Effect of Roasting Temperature for Copper Leaching of Sulfide Concentrate by Combined Methods

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Abstract
This study was undertaken to develop a cost-effective method of copper leaching in sulfide concentrate involving minerals as chalcopyrite and pyrite. The combined methods involving low temperature roasting of sulfide copper minerals with potassium chlorides without the formation of sulfurous gases and their evolution into the atmosphere is suggested. The effect of experimental parameters such as a roasting temperature and time has been presented and discussed in detail. This study was carried out in the roasting temperature range 400˚C - 600˚C and roasting time ranges 1 - 4 h with potassium chloride. The obtained cake is leached by an aqueous sulfuric acid 60 g/l concentrated at pH = 2 - 2.5 and 4 h. The concentrate, a roasting cake and after leaching solid residue were analyzed by chemical analysis, XRD and SEM-EDX. At temperature ranges 450˚C - 550˚C and 3 h of roasting, the process is activated. The recovery of copper into the solution at optimal roasting condition (500˚C, roasting time 3 h) is 93.2%. The advantage of the developed method is that, it not requires high roasting temperature and the use of autoclave for leaching. The method gives possibility to leach the concentrate at room temperature and atmospheric pressure, which gives possibility to reduce cost of the process.

Keywords
Copper Leaching, Chlorination, Potassium Chloride, Chalcopyrite

1. Introduction
Copper is found in various combinations of Cu, Fe, S, and other elements in na-
ture: among these naturally occurring compounds, chalcopyrite (CuFeS$_2$) is an abundant source that accounts for almost 70% of all copper resources in the world [1]. The pyrometallurgical process is widely used to extract copper from chalcopyrite; however, with increasing worldwide copper production, copper ores are becoming increasingly scarce, and more sulfur dioxide (SO$_2$) is being released into the atmosphere [1]. Concerns over air pollution and the environmental problem of acid rain have made governments all over the world tighten their regulations regarding the emission of sulfuric dioxide [2]. Mechanochemical leaching efficiency of chalcopyrite was very low at ambient temperature, the percentages of copper dissolved after 20 h between 28% - 33% [3]. Both circumstances warrant the development of enhanced copper extraction methods.

The combined methods involving low temperature roasting of sulfide copper minerals with potassium chlorides without the formation of sulfurous gases and their evolution into the atmosphere is suggested. Copper concentrates contain sulfide minerals such as chalcopyrite, pyrite, chalcosine, covelline and bornite. Therefore, the list of possible reactions accompanying their chlorinating roasting can be continued [4] [5]:

\[
\begin{align*}
\text{CuFeS}_2 + 4\text{KCl} + 4\text{O}_2 & = \text{CuCl}_2 + \text{FeCl}_2 + 2\text{K}_2\text{SO}_4 \\
\text{CuFeS}_2 + 4\text{KCl} + 4\text{O}_2 & = \text{CuCl} + \text{FeCl}_3 + 2\text{K}_2\text{SO}_4 \\
2\text{CuFeS}_2 + 8\text{KCl} + \frac{17}{2}\text{O}_2 & = \text{Cu}_2\text{O} + 2\text{FeCl}_3 + 4\text{K}_2\text{SO}_4 + 2\text{Cl} \\
\text{FeS}_2 + 4\text{KCl} + 4\text{O}_2 + \text{FeCl}_2 & = 2\text{FeCl}_3 + 2\text{K}_2\text{SO}_4 \\
\text{FeS}_2 + 4\text{KCl} + 4\text{O}_2 & = \text{FeCl}_3 + 2\text{K}_2\text{SO}_4 + \text{Cl} \\
\text{CuS} + 2\text{KCl} + 2\text{O}_2 & = \text{CuCl}_2 + \text{K}_2\text{SO}_4 \\
\text{Cu}_2\text{S} + 2\text{KCl} + 2\text{O}_2 & = 2\text{CuCl}_2 + \text{K}_2\text{SO}_4 \\
\text{CuCl} + \text{Cl} & = \text{CuCl}_2 \\
\text{FeCl}_2 + \text{Cl} & = \text{FeCl}_3
\end{align*}
\]

Chlorinating roasting of copper sulfide minerals under an atmosphere for removing of metals has continued to remain a subject of interest. Bayer and Weidemann have observed that the salt roasting is spontaneous for KCl, slower for NH$_4$Cl and variable rate for NaCl. They have studied on salt roasting of chalcopyrite at low temperatures (473 - 513 K) by thermoanalytical technique [6]. The chemistry of the salt-roasting process is very complex because several processes, such as oxidation, sulphation, in situ chlorination and evaporation of volatile species, occur either simultaneously or sequentially [7]. The non-isothermal analysis confirmed the chemical control mechanism at temperatures below 620 K [8].

2. Experimental
2.1. Materials

Sulfide copper concentrate originating from OyuTolgoi mine, Mongolia, with 28.68% of Cu, 34.52% of Fe, 32.2% of S, 4.6% other elements were used in the
investigation. The sample contains 21.49 g/ton of Au, 47.69 g/ton of Ag. The elemental composition of the copper concentrate was analyzed by ICP-OES. The sample was crushed and dry-sieved to different narrow size fractions, namely −150 + 100, −100 + 50, −45 + 32 μm. The XRD of concentrate is shown in Figure 1. The copper concentrate included chalcopyrite (CuFeS₂) 59.56%, pyrite (FeS₂) 14.23%, hematite (Fe₂O₃) 2.1% and albite (Na[AlSi₃O₈]) 5.95%, anorthite (CaAl₂Si₂O₈) 11.68%, quartz 6.45% were identified by XRD. The SEM-EDX of concentrate is shown in Figure 2. The elemental composition of concentrate determined Fe 34.89%, Cu 27.41% and S 26.11% from EDX analysis.

2.2. Experimental Condition
The 2 g of the sample was prepared for each roasting with potassium chloride. The concentrate/KCl weight ratio was held at 1/0.7. The roasting temperature was varied from 400°C to 600°C, the roasting time was changed 1, 2, 3 and 4 h, and each sample was dissolved after roasting. The leaching temperature at 25°C, the sulfuric acid concentration was 60 g/l, the solid/liquid (S/L) ratio was = 1/9, the rotation speed was 450 r/min in all leaching experiments. The leaching time was 4 h.

3. Result and Discussion
The effect of experimental parameters such as a roasting temperature, time have been presented and discussed in detail.

Effect of Roasting Temperature and Time
Experiments of roasting with KCl were performed according to the flowchart.
presented in Figure 3 at different roasting temperatures (400°C - 600°C) and roasting time (1 - 4 h). The roasted cake was leached at the ratio S/L was 1/9, the leaching temperature was 25°C, the sulfuric acid concentration was 60 g/l, the rotation speed was 450 r/min, and the leaching time was 4 h in all experiments. The effect of roasting temperature and time is shown in Figure 3. At 400°C, the not high recovery of 66.3% is observed at 2 h. At this temperature, the reaction system was not successful, because the molecules of copper sulfide minerals in the reaction were probably not possessed the enough energy which is needed to.

At 600°C, recovery of copper was nearly constant between 1 - 3 hours. After 3 h the recovery was increased (54.3%), but not enough. From Figure 3, it seen that, the high nearly recoveries of copper (91.1% - 93.2%) were observed at temperature range 450°C - 550°C. The significant dissolving degree was at 500°C and 3 h of roasting. The maximum recovery value was observed at 93.2%.

An evaluation of Gibbs energies calculation is showed that most of the above reactions were thermodynamically possible at a low temperature such as from 400°C to 600°C. Table 1 is shown the evaluation of Gibbs energies at 450°C, 500°C and 550°C that result of recovery copper was higher than other experiments.
The recovery of copper into the solution at optimum condition roasting temperature 500°C, roasting time 3 h, concentrate and potassium chloride 1:0.7 was 93.2%. Figure 4 and Figure 5 are shown SEM-EDX analysis results on roasting concentrate with KCl and solid residue after leaching. From Figure 4, it can be seen that roasting cake surface was changed, and the copper sulfide minerals oxidized with KCl, it consists of (wt%) 30.83 Cu, 11.03 Fe, 24.84 K, 11.73 S, 10.07 O and 7.98 Cl from the SEM-EDX analysis.

From SEM-EDX, the solid residue contains (wt%) 70.5Fe and 21.34O. But, hematite was observed in the solid residues, by XRD analysis. Contents of 1% Cu
Figure 4. SEM-EDX of copper concentrate after roasting.

Figure 5. SEM-EDX of solid residue after leaching.
and 0.31% S in solid residues shows that these elements were transferred to the solution during leaching.

Phases in concentrate were analysed by XRD after 3 h of roasting at temperature between 400˚C - 550˚C. From Figure 6 all phase analysis is shown potassium sulfide (K₂SO₄), copper chloride (CuCl₂), molybdenite (FeCl₃) and lawrencite (FeCl₂) were in samples. It is seen copper concentrate was oxidized with KCl according to above reactions. Concerning the XRD analysis after roasting at 400˚C, a potassium chloride was revealed. These results were showed that the roasting process of copper sulfide minerals was not fully oxidized with KCl at 400˚C.

For defining the mechanism of leaching, the solid residue was examined by XRD (Figure 7). Figure 7(A) shown that the solid residue contains following minerals hematite (Fe₂O₃), albite (Na[AlSi₃O₈]), and quartz (SiO₂). The XRD results are shown that the roasting process of copper sulfide minerals was oxidized with KCl and the oxidized products of copper were leached in sulfuric acidic solution completely.

4. Conclusions

Thus, we can conclude the following results according to development of processing the sulfide copper concentrate:

- This study demonstrated the possibility of the combined process for copper recovery at laboratory condition.
- The recovery of copper into the solution at feasible condition of roasting temperature 500˚C, roasting time 3 h, concentrate/potassium chloride weight ratio 1/0.7, leaching time 4 h, leaching temperature of 25˚C is 93.2%.

![Figure 6. XRD pattern of copper concentrate after roasting at temperature between 400˚C - 550˚C. (a) 400˚C, 3 h roasted; (b) 450˚C, 3 h roasted; (c) 500˚C, 3 h roasted; (d) 550˚C, 3 h roasted.](image)
A high iron and low sulfur contents in solid residue allow us to obtain high-quality copper from leaching solution. The combined method involving low temperature roasting of sulfide copper minerals with potassium chlorides without the formation of sulfurous gases and their evolution into the atmosphere is suggested.

**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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