric sulphate leaching processes are given in Figures 1 and 2, respectively.

As it can be seen in Figure 1, leaching time is important parameter for Cu minerals dissolving by ferric chloride. When leaching time increases, the leaching recovery of Cu also increases. The same effect was observed on Zn leaching efficiencies as seen in Figure 2. As it can be seen from the figure that Pb could easily be leached compared to other metals. 97.2% of Pb was leached in one hour of leaching time. According to the studies on the complex Cu-Pb-Zn concentrates, it was found that galena was sulphatized during the drying of samples at temperatures between 100-150°C [Çakır, 1976]. Therefore, Pb could be dissolved in the solutions without even ferric ion addition. Changes in the temperature and acid concentration do not show any effect on the Pb dissolution as the sulphates dissolve easily. Generally, two hours of leaching time was found sufficient for dissolving of other metals.

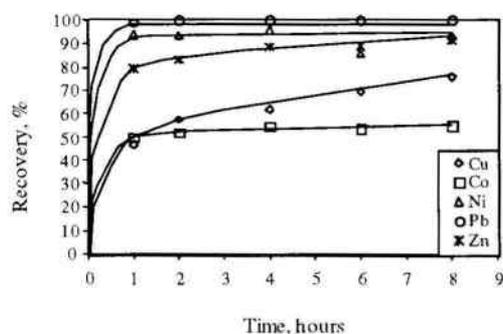


Figure 1. Effect of leaching time on metal leaching recoveries using ferric chloride.

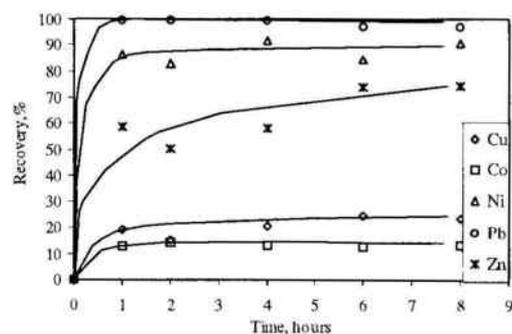


Figure 2. Effect of leaching time on metal leaching recoveries using ferric sulphate.

**Effect of Fe<sup>3+</sup> ion concentration:**

Constant experimental conditions for ferric chloride leaching were; leaching time: 2 hours, HCl concentration: 20 g/l, S/L ratio: 1/10, temperature: 90 °C. Fe<sup>3+</sup> ion concentration was changed as 15.5, 37.5, 75 and 150 g/l.

Constant experimental conditions for ferric sulphate leaching were; leaching time: 2 hours, H<sub>2</sub>SO<sub>4</sub> concentration: 10 g/l, S/L ratio: 1/10, temperature: 60 °C. Fe<sup>3+</sup> ion concentration was changed as 30, 60 and 90 g/l.

Effect of Fe<sup>3+</sup> ion concentration on ferric chloride and ferric sulphate leaching is given in Figure 3 and 4, respectively. From Figures 3 and 4, ferric chloride seems to be more effective than ferric sulphate in terms of Cu and Co leaching recoveries. When the concentration of ferric chloride reaches to 75 g/l, Cu and Co recoveries increase rapidly. Increasing ferric chloride concentration over 75 g/l had a decreasing effect on Cu, Co and Zn leaching recoveries.

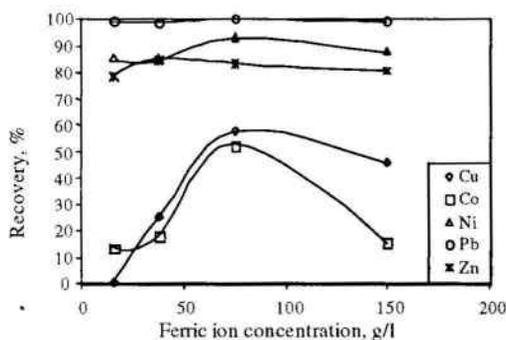


Figure 3. Effect of Fe<sup>3+</sup> ion concentration on metal leaching recoveries using ferric chloride.

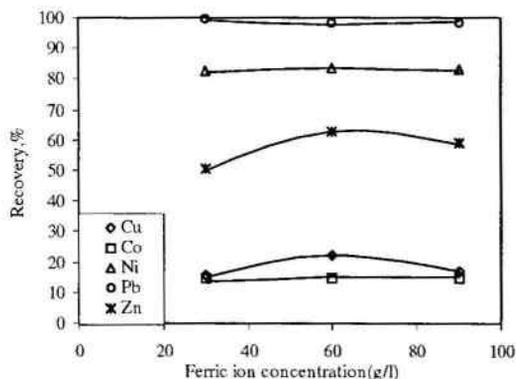


Figure 4. Effect of Fe<sup>3+</sup> ion concentration on metal leaching recoveries using ferric sulphate.

**Effect of acid concentration:**

Constant experimental conditions for ferric chloride leaching were; Fe<sup>3+</sup> ion concentration: 75 g/l,

leaching time: 2 hours, S/L ratio: 1/10, temperature: 90 °C and HCl concentration was changed as 10, 20 and 30 g/l.

Constant experimental conditions for ferric sulphate leaching were; Fe<sup>3+</sup> ion concentration: 60 g/l, leaching time: 6 hours, S/L ratio: 1/10, temperature: 90 °C and H<sub>2</sub>SO<sub>4</sub> concentration was changed as 10, 20 and 30 g/l.

Effect of acid concentration is given in Figures 5 and 6 for ferric chloride and ferric sulphate leaching, respectively. While acid (HCl) concentration seems to be an indifferent parameter in ferric chloride leaching, H<sub>2</sub>SO<sub>4</sub> concentration became a critical parameter in ferric sulphate leaching. Increasing H<sub>2</sub>SO<sub>4</sub> concentration had a decreasing effect on Cu and Co leaching recoveries and resulted in increase of Zn leaching recoveries.

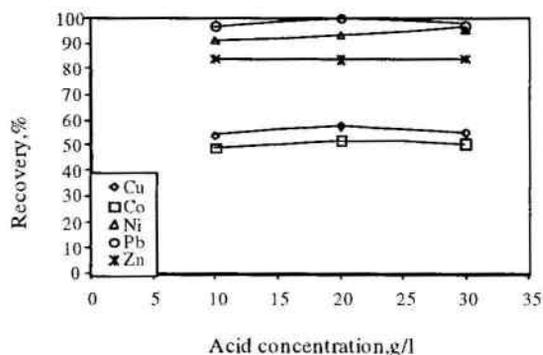


Figure 5. Effect of acid concentration on metal leaching recoveries using ferric chloride.

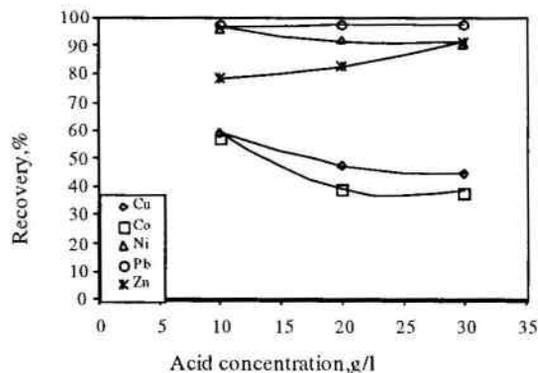


Figure 6. Effect of acid concentration on metal leaching recoveries using ferric sulphate.

**Effect of solid/liquid ratio:**

Constant experimental conditions for ferric chloride leaching were; Fe<sup>3+</sup> ion concentration: 75 g/l, leaching time: 2 hours, temperature: 90 °C, HCl concentration 10 g/l.

Constant experimental conditions for ferric sulphate leaching were; Fe<sup>3+</sup> ion concentration: 60 g/l,

leaching time: 6 hours, temperature: 90 °C, H<sub>2</sub>SO<sub>4</sub> concentration 10 g/l.

Solid/liquid ratio in both leaching tests changed as 1/10, 1/5 and 1/3. Effect of solid/liquid ratio is given in Figures 7 and 8 for ferric chloride and ferric sulphate leaching tests, respectively.

Effect of solid/liquid ratio was more distinguishable in ferric sulphate leaching than ferric chloride leaching. Leaching recoveries of Cu, Co, Zn and Ni decreased by increasing the amount of solid content in ferric sulphate leaching tests.

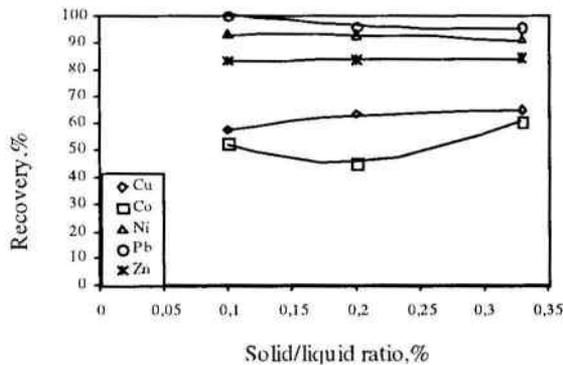


Figure 7. Effect of solid/liquid ratio on metal leaching recoveries using ferric chloride.

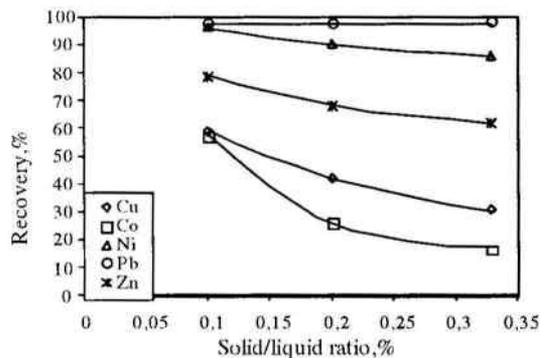


Figure 8. Effect of solid/liquid ratio on metal leaching recoveries using ferric sulphate.

#### Effect of Temperature:

Constant experimental conditions for ferric chloride leaching were; Fe<sup>+3</sup> ion concentration: 75 g/l, leaching time: 6 hours, HCl concentration: 10 g/l, S/L:1/10. Temperature was changed as 60, 75 and 90 °C.

Constant experimental conditions for ferric sulphate leaching were; Fe<sup>+3</sup> ion concentration: 60 g/l, leaching time: 6 hours, H<sub>2</sub>SO<sub>4</sub> concentration 10 g/l, S/L:1/10. Temperature was changed 60, 80 and 90 °C.

Effect of temperature is given in Figures 9 and 10 for ferric chloride and ferric sulphate, respectively.

Temperature change was very important in both leaching processes, whereas increasing temperature positively affected the metal leaching recoveries. The highest leaching recoveries were observed at 90 °C in both cases.

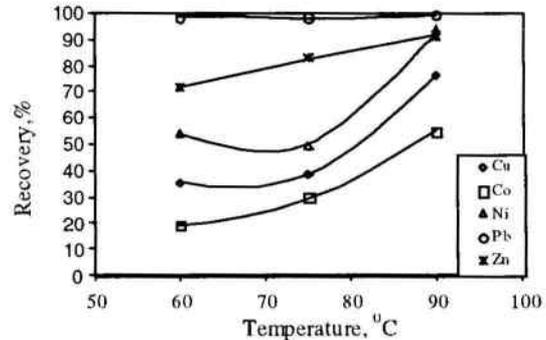


Figure 9. Effect of temperature on metal leaching recoveries using ferric chloride.

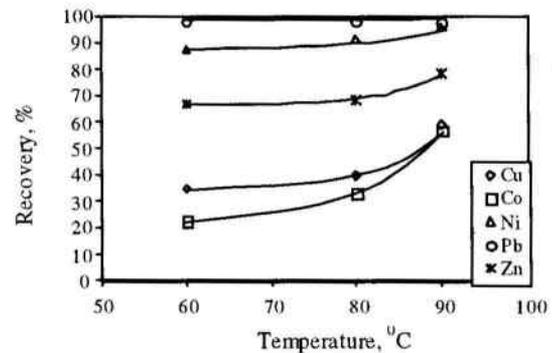


Figure 10. Effect of temperature on metal leaching recoveries using ferric sulphate.

## CONCLUSIONS

Ores sample taken from the rich zones of Küre contained 7.95% Cu, 2.13 % Pb, 0.341 % Zn, 0.087 % Co, 0.039 % Ni, 17 g/t Ag, 0.9 g/t Au.

As a result of these leaching experiments, ferric chloride seemed to be more effective reagent than ferric sulphate as expected according to the studies given in the literature (Jones et al. 1977). Optimum conditions of ferric chloride leaching were 75 g/l Fe<sup>+3</sup> ion and 20 g/l HCl concentration, 1/10 S/L ratio, 90 °C and 8 hours of leaching time. 76.19 % Cu, 99.91 % Pb, 91.37 % Zn, 54.92 % Co and % 93.43 % Ni leaching recoveries were observed at these conditions.

Optimum leaching conditions for ferric sulphate leaching were found as 60 g/l Fe<sup>+3</sup> ion and 10 g/l H<sub>2</sub>SO<sub>4</sub> concentration, 1/10 S/L ratio, 90 °C and 6 hours of leaching time. Metal leaching recoveries at these conditions were obtained as 58.84 % Cu, 97.42 % Pb, 78.46 % Zn, 56.84 % Co and % 95.98 Ni.

In conclusion, it can be said that ferric chloride leaching resulted in higher metal dissolution efficiencies than those of ferric sulphate.

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