A Generalized Kinetic Model for Hydrometallurgical Processes

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Abstract

In electrochemical leaching processes the solid must be an electric conductor, e.g., a metal, or a semiconductor, e.g., certain metal sulfides or oxides. Reaction takes place by the transfer of electrons at the solid surface and involves oxidation–reduction processes that take place simultaneously at two different locations not far from each other. At one location, electrons are picked up by a depolarizer, D, in solution, e.g., O$_2$, H$^+$, etc. (the cathodic zone) and at another location metal ions are released in solution (the anodic zone) where they react with reagent C. A single kinetic law derived theoretically is obeyed: Rate $= k_1k_2A[D][C] / (k_1[D] + k_2[C])$ where $k_1$ and $k_2$ are constants, and $A$ is the total surface area of the dissolving solid.

KEYWORDS: kinetics of leaching, leaching of metals, leaching of oxides, leaching of sulfides

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INTRODUCTION

Dissolution of minerals plays an important role in hydrometallurgy [1,2]. Mathematical models of leaching solids [3-7] are the basic ingredients of hydrometallurgical process simulators used for a variety of purposes [8,9]. For example:

- Plant design, i.e., selection of the leaching flowsheet and equipment size [10].
- Optimization of operating conditions of an existing plant, such as reagent flow rates, temperatures, solid / liquid ratio, particle size distribution of the material to be leached, and concentration of oxygen in the gas phase [11].
- Real-time optimization including automatic control and maximization of the metallurgical efficiency and / or economic value in the industrial context where the ore to be treated exhibits strong variations in properties [12,13].

The models involve a quantitative description of the mixing properties of the slurry, gas dissolution rate, equipment hydrodynamics, the chemical equilibrium, and the leaching kinetics. The latter usually is the most critical part of the process model since it requires a description of the dissolution mechanisms.

The kinetics of leaching of a solid in an aqueous phase depends primarily on the nature of the solid whether it is ionic, covalent, or metallic. Since bonding in solids is intermediate between these three extreme cases, a variety of leaching processes may be identified. These may be physical, chemical, and electrochemical. In electrolytic processes, an outside potential (EMF) is imposed on the solid which is made as anode in an electrolytic cell to cause its dissolution.

Physical processes

In this case the aqueous phase is water and there is no chemical transformation. This is the simplest case and applies mainly for ionic solids for example, sodium chloride. Physical processes are diffusion-controlled, therefore they are strongly influenced by the speed of agitation and less influenced by temperature.

Chemical processes

In these cases the crystalline solid may be partly ionic and partly covalent or mainly covalent. The first type of solids covers a variety of compounds: oxides, hydroxides, sulfides, sulfates, some halides and carbonates while the second type...
covers mainly silica and the silicates. These are insoluble in water but may be solubilized in the presence of a certain reagent in solution. Because of their slightly ionic character, partly ionic and partly covalent solids form minor amounts of ions when they are added to water. Thus, when a crystalline solid MX, where M is a divalent metal and X is a divalent anion, is in contact with water the following equilibrium will be set up:

\[
MX(s) \rightleftharpoons M^{2+}(aq) + X^{2-}(aq) \quad K = [M^{2+}][X^{2-}]
\]

The value of the equilibrium constant is so small and equilibrium is disrupted when the concentration of any of the ions \(M^{2+}\) or \(X^{2-}\) is decreased, thus more solid will go into solution to keep the value of \(K\) constant. Decreasing any of these ions may be the result of a neutralization reaction, complex formation, displacement, oxidation, or protonation. The rate of dissolution increases with increased concentration of the reagent and with increased temperature.

Covalent bond solids, e.g., that between silicon and oxygen in silica and the silicates, is a strong bond that cannot be broken easily by aqueous solutions. As a result of the strong Si–O bond, silica is not solubilized even by boiling with concentrated acids except hydrofluoric acid because of the formation of SiF\(_4\) which is a volatile gas.

**Electrochemical Processes**

These processes differ from the previous ones in the following aspects:

- The solid is a conductor, e.g., a metal, or a solid with partially ionic and partially covalent bonds that possesses semiconducting properties, e.g., UO\(_2\), ZnS, and CuFeS\(_2\).
- There is a transfer of electrons from the solid phase to the reacting species in solution, i.e., the process involves an oxidation–reduction couple. The ions or molecules in solution simply diffuse through the boundary layer to meet the solid surface to pick up electrons.
- The solid dissolves at certain localized points while the electron transfer takes place at other points usually much further.
- The oxidation and the reduction reactions proceed simultaneously.
- The kinetics of these reactions are influenced by the presence of lattice defects in the solid and/or the presence of trace impurity which may increase or decrease the electrical conductivity of the solid, and hence the availability of the electrons.
- The rate of dissolution exhibits three different forms:
  - Rate increases with increased reagent concentration.
- Rate increases with increased reagent concentration then levels off.
- Rate increases with increased reagent concentration, goes through a maximum, then decreases gradually.

**KINETICS OF ELECTROCHEMICAL REACTIONS**

In electrochemical leaching processes involving transfer of electrons the rate will depend on one of the reagents only within a certain concentration region beyond which it will change its dependence to the second reagent as shown in Figure 1 for metals, oxides, and sulfides. This behavior can be explained as follows. When a metal or a semi-conductor comes into contact with an aqueous phase to which oxygen or any depolarizer is added, oxygen or the depolarizer takes up electrons at one part of the surface (the cathodic zone) while the solid gives them up at another (the anodic zone) as shown in Figure 2. The cathodic reduction of oxygen for example, at the surface of the solid may lead to the formation of either hydrogen peroxide or hydroxyl ions as follows:

![Figure 1– Kinetics of electrochemical processes in solid-liquid reactions](image.png)
Figure 2– Mechanism of an electrochemical process in a solid-liquid reaction

\[ \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \]
\[ Fe^{3+} + e^- \rightarrow Fe^{2+} \]

The anodic reaction for a metal may be represented as follows:

\[ M \rightarrow M^{n+} + n\text{e}^- \]

while for a semiconducting oxide like UO$_2$ it would be:

\[ UO_2 \rightarrow UO_2^{2+} + 2e^- \]

and for a semiconducting sulfide like ZnS it would be:

\[ ZnS \rightarrow Zn^{2+} + S + 2e^- \]

The liberated metal ion would hydrolyze forming insoluble compounds that would block the anodic zone and the reaction would stop unless and acid or a

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complexing agent is present. If \([D] = \) the concentration of the depolarizer, \([C] = \) the concentration of the complexing agent, \(A_1 = \) the surface area of the cathodic zone, \(A_2 = \) the surface area of the anodic zone, \(k_1\) and \(k_2\) are the velocity constants at the cathodic and the anodic zones, respectively, then:

\[
V_1 = k_1 A_1 [D]
\]

and

\[
V_2 = k_2 A_2 [C]
\]

where \(V_1\) and \(V_2\) are the velocity of the cathodic and the anodic reactions, respectively. At the steady state, the rate of the cathodic reaction equals that of the anodic reaction, i.e.:

\[
k_1 A_1 [D] = k_2 A_2 [C]
\]

Therefore

\[
A \frac{k_2 [C]}{k_1 [D] + k_2 [C]} = A
\]

where \(A\) is the total surface area of the solid in contact with the solution:

\[
A = A_1 + A_2
\]

Substituting the value of \(A_1\) (or \(A_2\)) in any of the rate equations gives

\[
\text{Rate of dissolution} = \frac{k_1 k_2 A [D][C]}{k_1 [D] + k_2 [C]}
\]
This equation has the following characteristics:

- At low concentration of C, the second term in the denominator may be neglected in comparison with the first, and the rate equation simplifies to:
  \[ \text{Rate} = k_2[A][C] \]
i.e., the rate of dissolution in this case is only a function of the hydrogen ion or the complexing agent concentration.

- At high concentration of C, the first term in the denominator may be neglected in comparison with the second, and the velocity equation simplifies to
  \[ \text{Rate} = k_1[A][D] \]
i.e., the rate of dissolution under these conditions depends only on the concentration of the depolarizer.

- When the first and second terms in the denominator are of equal magnitude, i.e., when
  \[ k_1[D] = k_2[C] \]
then the rate of dissolution reaches its limiting value, i.e., when the rate curve changes its direction. This change takes place at a certain ratio of \([C]/[D]\), as can be deduced from the equation,

\[
\frac{[C]}{[D]} = \frac{k_1}{k_2} = \text{Constant}
\]

**Applications**

- **Dissolution of metals with hydrogen evolution**

  Evolution of hydrogen during the dissolution of metals may take place either in acidic or in an alkaline medium. In these cases the hydrogen ion acts as a depolarizer, and the reactions taking place are:

  \[
  \begin{align*}
  \text{Cathodic reaction: } & 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \\
  \text{Anodic reaction: } & M \rightarrow M^{n+} + ne^-
  \end{align*}
  \]

  The two cases will be considered separately.

- **Acidic medium.** In this case, beside acting as depolarizer, \(\text{H}^+\) ions also prevent the hydrolysis of metal ions:
\[ M^{n+} + nH_2O \rightleftharpoons M(OH)_n + nH^+ \]
i.e., preventing the deposition of insoluble products that may block the anodic zone. Such mechanism is shown schematically in Figure 3. The kinetic equation 5 for this process can be deduced from the general equation by substituting the hydrogen ion concentration for \([D]\) and \([C]\), thus getting:

\[
\text{Rate} = \frac{k_1k_2}{k_1 + k_2} A [H^+] \\
= k A [H^+]
\]

where \(k = \frac{k_1k_2}{k_1 + k_2}\)

This is the velocity equation for the dissolution of metals in acids with hydrogen liberation. Figure 4 shows the dissolution rate of titanium in hydrofluoric acid, in absence of air, which increases linearly with increasing
acid concentration as predicted by the equation derived theoretically above [14].

- **Alkaline medium.** An example of this case is the dissolution of aluminum in NaOH, which can be represented by the equations:
  
  Cathodic reaction: \(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\)
  
  Anodic reaction: \(\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-\)
  
  \(\text{Al}^{3+} + 4\text{OH}^- \rightarrow [\text{AlO(OH)}_2^-] + \text{H}_2\text{O}\)

  In this case, the hydrogen ions are acting as depolarizers, and the function of \(\text{OH}^-\) is to complex the liberated \(\text{Al}^{3+}\) ion into a soluble form. The overall reaction is, therefore:

  \(2\text{Al} + 2\text{OH}^- + 4\text{H}_2\text{O} \rightarrow 2[\text{AlO(OH)}_2^-] + 3\text{H}_2\)

  
  \[
  \text{Rate} = \frac{k_1k_2A[\text{H}^+][\text{OH}^-]}{k_1[\text{H}^+] + k_2[\text{OH}^-]} = \frac{k_1k_2A[\text{OH}^-]}{k_1 + \frac{k_2}{K}[\text{OH}^-]^2}
  \]

  where \(K = [\text{H}^+][\text{OH}^-]\).

  It can be seen from this equation that at low hydroxide concentration the second term in the denominator can be neglected and the rate equation reduces to:

  \[
  \text{Rate} = k_2A[\text{OH}^-]
  \]

  Further, at high hydroxide concentration the first term in the denominator can be neglected and the rate equation reduces to:

  \[
  \text{Rate} = k_1KA\frac{1}{[\text{OH}^-]}
  \]

  This equation shows that, beyond a certain hydroxide ion concentration, the rate of dissolution should decrease with increasing hydroxide concentration which was confirmed experimentally as shown in Figure 5 [15].
Dissolution of gold and silver in cyanide solution

The dissolution of gold and silver in cyanide solution, a process of great metallurgical importance (Figure 6), can be represented by the reactions:

Cathodic reaction: \( \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}^- + \text{H}_2\text{O}_2 \)

Anodic reaction: \( \text{Au} \rightarrow \text{Au}^+ + \text{e}^- \)
\( \text{Au}^+ + 2\text{CN}^- \rightarrow [\text{Au(CN)}_2]^– \)

Overall reaction:
\( 2\text{Au} + 4\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2[\text{Au(CN)}_2]^– + 2\text{OH}^- + \text{H}_2\text{O}_2 \)
The process was found to be strongly dependent on the speed of agitation, and the activation energy to be \(< 5\) kcal/mole which is characteristics of a diffusion-controlled process. According to Fick’s law of diffusion,

\[
\frac{d(O_2)}{dt} = \frac{\mathcal{D}_{O_2}}{\delta} A_1 \left\{ [O_2] - [O_2]_i \right\}
\]

\[
\frac{d(CN^-)}{dt} = \frac{\mathcal{D}_{CN^-}}{\delta} A_2 \left\{ [CN^-] - [CN^-] \right\}
\]

Figure 6 – Illustration of the dissolution of gold and silver in cyanide solution
\( \mathcal{D}_{\text{CN}^-} \) and \( \mathcal{D}_{\text{O}_2} \) the diffusion coefficients of cyanide and dissolved oxygen, \( \text{cm}^2 \cdot \text{sec}^{-1} \).

\([\text{CN}^-]\) and \([\text{O}_2]\) the concentration of \( \text{CN}^- \) and \( \text{O}_2 \) in the bulk of the solution in mole/mL.

\([\text{CN}^-]_i\) and \([\text{O}_2]_i\) the concentration of \( \text{CN}^- \) and \( \text{O}_2 \) at the interface in mole/mL.

\( A_1 \) and \( A_2 \) the surface area at which the cathodic and anodic reactions take place, in \( \text{cm}^2 \).

\( \delta \) the thickness of the boundary layer, in cm.

where

\[
\frac{d(\text{CN}^-)}{dt} \quad \text{and} \quad \frac{d(\text{O}_2)}{dt} \quad \text{the rates of diffusion of} \quad \text{CN}^- \text{ion and} \quad \text{O}_2, \quad \text{in mole/sec.}
\]

Since the process is diffusion-controlled, it can be assumed that the chemical reactions at the metal interface are very rapid as compared with the rates at which the cyanide ion and \( \text{O}_2 \) diffuse through the stagnant layer. These will then be consumed as soon as they reach the surface of the metal, i.e.,

\([\text{O}_2]_i = 0 \quad \text{and} \quad [\text{CN}^-]_i = 0 \)

Therefore,

\[
\frac{d(\text{O}_2)}{dt} = \frac{\mathcal{D}_{\text{O}_2}}{\delta} A_1[\text{O}_2]
\]

\[
\frac{d(\text{CN}^-)}{dt} = \frac{\mathcal{D}_{\text{CN}^-}}{\delta} A_2[\text{CN}^-]
\]

Since the amount of metal dissolved is twice that of oxygen consumed and half that of cyanide consumed as can be seen from the overall equation, therefore

Rate of dissolution \( = 2 \frac{d(\text{O}_2)}{dt} = 2 \frac{\mathcal{D}_{\text{O}_2}}{\delta} A_1[\text{O}_2] \)

\( = \frac{1}{2} \frac{d(\text{CN}^-)}{dt} = \frac{1}{2} \frac{\mathcal{D}_{\text{CN}^-}}{\delta} A_2[\text{CN}^-] \)
It follows from these equations that, at the steady state,

\[ 2 \frac{\partial}{\partial \delta} A_1 [O_2] = \frac{1}{2} \frac{\partial}{\partial \delta} A_2 [CN^-] \]

But, since \( A \), the total surface area of metal in contact with the aqueous phase = \( A_1 + A_2 \), therefore

\[ \text{Rate} = \frac{2 A}{\delta} \frac{\partial}{\partial \delta} \frac{[CN^-][O_2]}{[CN^-][CN^-] + 4 [O_2]} \]

From this equation it follows that, at low cyanide concentration, the first term in the denominator may be neglected in comparison with the second, so that the equation simplifies to

\[ \text{Rate} = \frac{1}{2} \frac{A}{\delta} [CN^-] \]

\[ = k_2 [CN^-] \]

![Figure 7](image.png)

Figure 7 – Kinetic results obtained experimentally for the dissolution of silver in cyanide solution in presence of oxygen

This coincides with the experimental facts (Figure 7) that at low cyanide concentration the rate of dissolution depends only on that concentration [16]. In the same manner, it follows also from equation 7 that at high cyanide concentration, the second term in the denominator may be neglected in comparison with the first, and the equation simplifies to
Rate = 2 \frac{A \mathcal{D}_{O_2}}{\delta} [O_2] \\
= k_2 [O_2]

This coincides also with the experimental facts in Figure 7 that, at high cyanide concentration, the rate of dissolution depends only on the oxygen concentration. It can also be deduced from equation 7 that, when

\[ \mathcal{D}_{CN^-}[CN^-] = 4 \mathcal{D}_{O_2}[O_2] \]

i.e. when

\[ \frac{[CN^-]}{[O_2]} = 4 \frac{\mathcal{D}_{O_2}}{\mathcal{D}_{CN^-}} \]

the rate of dissolution reaches its limiting value. The diffusion coefficients are as follows:

\[ \mathcal{D}_{O_2} = 2.76 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \text{ and } \mathcal{D}_{KCN} = 1.83 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}, \text{ i.e., the average ratio } \mathcal{D}_{O_2}/\mathcal{D}_{CN^-} = 1.5. \text{ Therefore, the limiting rate is reached when } \]

\[ \frac{[CN^-]}{[O_2]} = 6 \]

This means that, in order to maintain a cyanide consumption at the interface four times that of oxygen as demanded by the stoichiometry of reaction, the cyanide concentration in the bulk of the solution should be six times that of oxygen. The values found experimentally varied between 4.6 and 7.4 which is in good agreement.

- **Dissolution of copper in aqueous ammonia**

Metallic copper dissolves in aqueous ammonia according to the equation

Cathodic reaction: \[ \frac{1}{2} O_2 + H_2O + 2 e^- \rightarrow 2 OH^- \]

Anodic reaction: \[ Cu \rightarrow Cu^{2+} + 2 e^- \]

\[ Cu^{2+} + 4 NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2 OH^- \]

Overall reaction:

\[ Cu + 4 NH_3 + \frac{1}{2} O_2 + H_2O \rightarrow [Cu(NH_3)_4]^{2+} + 2 OH^- \]
Table 1 – Effect of speed of stirring and temperature (Activation Energy) on the rate of dissolution of copper in 0.5 mol/l NH₃

<table>
<thead>
<tr>
<th>Speed of stirring (rpm)</th>
<th>( P_{O_2} = 1.4 \text{ atm} )</th>
<th>( \Delta E )</th>
<th>( \text{Rate} )</th>
<th>( P_{O_2} = 7.8 \text{ atm} )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.cm(^{-2}).hr(^{-1})</td>
<td>Kcal</td>
<td>mg.cm(^{-2}).hr(^{-1})</td>
<td>Kcal</td>
<td></td>
</tr>
<tr>
<td>470</td>
<td>15.0</td>
<td>30.0</td>
<td>17.6</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>545</td>
<td>17.6</td>
<td>29.0</td>
<td>19.3</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>660</td>
<td>19.3</td>
<td>1.33</td>
<td>30.0</td>
<td>5.54</td>
<td></td>
</tr>
<tr>
<td>820</td>
<td>21.6</td>
<td>31.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Region of low oxygen pressure and high ammonia concentration; rate dependent only on oxygen partial pressure.
** Region of high oxygen pressure and low ammonia concentration; rate dependent only on ammonia concentration.

From the experimental data shown in Table 1 and Figure 8 [17] it can be concluded that:

- The cathodic reaction is a diffusion-controlled process
- The anodic reaction is a chemically-controlled process

From the first observation, it follows that the rate of oxygen diffusion through the Nernst boundary layer will be given by:

\[
\frac{d(O_2)}{dt} = \frac{\varphi_{O_2}}{\delta} A_1 [O_2]
\]

From the overall equation, two equivalents of copper are dissolved when one mole of oxygen is consumed, therefore,

\[
\text{Rate of copper dissolution} = 2 \frac{d(O_2)}{dt} = 2 k_1 A_1 [O_2]
\]

where \( k_1 = \frac{\varphi_{O_2}}{\delta} \)
From the second observation, it follows that the rate of chemical reaction between ammonia and copper is much slower than the rate at which NH₃ diffuses to the surface of the metal through the boundary layer, since the chemical reaction in this case is rate-controlling. This can be expressed as follows, after taking into consideration the stoichiometry of the reaction:

\[
\text{Rate of copper dissolution} = \frac{1}{4} k_2 A_2 [\text{NH}_3]
\]

At the steady state, the rate of cathodic reaction (diffusion of oxygen) = the rate of anodic reaction (chemical reaction with ammonia), i.e.,

\[
2 k_1 A_1 [\text{O}_2] = \frac{1}{4} k_2 A_2 [\text{NH}_3]
\]

\[
\text{Rate of copper dissolution} = \frac{2 k_1 k_2 A [\text{O}_2] [\text{NH}_3]}{8 k_1 [\text{O}_2] + k_2 [\text{NH}_3]}
\]

It can be seen from this equation that at low oxygen concentration and high ammonia concentration, the term \(2k_1 [\text{O}_2]\) can be neglected in the denominator, and the velocity equation becomes:

\[
\text{Rate} = 2k_1 [\text{O}_2]
\]

i.e. the rate of copper dissolution under these conditions depends only on the oxygen partial pressure. This is in agreement with experiments as shown in the above Figure 8. Further, the term \(k_1\) is a diffusion velocity coefficient which therefore should depend markedly on the rate of stirring of the solution and only slightly on the temperature, (i.e. the activation energy is low). This is in agreement with the...
experimental results in Table 1. Similarly, at high oxygen pressure and low ammonia concentration the term \( k_2 [\text{NH}_3] \) can be neglected in the denominator in equation 8 and the velocity equation becomes:

\[
\text{Rate} = \frac{1}{4} k_2 A[\text{NH}_3]
\]

which is also in agreement with the above Figure 8. Here, the constant \( k_2 \) is a true chemical reaction velocity constant, therefore it should be expected that the rate is independent of the speed of stirring and the activation energy should be higher than 4 Kcal. This is in agreement with experimental results in Table 1.

Figure 9 - Schematic representation of the electrochemical reactions during the leaching of uranium dioxide

- **Dissolution of uranium dioxide**

Uranium dioxide is a semiconductor; its dissolution in acid or in carbonate solution can be represented by the following reactions (Figure 9):

\[
\begin{align*}
\text{Dissolution in acid: } & \text{UO}_2(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{UO}_2^{3+} + 2\text{H}_2\text{O} \\
\text{Dissolution in carbonate: } & \text{UO}_2(\text{OH})_2 + 3\text{CO}_3^{2-} \rightarrow [\text{UO}_2(\text{CO}_3)_3]^{4+} + 2\text{OH}^-
\end{align*}
\]
In acid medium. The reduction of oxygen (or any oxidizing agent) at the cathodic zone:

\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \]

The oxidation of UO₂ at the anodic zone:

\[ UO_2 \rightarrow UO_2^{2+} + 2e^- \]

The overall reaction:

\[ UO_2 + 2H^+ + \frac{1}{2}O_2 \rightarrow UO_2^{2+} + H_2O \]

In carbonate medium:

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]
\[ UO_2 \rightarrow UO_2^{2+} + 2e^- \]
\[ UO_2^{2+} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} \]

Overall reaction:

\[ UO_2 + 3CO_3^{2-} + \frac{1}{2}O_2 + H_2O \rightarrow [UO_2(CO_3)_3]^{4+} + 2OH^- \]

Experimental data showed that the leaching process is chemically-controlled in both cases, an activation energy of about 15 Kcal/mole was obtained. Further at high acid concentration the rate is directly proportional to the oxygen pressure, while at high carbonate concentration the rate is proportional to the square root of the oxygen pressure (Figure 10 and 11) [18]. The velocity equations are, respectively:
Figure 10 – Dissolution of UO₂ in H₂SO₄ under oxygen pressure. Temperature 100°C, aqueous phase 400 mL, solid phase 1 gram, speed of stirring 600 rpm.

\[
\text{Rate} = \frac{k_1 k_2 A p_{O_2} [H^+]^2}{k_1 p_{O_2} + k_2 [H^+]^2}
\]

\[
\text{Rate} = \frac{k'_1 k'_2 A p_{O_2}^{1/2} [CO_3^{2-}]^2}{k'_1 p_{O_2}^{1/2} + k_2 [CO_3^{2-}]^2}
\]

- **Aqueous oxidation of sulfides**

Zinc sulfide is a semiconductor; its oxidation in acid medium can be represented by the following equations:

Cathodic reaction: \( \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \)

Anodic reaction: \( ZnS \rightarrow Zn^{2+} + S + 2e^- \)

Overall reaction: \( ZnS + 2H^+ + \frac{1}{2}O_2 \rightarrow Zn^{2+} + S + H_2O \)
Figure 11 – Dissolution of UO₂ in Na₂CO₃-NaHCO₃ mixture under oxygen pressure. Temperature 100°C, aqueous phase 400 mL, solid phase 1 gram, speed of stirring 600 rpm.

Figure 12 - Dissolution of ZnS in dilute sulfuric acid

Experimental data in Figure 12 [19] shows that at high acid concentration the rate is directly proportional to the oxygen pressure and the following equation applies:
Rate of dissolution = \[ \frac{k_1 k_2 A p_{O_2} [H^+]}{k_1 p_{O_2} + k_2 [H^+]}. \]

**SUMMARY**

A single kinetic law derived theoretically:

\[
\text{Rate} = \frac{k_1 k_2 A[D][C]}{k_1 [D] + k_2 [C]},
\]

for the dissolution of metals, semi-conducting oxides and sulfides was found to apply for many metallurgical processes; [D] and [C] are the concentrations of depolarizer and leaching agent, respectively.

**NOMENCLATURE**

- **D**: Depolarizer in solution, e.g., O\(_2\), H\(^+\), etc.
- **C**: Concentration of reagent in solution
- **k\(_1\), k\(_2\)**: Velocity constants
- **K**: Equilibrium constant
- **M**: A divalent metal
- **X**: A divalent anion
- **A**: The total surface area of the solid in contact with the solution
- **A\(_1\)**: Surface area of the cathodic zone
- **A\(_2\)**: Surface area of the anodic zone
- **V\(_1\)**: Velocity of the cathodic reaction
- **V\(_2\)**: Velocity of the anodic reaction
- \(\frac{d[CN^-]}{dt}\): Rate of diffusion of CN\(^-\) in gram ion/sec
- \(\frac{d[O_2]}{dt}\): Rate of diffusion of O\(_2\) in mole/sec
- \(D_{CN^-}\): Diffusion coefficient of cyanide, cm\(^2\)·sec\(^{-1}\)
- \(D_{O_2}\): Diffusion coefficient of dissolved oxygen, cm\(^2\)·sec\(^{-1}\)
- [CN\(^-\)]: Concentration of CN\(^-\) in the bulk of the solution in gram ion/mL
- [O\(_2\)]: Concentration of O\(_2\) in the bulk of the solution in mole/mL
- [CN\(^-\)]\(_i\): Concentration of CN\(^-\) at the interface in gram ion/mL
- [O\(_2\)]\(_i\): Concentration of O\(_2\) at the interface in mole/mL
- \(\delta\): Thickness of the boundary layer in cm
REFERENCES


