A comprehensive evaluation on leaching of non-ferrous metals from polymetallic tailings

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Abstract

There is a significant deficit between the supply and demand of critical metals, leading to look for new ways to get high-value elements from mine tailings. In this study, the atmospheric leaching method was applied to extract valuable elements, including copper, zinc, and copper oxide, from a polymetallic ore that was considered a tailing in the mining site. The sample contained 3.28% copper, 13.74% iron, 1.7% zinc, 5.71% lead, and 1.98% oxidized copper. The effect of time, stirrer speed, acid concentration, particle size, and temperature were investigated on the leaching of Cu, CuO, and Zn. The optimum recommended conditions for leaching of polymetallic ore were: acid concentration 0.5 mol L\(^{-1}\), %solid 25%, and leaching time 1 h. Leaching recoveries of 63.5% for Cu, 97.5% for CuO, 1% for Fe, and 100% for Zn can be achieved under the optimum conditions. The results for the dissolution of metals agreed with mineralogical studies.

1. Introduction

The global demand has been significantly increased for critical and valuable metals; on the other hand, a 50-year period is estimated to be sufficient to deplete Cu, Pb, Mn, Ag, Sn, and Zn \cite{1–3}. Therefore, the need for new resources like polymetallic ores and efficient processing methods attracts much attention \cite{4–7}. Utilization of this kind of ores may support the sustainable development of metals industries. Although oxide minerals have been treated historically by the hydrometallurgy method \cite{8–10}, the extraction of metals from complex or polymetallic ores has been developed recently. An appropriate lixiviant is required to leach ore to produce metal through hydrometallurgical treatment. In order to extract valuable metals from multi-metal ores, aqueous solutions of ammonia \cite{11–14}, sulfuric acid \cite{6, 15–17}, organic acids\cite{18}, and bioleaching\cite{2, 7, 19, 20} have been used as solvents. Sulfuric Acid (H\(_2\)SO\(_4\)) is the most common chemical reagent that is used for the leaching of various minerals, including copper; however, during the leaching process, in addition to copper, other metals in the matrix of the ore can be dissolved by this acid. Iron is the critical impurities that influence the final product’s quality as well as the current efficiency of the electrolytic process \cite{21, 22}. Therefore, the acid concentration should be low to limit the leaching of undesirable metals in the matrix of the ore. Thus, it may be advantageous to work on the essential leaching factors such as concentration of the reagent, pulp density, temperature, and time.

The leaching of polymetallic ores has been the subject of many studies. For example, the leaching process of non-ferrous metals from flotation tailings of copper converter slag using H\(_2\)SO\(_4\) as a leaching agent was studied by Muravyov et al. \cite{23}, and the effect of different factors on the leaching process was investigated. They found that 81.6% of copper and 37.7% of zinc can be dissolved under optimal conditions, while the iron recovery was only 26.2%. Cao et al. \cite{24} examined the factors controlling zinc and copper leaching rates for extracting valuable metals from the residue of zinc refineries. According to the results, under the optimum conditions, zinc and copper leaching rates were found to be 98.1% and 98.7%, respectively. Xiao-bo et al. \cite{25} proposed a three-step process for extracting iron and zinc from leaching tailings. As a result, concentrates containing 52% zinc and 32% iron were obtained in the flotation and magnetite separation processes.

Jamali et al. \cite{26} developed a process to leach a copper flue dust with 20% copper, 21% iron, and 3% zinc via a hydrometallurgical route. They found that 96% of zinc and 76.7% of copper have been transferred into PLS under the optimum conditions, whereas iron has dissolved at only 23.92%. The application of ionic liquids in
the extraction of metals was investigated by Kilicarslan et al. [27]. Their findings revealed that by using a convenient leaching agent, almost all of the zinc and more than 80% of copper were leached from the solution. An innovative method comprising roasting process, beneficiation and leaching had been developed by Zhuoyue et al. [28]. By utilizing this procedure, they extracted copper and zinc from a low-grade ore with recoveries of 86% and 69%, respectively.

Some studies applied a two-step leaching process to extract selectively non-ferrous metals, including copper and zinc, from the tailings of the flotation process, in which Zn &Cu was dissolved in the first stage, and iron was transferred into the solution in the second stage of leaching with H$_2$SO$_4$ agent [29]. Calcination prior to the leaching process was another way used by Ferron and Cuyper [30]. The calcination of copper-zinc sulfide concentrate followed by leaching with H$_2$SO$_4$ could recover 99% and 95% of copper and zinc, respectively. A mixture of lixiviants like sulfuric acid and chloride solution was used by Schueler et al. [31] for the extraction of Cu, Zn, and Pb from sulfide tailings. The results showed that the extraction of lead was dependent on NaCl concentration, and temperature positively affected the extraction efficiency of Cu and Pb. The leaching rates of copper, lead, and zinc were obtained as 94, 84 and 67%, respectively. Using direct reduction and magnetic separation as a processing method for obtaining valuable metals from jarosite residues was used by Wang et al. [32]. More than 90% of lead and zinc, and 50% of iron were recovered under the optimum conditions. Top [33] conducted a two-step study and recovered almost 90% of manganese and 57% of iron through leaching and magnetic separation.

Although the leaching of non-ferrous metals such as copper, zinc, lead, and iron by microbial leaching is quite promising, this process suffers from a low extraction rate. Contic et al. [19] worked on a polymetallic sulfide concentrate to extract copper, lead, and iron. The bioleaching efficiency was obtained at 68%, 83%, and 89% for iron, copper, and zinc, respectively. Muravyov [34] utilized bio-hydrometallurgy process to extract metals from pyritic wastes. Under the optimum oxidation conditions, more than 60% of copper and zinc and 85% of gold content was recovered from the tailings. Kovarikova et al. [35] showed that 47% of aluminum, 54% of iron, and 28% of Cu with the bioleaching method could be extracted from a polymetallic ore. Experiments on silver-bearing copper ore conducted by K.Zhappar et al. [36] demonstrated that bioleaching had higher extraction yield compared to conventional leaching method.

Several studies, such as Xi et al. [37], also applied the pressure oxidation process. They found that 98% copper and 99% zinc in the low-grade polymetallic chalcopyrite ore can be dissolved in the optimum condition while lead and iron remained in the residue. Karimo et al. [38] have studied the autoclave leaching of furnace electric filter dust to extract non-ferrous metals and analyze arsenic behavior. Oxidative leaching with sulfuric acid in an autoclave led to the extraction rate of 89 and 92 percent for copper and zinc, respectively. Copper and zinc leaching from a polymetallic concentrate was reported by Patel et al. [39] where 81% of copper and 54% of zinc can be extracted within a contact time of 30 and 90 minutes respectively.

The focus of this work is on the extraction of metals from a polymetallic ore that was historically lie in waste ores at the mine site because efficient metal extraction technologies were not available and at the same time the smelters impose financial penalties on copper concentrate because of the presence of certain impurities. As a result, further research is still necessary to effectively extract ores of this type. In this paper, to establish a
leaching process, various conditions were examined to determine the leaching efficiency for copper extraction from multi-metal oxide ores.

2. Materials And Methods

A representative sample (50 Kg) was collected from the overburden oxide ore deposit and sent to the laboratories for mineralogical analyses, including X-ray diffraction (Philips-Xpert Pro, the Netherlands) and X-ray fluorescence (Philips PW1730). Polished, thin sections and Scanning Electron Microscopy (LEO1450 UP, Zeiss, Germany) were also applied for characterizing the feed and the leaching residues. Chemicals such as sulfuric acid and sodium hydroxide with analytical grade and without dilution were purchased from Merck Co.

Total acid consumption tests were conducted in a 2.5 L glass bottle on a bottle roll machine at the acid concentration of 0.25 M, ambient temperature, and the solid-to-liquid ratio of 50 g L\(^{-1}\) within 32 h. The pH of the solution was measured at certain time intervals and fixed at the initial pH by adding the concentrate acid. This process continued until pH did not change during the leaching process. The total amount of acid consumed was then reported in Kg of acid per ton of ore.

Leaching tests were conducted in a 100 ml Round-bottom flask with a certain amount of solid sample and sulfuric acid solution. The temperature and stirrer speed was adjusted at the desired level until the end of the tests using a magnetic hot plate model HSD 330, MTOPS, Korea. The initial pH was also set at a certain value by a pH meter (pH-212, LUTRON). At the end of the test, solid and liquid phases were separated by filtration, and leachate was analyzed by atomic absorption spectroscopy (Contra aa700, Jena, Germany) to measure the content of the valuable metals in the aqueous solution. The metal recovery was then calculated using Eq. 1.

\[
R\% = \frac{100 \times C}{Wt(\%)} \times \frac{V}{m}
\]

Eq. 1

Where \(C\) and \(Wt(\%\) are the metallic concentration in the leaching solution and the metal grade in the solid sample, respectively. Volume of the leaching solution and mass of the solid sample are expressed in \(V\) and \(m\). Effective parameters on leaching and their levels are shown in Table 1.
Table 1
Studied variables and levels in the leaching of polymetallic ore

<table>
<thead>
<tr>
<th>Variables</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid sulfuric acid concentration</td>
<td>0.25, 0.5, 1, 1.5, 2</td>
</tr>
<tr>
<td>Time (h)</td>
<td>1, 3, 5, 8, 16, 24, 32</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25, 35, 45, 55, 65</td>
</tr>
<tr>
<td>Stirrer speed (rpm)</td>
<td>100, 250, 400</td>
</tr>
<tr>
<td>%Solid (%)</td>
<td>15, 25, 35, 50</td>
</tr>
<tr>
<td>Particle size (D_{80}, μm)</td>
<td>75, 150, 300</td>
</tr>
</tbody>
</table>

3. Results And Discussion

3.1 Sample characterization

Table 2 shows that the sample's dominant component was silica 31.25%, iron oxide 27.5%, and aluminum oxide 11.2% based on XRF analysis. In addition, the amount of copper and zinc oxide were reported as 2.3% and 1.3%, respectively. Mineralogical analysis, XRD, confirmed that the sample consists of Quartz, Clinohlore, Cerussite, Zincite, Hematite, Magnesite, Muscovite, and Smithsonite (Fig. 1). Copper-bearing minerals in the sample include CuFe$_2$O$_4$, Cu$_4$O$_3$, CuO and Cu$_6$Si$_6$O$_{18}$ according to the XRD pattern. However, the other copper oxide phases, such as malachite and azurite, can be expected since hematite exists in the sample. The concentration of Cu, Fe, Zn, Pb, and CuO were determined as 3.28%, 13.74%, 1.7%, 5.71%, and 1.98%, respectively, by wet chemical analysis. SEM–EDS analysis also confirmed the mineral composition of the ore (Fig. 2).

Table 2
Chemical composition of the sample by XRF analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>MnO</th>
<th>Fe$_2$O$_3$</th>
<th>CuO</th>
<th>ZnO</th>
<th>PbO</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>8.6</td>
<td>11.2</td>
<td>31.25</td>
<td>0.36</td>
<td>0.14</td>
<td>0.37</td>
<td>0.63</td>
<td>27.5</td>
<td>3.2</td>
<td>3.1</td>
<td>2.9</td>
<td>10.75</td>
</tr>
</tbody>
</table>

3.2. Determination of acid consumption

The amount of acid consumed during the leaching process was calculated at two different particle sizes of 75μm and 300μm. According to Fig. 3a, acid consumption for d$_{80}$ = 75μm was significant, and it reached the highest level (15.75 kg/ton) at 4 h of starting the test; no changes were observed for a longer period, which means the leaching reaction may have been completed. Total acid consumption for d$_{80}$ = 300μm was calculated as 13.56 kg/ton. Less acid consumption was expected since the finer particle size, the higher acid consumption. The reason may be due to the liberation of the mineral particles in finer size fractions and a more available contact area for the leaching process.
3.3 Atmospheric leaching experiments

In this section, several factors affecting the dissolution percentage of valuable elements by $\text{H}_2\text{SO}_4$ have been studied in detail. The stirring speed, reaction time, lixiviate concentration, temperature, particle size, and pulp density were examined, and the results have been discussed below.

3.3.1 Effect of stirring speed

The stirring speed at three different levels of 100 rpm, 250 rpm, and 400 rpm have been studied, and results have been illustrated in Fig. 4. The dissolution under no agitation is also reported in the figure. According to the results the dissolution rate of Cu, Zn, and CuO has increased by enhancing the agitation rate up to 100 rpm; however, no significant change was observed by further increasing. The reason may be attributed to the Nernst boundary layer [40]. It was also clear that the dissolution rates of iron-bear minerals are independent of the stirring speed. Also, lead-containing minerals did not dissolve in the sulfuric acid solution due to the formation of insoluble PbSO$_4$.

The recovery of zinc, total copper, and oxidized copper reached 70%, 30%, and 60%, respectively by $\text{H}_2\text{SO}_4$ 0.25 M within one hour at room temperature, while only 0.04% of Pb and 4.64% of Fe were transferred to the liquid phase.

3.4 Effect of leaching reaction time

The role of leaching reaction time on the extraction of Cu, Zn, and Fe was studied under these conditions: solid percentage of 25%, room temperature, 0.25 M $\text{H}_2\text{SO}_4$, and size fractions of 75µm and 300µm. Samples were taken in different time intervals (1h, 3h, 5h, 8h, 16h, 24h, and 32h) and sent for analysis. According to Fig. 5a, the recovery of copper ($\text{Cu}_t$) increases significantly at the first 3 hours of the reaction; then gradually increases until it reaches the maximum level. The final dissolution percentage of Cu$_t$ and CuO was determined by about 65% and 92%, respectively (Figs. 5a&b). The results indicated that copper dissolution was not influenced by particle size.

Almost the same results were obtained for the zinc dissolution (Fig. 5c), and the optimum dissolution was obtained at the first three hours; however, unlike copper dissolution, the effect of particle size on zinc recovery was considerable. According to Fig. 5d, the Fe content of the solution increased gradually over time and reached 11.92% after 32 hours in particle size 75µm.

3.5. The effect of sulfuric acid concentration

The effect of $\text{H}_2\text{SO}_4$ concentration on Cu, Zn, and Fe recoveries in five different acid concentrations of 0.25, 0.5, 1, 1.5, and 2 M was investigated while other conditions were kept constant. The result illustrated in Fig. 6a shows that the leaching of Cu has been increased by changes in the acid concentration from 0.25 M to 2 M, especially at the first 30 minutes of the reaction; however, when the reaction times rise, the effect of acid concentration was almost negligible.
According to Fig. 6b, almost all of the CuO content in the ore was leached at an acid concentration of 0.5 M, and there is no need for a stronger acid solution. It has also been found that increasing the leaching time cannot compensate for the lower acid concentration (0.25M) to reach high recovery. The same results were obtained for zinc, and at 0.5 M sulfuric acid concentration almost 90% zinc-bearing minerals were dissolved, and high concentration of acid enhanced the recovery to 98% at 2 M. (Fig. 6c). Unlike copper and zinc, increasing acid concentration significantly affected iron dissolution, whereas the iron recovery reached the maximum value of 6% by 2 M $\text{H}_2\text{SO}_4$ within 1 hour (Fig. 6d). According to the results, Cu and Zn dissolution kinetics were very fast and approached the optimal values after 5 to 15 minutes, while the iron-leaching rate was slow under this condition.

**3.6. The effect of pulp density**

Since the increasing pulp density may accelerate the corrosion of the equipment during the leaching process, and on the contrary, dilute solution will enhance the cost of downstream operations, the solid-to-liquid ratio should be considered an essential factor. In this section, the effect of %solid on the efficiency of leaching of Cu, CuO, Zn, and Fe was studied at four different values 15%, 25%, 35%, and 50%. According to Fig. 7, it is clear that the maximum recovery was obtained at a solid percentage of 25%, and thicker solutions led to a sharp decrease in the leaching efficiency due to an inadequate supply of $\text{H}^+$ or insufficient solid-liquid contact in the solution[26, 41]. Solid% 15 was not selected since it creates a dilute solution, making the process uneconomical.

**3.7. Effect of particle size**

Particle size is another critical parameter in leaching processes. Finer particles increase the extraction rate by enhancing the surface available for reaction. However, excess size reduction can exponentially raise energy consumption and, consequently the cost of the process. Therefore, it is essential to find the optimal particle size for improving the leaching efficiency by considering the economic and technical aspects. In order to study the effect of particle size, some experiments were conducted at $d_{80} = 75\mu\text{m}$, 150µm, and 300 µm, while other parameters were kept constant. As shown in Fig. 8, particle size's effect on leaching was insignificant; however, all elements' recovery decreased slightly for $d_{80} = 300 \mu\text{m}$ due to the smaller exposed surface area to the acid.

**3.8. Effect of temperature**

The effect of temperature on leaching processes was studied using the following conditions: 0.5 M $\text{H}_2\text{SO}_4$, 100 rpm, and pulp density of 25%. Experiments were conducted at five different temperatures in the range of 25–65°C. 5 ml Samples were taken at 1, 5, 10, 15, 30, 45, and 60 minutes and sent to determine Cu, Zn, and Fe content in the solution. As seen in Fig. 9a, the temperature has influenced the Cu dissolution, whereas rising temperature from 25 °C to 65 °C led to a 13% higher copper dissolution. The maximum value for the Cu$_t$, 62%, was reported at 65 °C within 60 minutes. The copper sulfide minerals seem responsible for the partial copper dissolution under the experiment's condition. A similar trend for CuO was observed (Fig. 9b), and the leaching efficiency percentage changed by about 20% with increasing temperature. It can be seen that 100% of the oxidized copper could be transferred into PLS at temperatures > 55 °C.
According to Fig. 9c, zinc recovery was temperature-dependent, whereas by changing the temperature from 25 °C to 65 °C, zinc dissolution increased from 59–97% only in 10 minutes. The Fe dissolution also showed an upward trend, increasing gradually to the value of 7% at a temperature of 65 °C (Fig. 9d).

According to the results, some experiments were conducted at the optimum condition of 65 °C, 30 minutes, 25%, 0.5 M, and 100 rpm to calculate the leaching efficiency based on the leaching residue. It is confirmed that 63.5%, 97.5%, and 100% of total Cu, CuO, and zinc can be recovered, respectively. Also, the chemical analyses of the feed and tailings illustrated that Fe and Pb content had been increased in the solid residue since they are insoluble in the sulfuric acid solution. This result was in agreement with the previous research[26]. The XRD patterns of tailings (Fig. 10) illustrated similar mineralogical phases to feed samples, including: quartz, clay minerals, hematite, muscovite, smithsonite, cerussite, and anglesite; however, SEM images (Fig. 11) confirmed that Cu and Zn bearing minerals were dissolved and the lead and iron oxides in the residue are more dominant. Chemical analysis by XRF was also in agreement with the other mineralogical studies (Table 3).

<table>
<thead>
<tr>
<th>Element</th>
<th>Feed sample</th>
<th>Residue of leaching process</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>8.6</td>
<td>7.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.37</td>
<td>0.47</td>
</tr>
<tr>
<td>PbO</td>
<td>2.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.2</td>
<td>9.3</td>
</tr>
<tr>
<td>MnO</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.25</td>
<td>28.51</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>27.5</td>
<td>35.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.36</td>
<td>0.4</td>
</tr>
<tr>
<td>CuO</td>
<td>3.2</td>
<td>0.58</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.1</td>
<td>0.12</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>1.9</td>
</tr>
<tr>
<td>L.O.I</td>
<td>10.75</td>
<td>9.77</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study, the dissolution rate of a polymetallic ore containing copper, zinc, and iron was studied at various conditions. According to observations, the acid concentration significantly affected the dissolution of Cu and
Zn. In contrast, all copper and zinc minerals were leached at an acid concentration of 0.5 M, and there is no need for stronger acid. It found that the effect of particle size, 75 µm, and 300 µm, on the dissolution of all elements except zinc was negligible, which helps the industry save energy in the grinding circuits. In contrast to concentration, temperature had little effect on dissolution of these elements. The results showed that all of the copper content in the matrix of the ore was leached, whereas only a part of zinc and iron were dissolved in H$_2$SO$_4$ solutions. According to the results, under the optimum condition of 65 °C, 30 minutes, 25%, 0.5 M, and 100 rpm, 63.5%, 97.5%, and 100% of Cu, CuO, and Zn could be recovered, respectively. Iron and lead-bearing minerals remained in the leaching residue, which was confirmed by XRD, XRD, and SEM analyses.

Declarations

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

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References

9. Jergensen, G.V., Copper leaching, solvent extraction, and electrowinning technology. 1999: SME.


14. Umarova, I., G. Salijanova, and S. Avinjanova, *Study on the enrichment of polymetallic ores of the deposit Handiza*. Recommended for publication by the Scientific Research Council of the University of Petrosani, 05.03. 2019 Recommended for publication by the Academic Board of the Kryvyi Rih National University, Minutes № 7, 26.02. 2019, 2018: p. 286.


Figures
Figure 1

XRD spectra of the feed sample for leaching experiments.

Figure 2
SEM analysis of the sample prior to the leaching process (A: lead oxide, B: Clinochlore, C: hematite or iron silicate, D: polymetallic oxide)

Figure 3

Acid consumption at two different particle sizes; (a) 75 µm, and (b) 300 µm.
Figure 4

The effect of agitation rate on leaching efficiency of metals (25 °C, % solid 25, 0.25 M, 1 h).
Figure 5

The effect of leaching time on the recovery of copper, iron and zinc (25 °C, % solid 25, 0.25 M, 100 rpm).
Figure 6

The effect of H$_2$SO$_4$ concentration on the metals recovery (25 °C, % solid 25, 100 rpm, 75 µm).
Figure 7

The effect of pulp solid percentage on the leaching of Cu, CuO, Zn, and Fe (25 °C, 100 rpm, 75 µm, 0.5M H₂SO₄, 15 min)
Figure 8

The effect of particle size on leaching efficiency of Zn, Cu, and Fe (25 °C, 100 rpm, %solid 25, 0.5M H$_2$SO$_4$, 15 min).
Figure 9

The effect of temperature on the recovery of metals (100 rpm, %solid 25, 0.5M H₂SO₄, 15 min, 75µm).
Figure 10

XRD pattern of feed and residue of leaching
Figure 11

SEM images of the residue of leaching (A: lead oxide, B: Clinochlore, C: hematite or iron silicate, D: polymetallic oxide)