Leach-cementation operations were applied to produce impure copper from the sulphating roasted ore. Effect of acid concentration and temperature on the extraction of copper from the ore into the leaching solution were studied. The cementation tests were conducted with two different stirring devices. One, mild steel disc and the second a propeller. The mild steel disc was used to provide a uniformly accessible surface for the kinetic study of cementation of copper with iron in sulphate solution.

Key words: leaching, cementation, copper ore

INTRODUCTION

High grade sulphide copper ores have been usually processed pyrometallurgically. However, in the past two decades, in order to eliminate emissions of sulphur dioxide, other approaches have been extensively investigated on both laboratory and pilot plant scales. Eventually, hydrometallurgy emerged as a very promising alternative technology for recovering of copper from the low grade sulphide ores.

The ore used in this study was taken from the low grade Ergani copper deposit that has 1,5 million tons of partly oxidized sulphide ore containing about 1–3% Cu (Canbazoglu, Cebeci and Kahriman, 1992). The ore was roasted to produce material...
which can be readily leached in a diluted sulphuric acid solution. The conditions of roasting of the ore are given by Yildirim (1980). This paper now presents the result on treatment of the roasted low grade Ergani copper ore sample by leach-cementation operations.

MATERIALS AND METHODS

The original ore sample (unroasted) contains mainly FeS\textsubscript{2}, CuFeS\textsubscript{2}, ZnS, FeS and PbS while gangue minerals are chlorides and silicates. The ore was roasted at 575\textdegree C in air for one hour. Particle size of the samples of the roasted ore used in the leaching experiments was (147+44) microns. Contents of the basic components of the roasted ore are shown in Table 1.

Table 1. Chemical analysis results of the roasted ore

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.48</td>
</tr>
<tr>
<td>Fe</td>
<td>29.66</td>
</tr>
<tr>
<td>Zn</td>
<td>0.22</td>
</tr>
<tr>
<td>Pb</td>
<td>0.28</td>
</tr>
<tr>
<td>S</td>
<td>10.50</td>
</tr>
<tr>
<td>Si</td>
<td>41.78</td>
</tr>
</tbody>
</table>

Perkin-Elmer 303 Atomic Absorption Spectrophotometer (AAS) was used to determine the copper and iron concentrations in the examined solutions. Particle size of the iron powder used for cementation was within the range of one micron. Its composition was 95% Fe, 0.02% N, 0.001% As and 2% acid insoluble matter.

The absorbance readings from the AAS were treated with a programmable Hewlett Packard desk calculator. This led to the direct copper and iron recoveries. The effect of different variables on the leaching of copper were studied.

Acid concentration. Twelve grams of the ore was leached in 40 ml (0.3 gr/ml) of the sulphuric acid solutions 5% to 45%. Tests were carried out at ambient temperature (20\textdegree C) for 30 minutes. The wrist shaker was used for the agitation. After completion the leaching, the liquor was filtered and adequate amount of the filtrate was diluted up to 250 ml for the AAS analysis. The remaining acidic solution was used for titration with sodium hydroxide and methyl red. More concentrated acid solutions were diluted with distilled water prior to the titration. The results of the titration and the AAS are shown in Figures 1 and 2 respectively.
Temperature. Forty-eight grams of the ore was leached in 160 ml of the 15% sulphuric acid solution at temperatures varying from 30° to 70° C. Temperature was controlled and maintained at defined level with a water bath. The results of experiments are shown in Figure 3.

Cementation tests. Two different stirring devices (mild disc and propeller) were applied to make comparison. The tests were conducted at various concentrations of (Cu²⁺), at constant temperature of 20° C, and for 20 minutes each. Concentrations of (Cu²⁺) were changed from 0,05 to 0,4 gr/l for the both mixing mechanisms. At the end of the each tests, concentrations of (Cu²⁺) were determined with AAS. The results are shown in Figure 4.

The use of mild disc. The steel rod between the disc and the main body of the stirrer was covered by a plastic pipe (Figure 1) in order to prevent the contact between the rod and the solution. After immersing the disc into the solution (400 ml) for cementation the stirring began at rate 800 rpm. After completion of the experiment the disc was removed from the solution and immersed into the acid solution to dissolve the cemented copper from the disc.

![Fig. 1. Illustration of the disc](image)

The use of propeller and iron powder. The same tests were repeated with iron powder introduced to the solution. Then the plastic covered rod with a propeller was used to mix the cementation mixture. No copper coverage on the propeller was observed.
RESULTS AND DISCUSSIONS

Consumption of acid during leaching of the ore studied at varying concentrations of acid is shown in Figure 2. The possible explanation of observed dependence is that the diluted acid preferentially attacks the more soluble copper and iron while the stronger acid attacks all of the species present in the ore.

However, Figure 3 shows that the copper recoveries are high throughout while the iron recoveries changes in the expected manner, i.e. the stronger the acid the larger the amount of leached iron. Copper recoveries in dilute acids might be more attributable to the temperature in contrary to the case of the stronger acids. Acid consumption results seem to reveal that the use of low acid concentration in beneficial. An improvement in copper recovery is advisable at elevated temperatures (Figure 4). The amount of iron extracted increases too. High concentration of iron in the solution causes severe problems in solvent extraction process which would be ideal for concentrating copper prior to electrowinning. The following reactions involve the recovering of copper from the acidic solutions by cementation with iron (Biswa, 1972; Tilyard, 1973).
Leaching and cementation of the sulphating roasted low grade ergani copper ore

\[ \text{Cu}^{2+} + \text{Fe}^0 \rightarrow \text{Cu}^0 + \text{Fe}^{2+} \quad \Delta \text{E}^0 = +777 \, V \quad (1) \]
\[ \text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e \rightarrow E_1^0 = +0.440 \, V \quad (2) \]
\[ \text{Cu}^{2+} + 2e \rightarrow \text{Cu}^0 \rightarrow E_2^0 = +0.337 \, V \quad (3) \]

According to reaction (1) one mole of Fe precipitates one mole copper. This means that 0.88 kg iron is necessary to precipitate 1 kg of copper. Iron consumed in the practical operations is 2-3 times greater (Biswas, 1980).

Cementation tests were carried out in solutions at varying initial CuSO\(_4\) concentrations. The percent recoveries of Cu increases with the decrease of copper concentrations (Fig 5). This was apparently caused by extremely rapid rates of copper precipitation at high solution concentrations, resulting in the formation of an almost impenetrable dense copper deposit on the steel disc. On the other hand, at high solution concentrations of copper, deposition of the cemented copper on the iron particles mixed with propeller caused low copper recoveries. However, as the concentration of copper decreases this effect ceases and therefore, the high copper recoveries are obtained.

The majority of previous investigations on cementation involved flow systems which were rather difficult to analyse allowing to interpret the data obtained qualitatively. Therefore, we chose the rotating disc by following Levich (1962) to provide information about the rate and activation energy. Effect of possible side reactions resulted from the presence of oxygen in the system were not considered.

Apparent rate constants of cementation in the experiments with mild steel disc were calculated for the each temperature using the heterogeneous first order rate equation. This equation may be written after Strickland and Lawson (1970) as follows:

\[ J = kC \quad (4) \]

where, \( J \)—apparent mass flux based on the initial exposed precipitant area ( kg m\(^{-2}\)sec\(^{-1}\)), \( k \)—rate constant (m sec\(^{-1}\)), \( C \)—bulk concentration of (Cu\(^{2+}\)) ions at time \( t \) (kg m\(^{-3}\)).
The rate constants of cementation at varying temperatures are shown in Table 2.

Table 2. Rate constants of copper cementation at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(1/T)*10^3 (K^-1)</th>
<th>k*10^-2 (cm.min^-1)</th>
<th>logk (-)</th>
<th>% Rec. (Cu^0/Cu^2+) *100</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.41</td>
<td>5.36</td>
<td>1.27</td>
<td>60.00</td>
</tr>
<tr>
<td>40</td>
<td>3.19</td>
<td>28.34</td>
<td>0.55</td>
<td>90.95</td>
</tr>
<tr>
<td>60</td>
<td>3.00</td>
<td>44.60</td>
<td>0.35</td>
<td>93.72</td>
</tr>
<tr>
<td>80</td>
<td>2.80</td>
<td>64.00</td>
<td>0.19</td>
<td>97.75</td>
</tr>
</tbody>
</table>

A – Frequency factor,
E – Activation energy (cal mole^-1 K^-1),
R – the gas constant (1.987 kcal mole^-1 K^-1)
T – the present temperature
The equation (5) could be written as follows:

\[ \log k = E/R \log e(1/T) + \log A \]  

(5)

It represents the plot in Figure 6 and its slope is: \((\log k)/(-E/R \log e(1/T))\), i.e., 0.90/1.50. Thus, the activation energy (E) equals to 2.747 (kcal mole^-1 K^-1). Activation energy of this magnitude remains in a close agreement with the experimental values of other works.

CONCLUSIONS

High copper recoveries were achieved in the leaching test of studied ore with aqueous sulphuric acid. Therefore, extraction of the copper was efficient which indicates that required surface area of the particles for the leaching reactions is reached with applied granulation of ore. Copper present in the ore was readily soluble due to the roasting and leaching with the weakly acidic solutions. The leaching for 30 minutes was sufficient so that higher recoveries of copper can be reached only at elevated temperatures.
Better results of cementation of copper for the leach solutions were obtained at lower concentrations of solutions at room temperature. From comparison of the two different cementation systems, it might be concluded that the propeller method was more efficient than the steel disc. The first method gives an impure product. The copper cementation deposition rate per initial unit area of iron increases with increasing temperature. This rate depends on hydrodynamic conditions and viscosity of the solution.

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Mehmet Yildirim, Ługowanie i cementacja prażonej siarczanująco rudy z Ergami o niskiej zawartości miedzi, Fizykochemiczne Problemy Mineralurgii, 34, 133–140 (w jęz. angielskim)

Zastosowano ługowanie i cementację do otrzymywania miedzi po prażeniu siarczanizującym rudy. Badano wpływ stężenia kwasu i temperatury na proces ekstrakcji. Cementację przeprowadzono w dwóch różnych urządzeniach mieszających tj. stalowym mieszadłem dyskowym oraz śmigłowym. Zastosowane mieszadło dyskowe zapewniło jednorodną powierzchnię do badania kinetyki cementacji Cu za pomocą Fe w roztworach siarczanowych.