Optimal pH for Heap Leaching of Low Grade Copper-Cobalt-Iron Ore

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Summary

Acid heap leaching is a metal extraction process from low grade ores normally 1-2% oxidised valuable mineral using a leachant (e.g. concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}). The ore is crushed, cured, agglomerated and stacked on an impermeable pad. Raffinate dosed with concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) acid is sprayed onto the stacked ore to produce a pregnant leach solution. Though cheap the process maybe, it is affected by the pH of the leaching liquor, nominal crushing size, temperature, optimal stacking height, irrigation rate, solid-to-liquid ratio, permeability, gangue minerals, temperature, nominal crush size, ore particle size distribution affect. The aim of this paper is to investigate the most effective raffinate pH for leaching out copper and cobalt from low grade ore. The ore contains malachite (Cu\textsubscript{2}(CO\textsubscript{3})\textsubscript{2})(OH\textsubscript{2}), cobalt oxide, hematite (Fe\textsubscript{2}O\textsubscript{3}) and about 94 wt. % gangue mineral (CaCO\textsubscript{3}, CaO and SiO\textsubscript{2}) content. CaO is highly soluble in acid and SiO\textsubscript{2} is also soluble in acid when present in the form complex compounds such as calcium silicate (CaSiO\textsubscript{3}, Ca\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}) or feldspar (KAlSi\textsubscript{3}O\textsubscript{8}) and hence they significantly interfere the heap leaching process. In order to analyse the optimal pH, three samples of different composition were used in our experiments. The samples were ground to a particle size of ≤ 50mm, cured and agglomerated before leaching with the raffinate solution containing Ca\textsuperscript{2+}(12.095%), Fe\textsuperscript{3+}(0.158%), Cu\textsuperscript{2+}(0.1185%), and Co\textsuperscript{2+}(0.216%) from the solvent extraction dosed with concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) acid (98%) at different pH ranges (0.3-0.4, 0.54-0.6 and 0.7-1). The effect of the raffinate pH was analyzed by leaching the samples at different pH (0.3-0.4, 0.54-0.6 and 0.7-1) and analyzing the solution and the leach residue via atomic absorption spectrometry (AAS) technique. The one treated at a pH range of 0.54-0.6 yielded the highest concentration of copper (24gpl), cobalt (0.28gpl) and iron (3.65gpl) in the pregnant leach solution and the highest recovery of copper (42.23%), cobalt (21.90%) and iron (47.87%). The leach residue for samples 1 treated with leaching liquor (pH 0.3-0.4) were Cu\textsuperscript{2+} (0.50%), Fe\textsuperscript{3+} (1.12%), Co\textsuperscript{2+} (0.354%) and Ca\textsuperscript{2+} (0.057%). The leaching residue for sample 2 treated with leaching liquor (pH 0.54-0.6) were Cu\textsuperscript{2+} (0.065%), Fe\textsuperscript{3+} (0.057%), Co\textsuperscript{2+} (0.27%), Ca\textsuperscript{2+} (0.097%) and SiO\textsubscript{2} (0.31%). The leach residue for sample 3 treated with leaching liquor (pH 0.7-1) were Cu\textsuperscript{2+} (0.24%), Fe\textsuperscript{3+} (0.31%), Co\textsuperscript{2+} (0.31%), Ca\textsuperscript{2+} (0.25%) and SiO\textsubscript{2} (0.64%). Since almost all silica was consumed by the leaching liquor in sample 1, more silicic acid was produced as shown in equation (1) which decomposed in equation (2) to produce silica gel. The silica gel reduced the permeability of the leaching liquor by preventing its reaction with the entire ore leading to less concentrations and recoveries of the valuable (Cu, Co and Fe). The experimental results were compared with the thermodynamic prediction from the FactSage software.

\[
\begin{align*}
2\text{CaO} \cdot \text{SiO}_2(s) + 2\text{H}_2\text{SO}_4(\text{aq}) & \rightarrow 2\text{CaSO}_4(s) + \text{H}_4\text{SiO}_4(\text{aq}) \\
\text{H}_4\text{SiO}_4(\text{aq}) & \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{SiO}_2(\text{gel})
\end{align*}
\]

Keywords: raffinate, leaching, gangue, silica, pH

Introduction

Heap leaching is a metal extraction process that is commonly used for the extraction of copper, cobalt, nickel, gold, iron, silver and uranium from their low grade oxide ores using a leachant (e.g. concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}). (Hiskey, 1986; McMahon, 1964; ). The ore is crushed, cured, agglomerated and stacked on an impermeable pad. Raffinate from the solvent extraction dosed with concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}, 98%) acid is sprayed onto the stacked ore to produce a pregnant leach solution as shown in figure 1. Concentrated sulphuric acid is used in heap leaching and its cost is the most vital economic factor (Rich, 2008). This process is preferred to other leaching processes due to; (i) its low energy requirement, (ii) absence of the tailings disposal, (iii) absence of the counter-current decantation (CCD) circuits, (iv) no additional tailings impoundment, (v) suitable for treating the low grades, (vi) quick installation of the needed equipments (vii) requires low capital, operation costs and high operating flexibility because the raffinate is recycled (vii) the process is simple including the equipments (viii) integration with other treatment options (viii) by-passes the ore capital intensive stages of fine crushing, grinding and agitation leaching (ix) forecasted copper market prices (x) no solid/liquid separation that is needed after the process and (xi) less exposure to environmental risks (Bartlett, 1998). The main minerals are malachite (Cu\textsubscript{2}CO\textsubscript{3}(OH\textsubscript{2}) and cobalt monoxide (CoO) minerals whereas the major gangue minerals are calcite (CaCO\textsubscript{3}), quicklime (CaO), hematite (Fe\textsubscript{2}O\textsubscript{3}) and calcium silicate (2CaO.SiO\textsubscript{2}). Apart from the pH of the leaching liquor, the process is also influenced by ore mineralogy, surface properties, solid-to-liquid ratio, permeability, irrigation flow rate, pore size distribution, air distribution, height of the heap, gangue minerals, temperature, liberation characteristic of an ore and ore particle size distribution affect (Mular et al., 2005; Kunkel, 2008). However, the optimal pH of the leaching liquor on the ore containing low grade copper, cobalt and iron oxides has never been investigated. When the pad is treated with leaching liquor, reactions 1-7 take place. The silicic acid produced breaks down to silica gel and water as shown in equation 7.

Thermodynamic Prediction

The Cu-Co-Fe-Ca-SiO\textsubscript{2} system at 298K is shown in as
figure 2 and a number of observations can be made:
1. Calcium oxide and cobalt oxide are soluble in acidic media.
2. SiO$_2$ from calcium silicate can transform to H$_2$SiO$_4$, both under reducing or oxidizing atmospheres.
3. Malachite is reduced to metallic copper at low electrode potential or under reducing atmosphere.
4. Fe$_2$O$_3$ is generally insoluble at pH>3.1
5. Fe$_2$O$_3$ is insoluble at pH<3, under oxidizing atmosphere (higher electrode potential).
6. Calcium is soluble both under reducing and oxidising atmosphere.

Based on the EpH diagram in figure 2, it can be concluded that CaO and SiO$_2$ are the difficult impurities to deal with during acid leaching of the Cu-Co oxide minerals.

This is because they are soluble under reducing and oxidizing atmosphere. Iron can be precipitated as Fe$_2$O$_3$ by raising the electrode potential or through oxidizing the solution with air. It is for this reason that iron is commonly removed from the leach solution through precipitation under atmospheric conditions (21% O$_2$).

**Experiment**
The mineral sample was determined by the X-ray diffraction analysis. The main crystalline phases in the ore were malachite (Cu$_2$(CO$_3$)(OH)$_2$), cobalt (II) oxide (CoO), hematite (Fe$_2$O$_3$), calcium carbonate (CaCO$_3$), calcium silicate (CaO.SiO$_2$) and quick lime (CaO). The composition of metallic phases were determined by the atomic absorption spectrometry shown in table 1. The ore was dried in

<table>
<thead>
<tr>
<th>Cu</th>
<th>Fe</th>
<th>Co</th>
<th>Ca</th>
<th>C</th>
<th>SiO$_2$</th>
<th>H$_2$O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.51</td>
<td>2.81</td>
<td>0.682</td>
<td>2.61</td>
<td>1.31</td>
<td>1.42</td>
<td>0.51</td>
<td>88.15</td>
</tr>
</tbody>
</table>

**Fig. 1 Flowsheet for the production of copper cathodes through heap leach operation**
Rys. 1 Schemat technologiczny produkcji katod miedzianych po wyługowania hałd

**Fig. 2 EpH diagram for the Cu-Co-Fe-Ca-SiO$_2$ system at 298K, constructed using HSC software**
Rys. 2 Diagram EpH dla układu Cu-Fe-Ca-SiO$_2$ w temperaturze 298K stworzony przy użyciu oprogramowania HSC
Cu₂CO₃(OH)₂(aq) + 2H₂SO₄(aq) → 2CuSO₄(aq) + 3H₂O(l) + CO₂(g)  \quad (1)

CoO(s) + H₂SO₄(aq) → CoSO₄(aq) + H₂O(l)  \quad (2)

Fe₂O₃(s) + 3H₂SO₄(aq) → Fe₂(SO₄)₃(aq) + 3H₂O(l)  \quad (3)

CaCO₃(s) + H₂SO₄(aq) → CaSO₄(aq) + H₂O(l) + CO₂(g)  \quad (4)

CaO(s) + H₂SO₄(aq) → CaSO₄(aq) + H₂O(l)  \quad (5)

2CaO·SiO₂(s) + 2H₂SO₄(aq) → 2CaSO₄(aq) + H₂SiO₄(aq)  \quad (6)

H₂SiO₄(l) → 2H₂O(l) + SiO₂(g)  \quad (7)

The moisture content was calculated by subtracting the weight of dried sample (Mdry) from the initial or undried sample (equation 5). The presence of carbon from malachite and calcium carbonate was determined by LECO-444 SC analyser.

Three samples 1, 2 and 3 were determined by atomic absorption spectrometry shown in table 2. The metallic phases in the residues for samples 1, 2 and 3 were determined by atomic absorption spectrometry (equation 6). The presence of carbon from malachite and calcium carbonate was determined by LECO-444 SC analyser.

Moisture content (\(\mu\) %) = \(\frac{M_{wet} - M_{dry}}{M_{wet}} \times 100\)  \quad (8)

Results and Discussion

The analyses of Cu, Co, Fe, Ca and SiO₂ in the leach residue after leaching show that SiO₂ is absent in the leach residue for sample 1. The absence of SiO₂ in the leach residue for sample 1 shows that all SiO₂ was dissolved into the acid during the leaching process. It can also be noticed from table 2 that the concentration of calcium is very low in the leach residues for all the samples implying that it was mainly dissolved during the process since it is more reactive than the other metals in the samples. The dissolution of calcium in acid agrees with the thermodynamic prediction in figure 2 as calcium is soluble in acid at pH below 7. The presence of calcium in the pregnant solution is undesirable as it is expensive to remove. However, the silicic acid produced disintegrated producing silica gel (SiO₂(gel)) (Banza et al., 2002) as shown in equation 7 on the ore thereby reducing its permeability. The permeability of the samples ores affects the extracted metal concentrations and recoveries. The more permeable the ore, the more are the extracted metal concentrations and recoveries in the pregnant leach solution. This is because the sulphuric acid will not penetrate to all the parts of the ore to react with it. During the early days of the experiment, the concentrations and recoveries produced were very promising. However, with the increase in the production and disintegration of the silicic acid, the concentrations of the metals in the pregnant leach solution decreased.

From the results in figure 3, the copper concentration in this pH (0.3-0.4) increased from 3gpl on the first (1) day to 16gpl on the third (3) day. However, due to the increase in calcium and silica gel, the concentration of the copper decreased until on the six (6) day to 3.0gpl. In figure 4 and 5, the highest concentration of cobalt and iron were 0.18gpl on the fourth (4) day and 3gpl on the third (3) day. Moreover, copper ore remained as compared to the other samples as shown in table 2. This was because more leaching liquor reacted with calcium which is more soluble that Cu, Fe and silica. The remaining leaching liquor could not actively react with the valuable metals because of reduced permeability. The total leaching time was 6 days.

Sample 2 ore was leached with leaching liquor (0.54≤pH≤ 0.6) and according to table 2, its silica was 0.31% wt. This implied that though silicic acid was produced and disintegrated, it was not as much as in sample 1 ore. Hence reduction in permeability was inevitable but not compared to sample 1 ore. This is the reason why sample 2 produced highest concentrations of copper (24gpl on 4th day), cobalt (0.28gpl on 3rd day) and iron (3.65gpl on 2nd day). The total leaching time was 6 days.

However, as shown in table 2 sample 3 had more silica in the residue than any other sample hence permeability must be expected to be more as compared to other samples. However, though it produced better concentration of the valuable metals than sample 1 due to the pH of the leaching liquor, its total leaching time was 7 days.

When the metal concentration in the pregnant leach solution is affected the recovery is equally affected. Since the metal concentration was affected by the reduction in permeability, the highest recovery and net recovery of copper, cobalt and iron in all samples ores took place in sample 2 ore as shown in figures 6, 7 and 8. The highest recovery of copper, cobalt and iron were 42.23% on the third day, 21.90% on the fourth day and 47.87% on the fourth day. However, the net recoveries of copper, cobalt and iron as shown in figures 6, 7 and 8 were 97%, 60% and 92%.

Conclusion

1. The optimum pH was between 0.54-0.6 since the recovery and concentrations of the copper, cobalt and iron were higher in the pregnant leach solution. This was because pH range 0.3-0.4 consumed more gange materials especially CaO, CaCO₃ and CaSiO₃ than other pH ranges and pH range 0.7-1 produced promising recoveries and
Fig. 3 Concentration of Cu in pregnant leach solution against time
Rys. 3 Zmiana stężenia Cu w roztworze w czasie ługowania

Fig. 4 Concentration of Co in pregnant leach solution against time
Rys. 4 Zmiana stężenie Co w roztworze ługującym w czasie

Fig. 5 Concentration of Fe in pregnant leach solution against time
Rys. 5 Stężenie Fe w roztworze ługującym w czasie
Tab. 2 Chemical composition of the leach residues (%wt)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Fe</th>
<th>Co</th>
<th>Ca</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.30</td>
<td>1.12</td>
<td>0.354</td>
<td>0.057</td>
<td>-</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.065</td>
<td>0.057</td>
<td>0.27</td>
<td>0.097</td>
<td>0.31</td>
</tr>
<tr>
<td>Sample 3</td>
<td>30.24</td>
<td>0.31</td>
<td>0.27</td>
<td>0.25</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Fig. 6 Recovery of Copper from pregnant leach solution
Rys. 6 Uzysk miedzi z roztworu ługującego

Fig. 7 Recovery of Fe from the pregnant leach solution
Rys. 7 Uzysk żelaza z roztworu ługującego

Fig. 8 Recovery of Co from the pregnant leach solution
Rys. 8 Uzysk Co z roztworu ługującego
concentrations except that its leaching time was 7 days.
2. The more gangue minerals leached the less the recovery as shown in table 2.
3. The experimental results were in harmony with the thermodynamic prediction.

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Literatura - References


Optymalne pH dla ługowania zwałów rudy o niskiej jakości miedzi, kobaltu i żelaza

Kwaśnie ługowanie zwału jest procesem ekstrakcji metali z rud o niskiej klasie zazwyczaj 1-2% utlenionego wartościowego minerału przy zastosowaniu ługowania (na przykład stężonym kwasem siarkowym (H₂SO₄). Rudę kruszy się, konserwuje, aglomeruje i umieszcza na nieprzepuszczalnej podkładce. Rafinat dozowany ze stężonym kwasem siarkowym (H₂SO₄) jest natryskiwany na ułożoną rudę w celu wytworzenia macierzystego roztworu ługowego. Chociaż sposób ten może być tani, to zależy on od pH roztworu ługującego, nominalnej wielkości kruszca, temperatury, optymalnej wysokości spiętrzania, stopnia izracji, stosunku ciała stałego do cieczy, przepuszczalności, skaly płonnej, Temperatury, nominalnej wielkości zgniatania, wpływu rozkładu wielkości cząstek rudy. Celem niniejszej pracy jest zbadanie optymalnej wartości pH, w eksperymencie zostały użyt trzy próbki o różnej kompozycji. Próbki zostały zmielone do rozmiaru ≤ 50mm, zakonserwowane (CaSiO₃) i aglomerowane przed ługowaniem w roztworze rafinatu zawierającym CaO, Al₂O₃, SiO₂. CaO jest wysoko rozpuszczalny w kwasie i SiO₂ jest również rozpuszczalny w kwasie, jeśli jest obecny w formie związków kompleksowych, takich jak krzemian wapnia (CaSiO₃) i skaleń (KAlSi₃O₈), a tym samym może znacznie zakłócić proces ługowania zwału. W celu analizy optymalnej wartości pH, w eksperymencie zostały użyt trzy próbki o różnej kompozycji. Próbki zostały zmielone do rozmiaru ≤ 50mm, zakonserwowane i aglomerowane przed ługowaniem w roztworze rafinatu zawierającym CaO (12,095%), FeO (0,158%), CaO (0,1185%), oraz CoO (0,216%) pochodzącym od ekstrakcji rozpuszczalnikowej dawkowanej z stężonym kwasem siarkowym (98%) w różnych zakresach pH (0,3-0,4, 0,54-0,6 oraz 0,7-1). Wpływ pH rafinatu był analizowany przez ługowanie próbek o różnym pH (0,3-0,4, 0,54-0,6 oraz 0,7-1) oraz 0,6 oraz 0,7-1) i analizę roztworu a także pozostałości ługu za pomocą techniki absorpcji specyficznej absorpcji spektroskopii atomowej (ASA). Próbki, która traktowano roztworem o zakresie pH 0,54-0,6 wykazuje najczęściej w stężenie miedzi (24gpl), kobaltu (0,28gpl) i żelaza (3,65gpl) w macierzystym roztworze ługowym i największy odkaz miedzi (42,23%), kobaltu (21,90%) i żelaza (47,87%). Ostateczna masa dla próbki 1 traktowana płynem ługującym (pH 0,3-0,4) miała CaO (0,50%), FeO (1,12%), Co (0,354%) oraz CaO (0,07%). Ostateczna masa dla próbki 1 traktowana cieccią ługującą (pH 0,54-0,6) miała CaO (0,354%), FeO (0,07%), CaO (0,27%), CaO (0,097%) oraz SiO₂ (0,31%). Ostateczna masa dla próbki 2 traktowana płynem ługującym (pH 0,7-1) zawierała CaO (0,24%), FeO (0,31%), Co (0,31%), CaO (0,25%) oraz SiO₂ (0,64%). Ponieważ prawie cała krzemionka została zużyta przez płyn ługujący w próbie 1, większość kwasu krzemionkowego została wytworzone, jak przedstawiono w równaniu (1), który rozkłada się w równaniu (2), z wytworzeniem żelu krzemionkowego. Żel krzemionkowy zmniejsza przepuszczalność cieczy ługującej, zapobiegając przed reakcją z całą rudą, co prowadzi do mniejszych stężeń i odzyskiwaniu wartościowych Cu, Co i Fe. Wyniki doświadczalne porównano z prognozami termodynamicznymi z oprogramowania FactSage.

\[
\begin{align*}
2\text{CaO} \cdot \text{SiO}_2(s) + 2\text{H}_2\text{SO}_4(aq) & \rightarrow 2\text{CaSO}_4(s) + \text{H}_2\text{SiO}_4(aq) \\
\text{H}_2\text{SiO}_4(aq) & \rightarrow \text{H}_2\text{O}(l) + \text{SiO}_2(g) 
\end{align*}
\]

Słowa kluczowe: rafinacja, ługowanie, skala płonna, krzem, pH

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