A semi-empirical kinetic model was developed for the atmospheric leaching of a Ni-Cu converter matte in copper sulphate-sulphuric acid solution.

by R.M. Lamya* and L. Lorenzen†

Synopsis

A semi-empirical kinetic model was developed for the atmospheric leaching of a Ni-Cu matte in copper sulphate-sulphuric acid solution. Kinetics of the leaching process was studied as a function of initial copper ion concentration, initial acid concentration, temperature, stirring rate and particle size distribution. The kinetic model was developed on the basis of the leaching mechanism and chemical reactions of the leaching system investigated, and was evaluated by comparing the model predictions to experimental data. The model was found to satisfactorily fit the trends in the leaching of the metals, namely copper, nickel, cobalt and iron.

Introduction

Nickel-copper matte is hydrometallurgically treated to produce marketable base metals, namely nickel, copper and cobalt, as well as precious metals. The hydrometallurgical processing of the Ni-Cu matte involves leaching stages in which the metal values are first dissolved and later recovered as final products in the subsequent stages. The leaching process is normally carried out in acidic copper-nickel sulphate solution, with oxygen being the oxidizing agent. Numerous studies have been conducted on the leaching of the Ni-Cu matte under atmospheric conditions. Other workers have studied the operations and improvements made to the existing Ni-Cu matte refining processes. Nickel-copper matte leaching processes may entail an atmospheric leach followed by pressure leaching stages, or the leaching process route may involve a preleach stage (repulping stage) prior to pressure leaching stages. During atmospheric leaching and in the preleach stage substantial quantities of nickel and cobalt are dissolved while copper is precipitated via the cementation process; any precious metals present remain in the solids. The precipitated copper and unleached nickel and cobalt are leached in the subsequent pressure leaching stages in order to produce precious metal concentrates without or with only traces of base metals.

Material

The material used in this study was a Ni-Cu converter matte with the following chemical composition: 47.9 per cent nickel, 31.0 per cent copper, 20.4 per cent sulphur and small amounts of iron and cobalt. The principal phases present in the matte were heazlewoodite (Ni₃S₂), chalcocite (Cu₂S), djurleite (Cu₁.₉S) and nickel-rich alloy. The as-received matte was ground to 50 per cent -45 µm. A portion of the matte was screened in three different size fractions namely -300+150, -106+45 and -45 although only the -106+45 and -45 µm size fractions were used in the kinetic model. The leaching solution was acidic copper...
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The chemical reaction rates are presented in terms of the rate of disappearance of a species, according to Equation [1]:

\[ r_A = \frac{1}{V} \frac{dN_A}{dt} = \text{moles of } A \text{ formed} \quad \text{(reaction volume)/(time)} \quad [1] \]

where \( V \) is the reaction volume, \( N_A \) is the number of moles of species \( A \), and \( t \) is the reaction time. Assuming a constant reaction volume, the rate of disappearance of \( A \) is given by:

\[ \frac{dN_A}{dt} = k_A \cdot C_B \quad [5] \]

This reaction rate expression takes the form shown in Equation [5].

The actual volume of the reaction mixture decreased slightly during the experiments as samples were taken out for analysis. However, the volume taken out was considered insignificant in comparison to that which remained. Thus the reaction volume term in Equation [2] was taken as a constant, and was absorbed into the rate constants used in the model.

If we consider a single elementary homogeneous reaction with a stoichiometric equation given by:

\[ A = B \leftrightarrow D \quad [3] \]

the rate of disappearance of \( A \) is given by:

\[ -r_A = k_C \cdot C_B \quad [4] \]

where \( k \) is the reaction rate constant and \( C_A \) and \( C_B \) are the concentrations of species \( A \) and \( B \) respectively. The negative sign indicates the disappearance of species \( A \).

Combining Equations [2] and [4], the reaction rate expression takes the form shown in Equation [5]:

\[ \frac{dN_A}{dt} = k_A \cdot C_B \quad [5] \]

### Experimental procedure

The leaching experiments were performed in a 3-litre stainless steel vessel provided with baffles, a cover, a thermometer, a pH electrode and equipped with a variable speed overhead stirrer. The stirrer had a flat-blade turbine type impeller and the rate of stirring was set by a tachometer. The set-up was placed in a water bath with temperature controls. The cover of the reaction vessel was fitted such that air ingression into the reactor during the experiments was minimal. This was done to simulate conditions existing in the preleach tank in the commercial plant. The cover of the vessel had ports for holding a thermometer, a pH electrode and for taking samples. Solution samples were analysed for Ni, Cu, Co and Fe using inductively coupled plasma (ICP). Solid samples were mostly analysed by ICP, although some were analysed by dissolving the solid sample in perchloric acid and/or aqua regia and analysing for the same elements using the ICP.

### Reaction kinetic modelling

The semi-empirical kinetic model was developed on the basis of the leaching mechanism and chemical reactions occurring during the leaching process investigated. The model makes allowance for variations in the values of the leaching parameters such as initial copper concentration, temperature, stirring rate, particle size and initial acid concentration. Under the leaching conditions employed in this study (where no oxidant was added) the sulphide minerals were expected to be marginally leached. Therefore, the chemical reactions considered in the model are those that are most likely to occur to a significant degree during the leaching process.

### Chemical reaction rates

The chemical reaction rates are presented in terms of the rate of change of the number of moles of the species in the reaction volume, according to Equation [1]:

\[ r_A = \frac{1}{V} \frac{dN_A}{dt} = \text{moles of } A \text{ formed} \quad \text{(reaction volume)/(time)} \quad [1] \]

\[ \frac{dN_A}{dt} = k_A \cdot C_B \quad [5] \]

\[ -r_A = k_C \cdot C_B \quad [4] \]

\[ \frac{dN_A}{dt} = k_A \cdot C_B \quad [5] \]

### Table I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>60, 80</td>
</tr>
<tr>
<td>Stirring rate (rpm)</td>
<td>205, 400</td>
</tr>
<tr>
<td>Initial particle size (µm)</td>
<td>-106+45, -45</td>
</tr>
<tr>
<td>Initial spent electrolyte copper concentration (g/l)</td>
<td>25, 48</td>
</tr>
<tr>
<td>Initial spent electrolyte acid concentration (g/l)</td>
<td>90, 125</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leaching parameter values that were investigated</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>60, 80</td>
</tr>
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</tr>
</tbody>
</table>
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The reaction rate expression for Equation [10] is given by:

\[
\frac{dN_{\text{A}(10)}}{dt} = n_A K_{10} C_{\text{Cu}^{1.2}}
\]

where \( \frac{dN_{\text{A}}}{dt} \) is the rate of production of species A, \( n_A \) is the stoichiometric coefficient of species A and K is a first-order rate constant incorporating the reaction volume term from Equation [2].

Equation [11] was used to develop the reaction rate expressions for the dissolution and formation of various species during the leaching process, as a result of the cementation process (Equations [10A]–[10G]).

\[
\frac{dNi^{2+}}{dt} = \frac{8}{3} K_{10} C_{\text{Cu}^{1.2}}
\]

[10A]

\[
\frac{dCu^{2+}}{dt} = -\frac{8}{3} K_{10} C_{\text{Cu}^{1.2}}
\]

[10B]

\[
\frac{dNi^{0}}{dt} = -\frac{2}{3} K_{10} C_{\text{Cu}^{1.2}}
\]

[10C]

\[
\frac{dNi_{2}S_{2}}{dt} = -K_{10} C_{\text{Cu}^{1.2}}
\]

[10D]

\[
\frac{dCu_{S}}{dt} = K_{10} C_{\text{Cu}^{1.2}}
\]

[10E]

\[
\frac{dNiS}{dt} = K_{10} C_{\text{Cu}^{1.2}}
\]

[10F]

\[
\frac{dCu^{0}}{dt} = \frac{2}{3} K_{10} C_{\text{Cu}^{1.2}}
\]

[10G]

The leaching of iron by the cementation process (Equation [12]) was assumed to be insignificant due to the presence of the iron alloy as small inclusions randomly distributed in the matte. The matte had to be attacked by the acid and penetrated to leach the iron grains embedded in the matte; besides the quantity of iron in the matte was very small (0.60%). It was therefore assumed that the iron was leached mainly by the acid according to Reaction [15].

\[
Fe^{0} + Cu^{2+} = Fe^{2+} + Cu^{0}
\]

[12]

Matte leaching by direct acid attack

The nickel alloy was leached by acid according to the following reaction:

\[
Ni^{0} + 2H^{+} + 1/2O_{2} \rightarrow Ni^{2+} + H_{2}O
\]

[13]

The rate expression for Reaction [13] is given by Equation [14]:

\[
\frac{dN_{\text{A}(8.13)}}{dt} = n_A K_{13} C_{H^{+}}, P_{O_{2}}
\]

[14]

where \( \frac{dN_{\text{A}}}{dt} \), \( n_A \), and \( K_{13} \) are as explained earlier for Equation [11], \( C_{H^{+}} \) is the acid concentration and \( P_{O_{2}} \) is the partial pressure of oxygen. But no oxygen was added to the system, so the \( O_{2} \) partial pressure was taken to be the same as the atmospheric pressure and was assumed to be constant.

Therefore, the oxygen partial pressure term in all the rate expressions for the dissolution and formation of species due to leaching by acid has been omitted. The rate expressions for Reaction [13] are given by Equations [13A]–[13C]:

\[
\frac{dNi^{2+}}{dt} = k_{13} C_{H^{+}}
\]

[13A]

\[
\frac{dH^{+}}{dt} = -2k_{13} C_{H^{+}}
\]

[13B]

\[
\frac{dNi^{0}}{dt} = -k_{13} C_{H^{+}}
\]

[13C]

It should be noted that for modelling purposes, reactions of sulphide minerals with acid have not been considered due to the fact that the acid will mainly attack metal alloys, especially in this case where no oxidant was added.

The iron alloy present in the matte was leached according to Reaction [15]:

\[
Fe^{0} + 2H^{+} + 1/2O_{2} \rightarrow Fe^{2+} + H_{2}O
\]

[15]

\[
Fe^{3+} + 3H_{2}O \rightarrow Fe(OH)_{3} + 3H^{+}
\]

[16]

When the pH of the leaching system rose sufficiently, iron precipitated from the solution. For modelling purposes, it has been assumed that the precipitation occurs via Equation [16]. The rate expressions for Reaction [15] are represented by Equations [15A]–[15C], and again the \( O_{2} \) partial pressure term has been assumed constant.

\[
\frac{dFe^{2+}}{dt} = k_{15} C_{H^{+}}
\]

[15A]

\[
\frac{dFe^{0}}{dt} = -k_{15} C_{H^{+}}
\]

[15B]

\[
\frac{dFe(OH)_{3}}{dt} = k_{15} C_{Fe^{3+}}
\]

[15C]

It was noted that any iron present as FeS would not have leached to a significant degree under the conditions employed in this study. The cobalt alloy was leached according to Reaction [17]:

\[
Co + 2H^{+} + 1/2O_{2} \rightarrow Co^{2+} + H_{2}O
\]

[17]

The reaction rate expressions for Equation [17] are given below. As stated earlier, the oxygen partial pressure was constant (atmospheric pressure) and hence it was absorbed into the rate constant, \( K_{17} \).

\[
\frac{dCo^{2+}}{dt} = k_{17} C_{H^{+}}
\]

[17A]
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\[
\frac{dH^+}{dt} = -2k_{17}C_{H^+}. \tag{17B}
\]

\[
\frac{dCo^2}{dt} = -k_{17}C_{H^+}. \tag{17C}
\]

**Reaction rate constants**

The empirical rate constants $K_{10}$, $K_{13}$, $K_{15}$, $K_{16}$ and $K_{17}$ were estimated and fine tuned to provide the best possible fit to the experimental data. A set of constants that enabled the model to accurately simulate the experimental data is presented in Table II. The reaction rate constants incorporate expressions that can predict effect of variations in temperature, particle size, stirring rate, initial acid and copper concentrations. The leaching rate constants also incorporate a term for the shrinking core leaching effect. This is because the Ni alloy occurs as small inclusions randomly distributed in the matte particles. Hence, pores have to form for the leaching solution to reach the Ni alloy particles. In general the reaction rate constants are of the form:

\[
K_i = A K_{H^+}/Cu_{i} K_{T,i} Z
\]

where $K_i$ is the reaction rate constant for Reaction (i).

The terms in the reaction rate constant expression represent the following:

- $A$ is the surface area factor that accounts for the effect of variation in the effective surface area of the matte particles.
- $K_{H^+}/Cu_{i}$ is the reaction rate constant that accounts for the effect of initial acid or copper concentration.
- $K_{T,i}$ is the term that accounts for the effect of variations in the temperature. The effect of temperature is represented by the Arrhenius law, and may be written as:

\[
A_{i} = A_{i}e^{\frac{-E_a}{RT}}
\]

where $A_{i}$ is the frequency factor of reaction (i), $R$ is the gas constant and $E_a$ is the activation energy of Reaction (i).

- $Z$ is the term that accounts for the shrinking core leaching effect, and in this case applies to reactions where Ni alloy leaching takes place. This term is of the form:

\[
Z = \left( \frac{N_{Ni alloy}}{N_{Ni alloy(0)}} \right)^{\frac{1}{3}}
\]

where $N_{Ni alloy}$ is the moles of the Ni alloy at time $t$, and $N_{Ni alloy(0)}$ is the initial moles of the alloy in the matte.

**Combined reaction rate expressions**

The combined reaction rate expressions for the dissolution and formation of various species during the leaching process are represented by Equations [21]-[31]. These rate expressions were solved numerically by the 4th order Runge-Kutta method using the Excel spreadsheet, after values of the rate constants $K_{10}$, $K_{13}$, $K_{15}$, $K_{16}$ and $K_{17}$ were determined.

It should be noted that in the case of iron it was not possible to distinguish between Fe$^{2+}$ and Fe$^{3+}$, hence they have been represented as total Fe concentration.

\[
\frac{dNi^{2+}}{dt} = \frac{8}{3} k_{10}C_{Cu^{2+}} + k_{13}C_{H^+} \tag{21}
\]

\[
\frac{dCu^{2+}}{dt} = \frac{8}{3} k_{10}C_{Cu^{2+}} \tag{22}
\]

\[
\frac{dFe_{Total}}{dt} = -k_{15}C_{H^+} - k_{16}C_{Fe^{2+}} \tag{23}
\]

\[
\frac{dCo^{2+}}{dt} = k_{17}C_{H^+} \tag{24}
\]

\[
\frac{dH^+}{dt} = -2k_{17}C_{H^+} \tag{25}
\]

\[
\frac{dNi^0}{dt} = -\frac{2}{3} k_{10}C_{Cu^{2+}} - k_{15}C_{H^+} \tag{26}
\]

\[
\frac{dCu^0}{dt} = \frac{2}{3} k_{10}C_{Cu^{2+}} \tag{27}
\]

\[
\frac{dCu_{S}}{dt} = k_{10}C_{Cu^{2+}} \tag{28}
\]

\[
\frac{dNiS}{dt} = k_{10}C_{Cu^{2+}} \tag{29}
\]

\[
\frac{dFe^0}{dt} = -k_{15}C_{H^+} \tag{30}
\]

**Table II**

**Reaction rate constants used in the kinetic model**

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>$K_{10}$</th>
<th>$K_{13}$</th>
<th>$K_{15}$</th>
<th>$K_{16}$</th>
<th>$K_{17}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td>60</td>
<td>0.298</td>
<td>0.679</td>
<td>0.0881</td>
<td>0.082</td>
</tr>
<tr>
<td>Stirring rate (rpm)</td>
<td>80</td>
<td>1.728</td>
<td>0.979</td>
<td>0.0981</td>
<td>0.082</td>
</tr>
<tr>
<td>205</td>
<td>0.298</td>
<td>0.679</td>
<td>0.0881</td>
<td>0.082</td>
<td>0.032</td>
</tr>
<tr>
<td>400</td>
<td>0.249</td>
<td>3.19</td>
<td>0.1109</td>
<td>2.02</td>
<td>0.032</td>
</tr>
<tr>
<td>-45</td>
<td>1.161</td>
<td>1.409</td>
<td>0.171</td>
<td>0.261</td>
<td>0.035</td>
</tr>
<tr>
<td>-106.45</td>
<td>0.498</td>
<td>0.976</td>
<td>0.124</td>
<td>0.095</td>
<td>0.035</td>
</tr>
<tr>
<td>Initial acid (g/l)</td>
<td>90</td>
<td>0.298</td>
<td>0.679</td>
<td>0.0981</td>
<td>0.082</td>
</tr>
<tr>
<td>125</td>
<td>0.173</td>
<td>1.532</td>
<td>0.086</td>
<td>0.082</td>
<td>0.032</td>
</tr>
<tr>
<td>Initial Cu (g/l)</td>
<td>25</td>
<td>0.298</td>
<td>0.679</td>
<td>0.0881</td>
<td>0.082</td>
</tr>
<tr>
<td>48</td>
<td>0.0867</td>
<td>1.545</td>
<td>0.0881</td>
<td>0.082</td>
<td>0.032</td>
</tr>
</tbody>
</table>
Evaluation of the kinetic model

The kinetic model was evaluated by comparing the model predictions to experimental data. The model was found to satisfactorily fit the trends in the leaching of the metals. Due to the fact that in most of the experiments only solution samples were analysed for metal concentrations when determining the effect of variations in the leaching parameters, the accuracy of the model is mainly determined by how well its predictions fit the nickel, copper, cobalt, total iron and acid concentrations in the solution. It was not possible to analyse all the solid samples because of the difficult inherent in the analysis of large numbers of solid samples. The accuracy of analysis of solid samples was also a concern as the matte did not leach to a significant degree under the conditions employed in this study. Therefore, the rates of decrease and formation of solid species during the leaching of the matte were not evaluated. However, Equations [26]–[31] could be used to predict the leaching and formation the solid species, since any transformation in the mineral phases are caused by the leaching process.

A comparison of the model predictions and experimental data for the dissolved species during the leaching process for different conditions is presented in Figures 1–7. It can be seen that the kinetic model was able to predict the leaching of the matte reasonably accurately. However, it should be mentioned that some of the model graphs could not fit the experimental data well probably due to the fact that a complex reaction mechanism takes place in the system where some metals dissolve and others precipitate. It is also understood that the model is basic and was intended to give a general trend in the leaching behaviour of the metals, and can be improved upon.

Conclusion

A semi-empirical kinetic model was developed on the basis of the leaching mechanism and chemical reactions of the leaching system investigated. The model makes allowance for variations in the values of the leaching parameters such as initial copper concentration, temperature, stirring rate, particle size and initial acid concentration. Under the leaching conditions employed in this study (where no oxidant was added) the sulphide minerals were not expected to leach to a significant degree. Therefore, the chemical reactions considered in the model were those that are most likely to occur to a significant degree during the leaching process. The kinetic model was evaluated by comparing the model predictions to experimental data. A comparison of the model predictions and the experimental data for the dissolved species during the leaching process showed that the model was able to satisfactorily fit the trends in the leaching of the metals. The model can be used to give an indication of the effect of variation in process parameters, such as initial acid and aqueous copper concentrations of the leaching solution, on the leaching process.
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References


