Leaching mechanism of tetrahedrite in alkaline sulfide solution

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ABSTRACT

The dissolution kinetics of tetrahedrite in aqueous alkaline sodium sulfide solutions was investigated in this present study. The effect of mineral particle size, reaction temperature, sodium sulfide and sodium hydroxide concentrations on the rate of dissolving antimony from tetrahedrite were studied. The result reveals that the rate of reaction increases with increasing reaction temperature, sodium sulfide concentration, sodium hydroxide concentration and with decreasing mineral particle size. The kinetics study indicates that tetrahedrite leaching rate by the lixiviant under the selected conditions is chemically controlled through the particle surface reaction. Therefore, the activation energy of antimony dissolution from tetrahedrite was estimated to be 81 kJ/ mol, which is in agreement with the value reported for the chemically controlled reactions process.

Keywords: Tetrahedrite, Leaching mechanism, Alkaline sodium sulfide, Leaching, Lixiviant

1. Introduction

Copper has immensely contributed to the civilization development of humans. From the dawn of civilization until today, copper has made, and continues to make, a vital contribution to sustaining and improving society due to its unique properties. Economic, technological and societal factors have influenced the demand and supply of copper in the recent time. The increasing demand for copper Worldwide has increased its production and therefore, new mines and plants are introduced and the existing ones are expanded. Unfortunately, today, most of the new copper sulfide mineral deposits found are complex in nature and often found in association with minerals like tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$), enargite (Cu$_3$AsS$_4$) and tennantite (Cu$_{12}$As$_4$S$_{13}$) (Riveros and Dutrizac, 2008), which render the concentrate unsuitable as a feedstock for smelting due to its antimony, arsenic and mercury contents which create serious environmental problems (Curreli et al., 2009; Filippou et al., 2007; Lattanzi et al., 2008).

Tetrahedrite is a complex sulfide of copper and antimony which can be an interesting and important resource of copper (40-46%), antimony (27-29%) (Baláz et al., 1998) and or other non-ferrous metals as is evident from its general chemical formula (Cu,Ag)$_{10}$(Cu,Zn,Fe,Cd,Hg)$_2$(Sb,As)$_4$S$_{13}$ (Baláž, 2000; Ukasik and Havlik, 2005). Tetrahedrite is often described as the “sulphosalts” which indicates a certain type of un-oxidized sulphur mineral that is structurally distinct from a sulfide (King, 2001). The tetrahedrite group is notable for the variety of elements which are stable in its structure. It is very difficult to find pure tetrahedrite naturally due to its original constituents which are always substituted partially by other elements. Hence, copper can be substituted by silver, zinc, iron, mercury, cadmium, lead etc, while arsenic can substitute for antimony leading to
tannantite and some sulphur may be replaced by selenium and tellurium (Filippou et al., 2007; King, 2001; Neiva Correia et al., 1993). Mining of tetrahedrite mineral has been more economically attractive due to the substantial amount of copper, silver and gold usually found in association with the mineral. As a result of increasing demand for copper globally, the need to source for copper from all resources including those that contain high antimony and arsenic are indispensable and therefore more economical and environmentally friendly treatment options are required.

Leaching of native tetrahedrite concentrate in acidic ferric chloride solution at temperature range of 40-90 °C has been investigated (Havlik et al. 1999). The leaching rate shows a slow behaviour exhibiting apparent parabolic kinetics. Increase in the leaching temperature improves the metal extraction and the apparent activation energy was estimated to approximately 38 kJ/mol, indicating that the process occurs in the mixed regime of both the diffusion and chemical reaction. The leaching of tetrahedrite with ferric chloride, sodium chloride and hydrochloric acid solutions was reported to involve the breakdown of the tetrahedrite crystal structure with the simultaneous liberation of all its components without the formation of sulphate in the leaching reaction (Correia et al., 2000). At chloride concentrations less than 3 M, antimony precipitates were observed and the leaching kinetics is described by the shrinking core model. The rate of leaching tetrahedrite in the lixiviant is controlled by a surface reaction and the apparent rate constant is proportional to the inverse of the mean mineral particle size.

In a recent study, Riveros and Dutrizac (2008) performed a series of leaching test on tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) in acidic media using Fe$_2$(SO$_4$)$_3$, FeCl$_3$ or O$_2$ as oxidizing agents. At temperatures <100°C, the dissolution kinetics of disks of synthetic iron-bearing tetrahedrite in Fe$_2$(SO$_4$)$_3$ - H$_2$SO$_4$ media are linear; the leaching rates are slow but increase significantly with increasing temperature with an apparent activation energy of 120 kJ/mol. The dissolution of sized particles of natural Ag-bearing tetrahedrite in FeCl$_3$-HCl solutions proceeds according to the shrinking core model and both copper and silver dissolve at about the same rate provided that the total chloride concentration of the solution is sufficiently high to solubilize the AgCl reaction product. The leaching rates were slow and the activation energy was estimated to be 116 kJ/mol. The addition of sulphate ions to the FeCl$_3$-HCl system reduces the tetrahedrite leaching rate to values similar to those realized in the Fe$_2$(SO$_4$)$_3$-H$_2$SO$_4$ system. However, the rate of dissolving mineral particle in leaching process decreases with time and is therefore, directly dependent on the activation energy. If the rate of reaction is slow, it will control the overall process and the process will be chemically controlled but if the rate of reaction in the bulk of the solution is fast, the solution will be governed by the rate of diffusion of the ions from the surface of the solid through the boundary layer. The activation energy of a chemically controlled process is usually greater than 42 kJ/mol while a diffusion-controlled process is characterised as being 4 – 12 kJ/mol (Habashi, 1980).

Leaching of copper-antimony-arsenic sulfide minerals in alkaline sulfide solution has been studied extensively and reported elsewhere in the literatures (Baláz and Achimovicová, 2006a; Baláz and Achimovicová, 2006b; Baláz et al., 1998; Baláz et al., 1992; Balaz et al., 2001; Delfini et al., 2003; Frohlich and Miklos, 2001; Samuel, 2008; 2005), however, detailed information regarding the dissolution kinetics of natural tetrahedrite in alkaline sulfide solutions has not been fully documented. In the current study, the effect of the reaction temperature, mineral particle size, and the concentration of sodium sulfide and sodium hydroxide were investigated to study the reaction kinetics of tetrahedrite in aqueous alkaline sodium sulfide solution and identify the rate-determining process for Cu$_{12}$Sb$_4$S$_{13}$ in Na$_2$S-NaOH media.
2. Material and methods

The investigations were carried out with the tetrahedrite crystals purchased from Gregory, Bottley & Lloyd Company, UK, which originated from Casapalca, Huarochiri, Departamento Lima, Peru, containing mainly sharp tetrahedrite crystals accompanied by an excellent brilliance and striation growth of sphalerite and partially covered by quartz. The tetrahedrite mineral was crushed, ground and sieved into the following size fractions: -106 +75 µm, -75 +53 µm and -53 +38 µm, which were used in the study. The various size fractions were divided into appropriate portions before used in the leaching experiments. The chemical composition of these size fractions is given in Table 1. X-ray diffraction (XRD) analysis of the sample shows that tetrahedrite, chalcopyrite, sphalerite, galena, pyrite and quartz are the major mineralogical phases found in the mineral sample.

Table 1. Chemical composition (%).

<table>
<thead>
<tr>
<th>Size fraction</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>Sb</th>
<th>As</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>+75 µm</td>
<td>15.6</td>
<td>11.12</td>
<td>16.1</td>
<td>5.78</td>
<td>1.86</td>
<td>28.0</td>
</tr>
<tr>
<td>+53 µm</td>
<td>15.2</td>
<td>14.20</td>
<td>16.8</td>
<td>5.43</td>
<td>1.87</td>
<td>31.5</td>
</tr>
<tr>
<td>+38 µm</td>
<td>15.7</td>
<td>13.29</td>
<td>16.9</td>
<td>5.71</td>
<td>1.77</td>
<td>26.5</td>
</tr>
</tbody>
</table>

The leaching experiments were conducted batch-wise in a four-necked round bottomed glass reactor which was mechanically stirred with a paddle stirrer at 600 rpm and heated with an auto-regulated system. The leaching solution (500 mL) was added to the reactor and when the desired temperature was reached, the solid sample was added. In the entire leaching test, 2.5 g of tetrahedrite was leached in 500 mL of the lixiviant. At a regular time interval, 5 mL sample of the leach solution was collected for the analysis of the metals dissolved in the leach liquor. The following experimental conditions: sodium sulfide (Na$_2$S.3H$_2$O) concentration (100 g/L, 150 g/L and 250 g/L); sodium hydroxide (NaOH) concentration (30 g/L and 60 g/L); leaching temperature (84, 91, 98 and 105 ºC), mineral particle size (38, 53 and 75 µm) and reaction time of 360 minutes were used in all cases. The mineral samples and leach liquors were chemically analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Sector Field Mass Spectrometry (ICP-SFMS).

3. Results and discussion

3.1 Effect of Na$_2$S concentration

When antimony reacts with sulfide ions complex compounds are formed, however, leaching of tetrahedrite in alkaline sulfide solution will result in a variety of reaction products. These include chalcocite (Cu$_2$S) or covelite (CuS), while antimony is dissolved as thioanions: thioantimonite (SbS$_3^{3-}$), thioantimonate (SbS$_4^{5-}$) etc depending on the feed composition and the reaction conditions (Filippou et al., 2007). Therefore, the influence of sodium sulfide concentration on tetrahedrite leaching is an important parameter to investigate. The dissolution reaction of tetrahedrite in alkaline sulfide solutions is expressed as follows:

$$\text{Cu}_{12}\text{Sb}_4\text{S}_{13(s)} + 2\text{Na}_2\text{S}_{(aq)} \rightarrow 5\text{Cu}_2\text{S}_{(s)} + 2\text{CuS}_{(s)} + 4\text{NaSbS}_2_{(aq)}$$  \hspace{1cm} (1)

$$\text{NaSbS}_2_{(aq)} + \text{Na}_2\text{S}_{(aq)} \rightarrow \text{Na}_3\text{SbS}_3_{(aq)}$$  \hspace{1cm} (2)
Leaching experiments were carried out to investigate the effect of changes in the initial concentration of sodium sulfide in the range of 100 – 250 g/L at 105 ºC in solutions containing 60 g/L NaOH. The amount of solid leached was kept constant at 2.5 g which was taken from +53 µm size fraction. It is apparent from Fig. 1 that antimony dissolution rate from tetrahedrite by the lixiviant increases steadily with increasing sodium sulfide concentration, and the dissolution rate at Na\(_2\)S concentration of 250 g/L is much higher than that at 150 and 100 g/L Na\(_2\)S. The result shows that tetrahedrite leaching is strongly dependent on the concentration of sodium sulfide.

**Fig. 1.** Effect of Na\(_2\)S concentration on tetrahedrite leaching; leaching conditions: 60 g/L NaOH, 2.5 g sample from +53 µm particle size, stirring rate of 600 rpm at a temperature of 105 ºC for 6 hours.

3.2 Effect of NaOH concentration

The influence of sodium hydroxide concentration on tetrahedrite leaching is presented in Fig. 2. The leaching experiments were conducted using the following conditions: 150 g/L Na\(_2\)S; particle size of +53 µm; 2.5 g of tetrahedrite leached in 500 mL Na\(_2\)S-NaOH solution at reaction temperature of 105 ºC for 360 minutes. From Fig. 1, it is evident that tetrahedrite dissolution rate by the lixiviant is strongly dependent on NaOH concentration. This effect is seen from the plot that the percentage of antimony reported into the leach liquor after 360 minutes at a concentration of 60 g/L NaOH is greater than that obtained at NaOH concentration of 30 g/L. Increase in NaOH concentration accelerates the rate at which antimony solubilises from tetrahedrite into the leach liquor.
3.3 Effect of temperature

The influence of reaction temperature on antimony dissolution was investigated by conducting leaching experiments at: 84 °C to 105 °C using +53 µm tetrahedrite fraction while keeping reagent concentration fixed at 150 g/L Na$_2$S + 60 g/L NaOH and the results obtained are presented in Fig. 3. The amount of solid leached was kept constant at 2.5 g/L. The data obtained show that the reaction temperature exerts the most significant effect on the rate of antimony dissolution from tetrahedrite. The conversion rate increases rapidly with increasing time and temperature. At 84 °C, antimony dissolution reached only 10% in 240 min and shows no significant improvement thereafter. By increasing the reaction temperature to 91 °C, antimony dissolution is 16% in 240 min and reaches 25% in 360 min. When the temperature was increased further to 105 °C, antimony dissolution is about 57% in 360 min which is quite significant. The leaching profile shown in Fig. 3 reflects that there will be further increase in the percentage of antimony reported into the leach solution, if the leaching time is increased further.
Fig. 3. Effect of reaction temperature on tetrahedrite dissolution rate; leaching conditions: 150 g/L Na$_2$S, 60 g/L NaOH, 2.5 g sample from +53 µm particle size, stirring rate of 600 rpm for 6 hours.

3.4 Leaching kinetic model

The rate of reaction in fluid-solid systems could be determined by a non-catalytic heterogeneous model which has a number of applications in chemical and hydrometallurgical processes. The shrinking particle model and the shrinking core model are the most commonly used. The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary layer, or through a solid product layer, or by rate of the surface chemical reaction (Aydogan et al., 2005). The experimental data obtained at different temperatures in this study have been evaluated using diffusion controlled mechanisms (Eq. 3) and surface chemical reaction control model (Eq. 4).

\[
1 - \frac{2}{3} X - (1 - X)^{2/3} = \frac{2M_S DC_A}{\rho_S \beta r_0^2} t = k_d t \tag{3}
\]

\[
1 - \left(1 - X\right)^{1/3} = \frac{k_r M_S C_A}{\rho_S \beta r_0} t = k_r t \tag{4}
\]

where $X$ is the fraction reacted, $k_c$ is the kinetic constant, $M_S$ is the molecular weight of the solid, $C_A$ is the concentration of the dissolved lixiviant A in the bulk of the solution, $\rho_S$ is density of tetrahedrite, $\beta$ is the stoichiometric coefficient of the reagent in the leaching reaction, $r_0$ is the initial radius of the solid particle, $t$ is the reaction time, $D$ is the diffusion coefficient in the porous product layer, $k_d$ and $k_r$ are the rate constants which are calculated from Eqs. (3) and (4), respectively.

By fitting the experimental data to the diffusion controlled model equation describes in Eq. 3 and the result shown in Fig. 4, it is found that the data do not correlate to this model, since neither a straight line nor a zero point intercept was obtained.
When surface chemical reaction control model (Eq. 4) was applied to the experimental data got, at different temperatures, linear plot was obtained as presented in Fig. 5. A good linearity was observed during the whole reaction time which indicates that the rate of the reaction is chemically controlled through the particle surface reaction. The rate constant, \( k_r \), was estimated, which is equivalent to the slope of the straight lines shown in Fig. 5.

**Fig. 4.** A plot of \( 1 - \frac{2}{3}X - (1 - X)^{2/3} \) against time at different reaction temperatures.

**Fig. 5.** A plot of \( 1 - (1 - X)^{1/3} \) against time at different reaction temperatures.
3.4.1 Activation energy calculation

The temperature dependence of the chemical reactions can be given by the Arrhenius equation (Habashi, 1980; Ray, 1993) as follows:

\[ k_r = A \exp\left(\frac{-E_a}{RT}\right) \]  

(5)

where \( A \) is the frequency factor and \( E_a \) is the apparent activation energy. Kinetic constant values from Fig. 5 were used to construct an Arrhenius plot for determination of activation energy as shown in Fig. 6, giving an excellent linear dependency of the kinetic constant with temperature. Fig. 6 was made by plotting the natural logarithm of the rate constant (\( \ln k_r \)) against the reciprocal of the temperature (1/T) and the activation energy was determined from the slope of the Arrhenius plot as 81 kJ/mol, which is in conformity with the activation energy reported for a chemically controlled process (Habashi, 1980). Because of high activation energy obtained, conclusion can be drawn that the rate of tetrahedrite leaching by the lixiviant is temperature sensitive.

![Fig. 6. Arrhenius plot of tetrahedrite leaching in alkaline sulfide solution.](image)

3.5 Effect of particle size

The effect of mineral particle size in mineral processing as well as hydrometallurgical treatment of mineral ore can not be overemphasized. Therefore, this effect was investigated on the leaching of tetrahedrite by alkaline sulfide solution. The tests were conducted by using three particle sizes (+38, +53 and +75 µm) at 105 °C in leach solutions containing 150 g/L \( \text{Na}_2\text{S}.3\text{H}_2\text{O} \) and 60 g/L \( \text{NaOH} \). According to Fig. 7, the rate at which tetrahedrite is leaching increases with increase in time and decreases with increase in particle size and hence the smaller the particle size, the faster was tetrahedrite leaching by the lixiviant. By plotting the kinetic data using Eq. 4, linearity of the data were obtained as contained in Fig. 8. The values of the rate constants from Fig. 8 were plotted against the reciprocal of the mineral particle radii yielding a linear relationship with correlation coefficients of 0.9705 (Fig. 9).
Furthermore, the linear dependence of the rate constant on the inverse particle radius is more evidence in support of the surface reaction shrinking core model for this process.

**Fig. 7.** Effect of mineral particle size on tetrahedrite leaching.

**Fig. 8.** A plot of $1 - (1 - X)^{1/3}$ against time at different mineral particle sizes.
Fig. 9. A plot of rate constant versus the reciprocal of mineral particle radius.

4. Conclusions

Leaching mechanism of tetrahedrite in aqueous alkaline sulfide solution was studied. It was found that the rate of reaction increases with increase in reaction temperature, sodium sulfide concentration, sodium hydroxide concentration and with decrease in mineral particle size. The kinetic equation from evaluation of experimental data using heterogeneous and pseudo-homogeneous reaction models was determined to be \( 1 - \left(1 - X\right)^{\frac{1}{2}} = k_r t \) and from the Arrhenius plot using \( k_r \) values obtained experimentally, an activation energy of 81 kJ/mol was estimated, which is consistent with the value of activation energy reported for the chemically controlled reaction process.

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Nomenclature

\[ \beta \]  Stoichiometric coefficient of the reagent in leaching solution
\[ C_A \]  Concentration of the dissolved reagent A in the bulk of the liquid  \([\text{mol/L}\] \]
\[ D \]  Diffusion coefficient in the porous layer  \([\text{L}^2/\text{t}]\]
\[ E_a \]  Activation energy of the leaching reaction  \([\text{M L}^2 \text{t}^2]\]
\[ k_c \]  Kinetic constant  \([\text{M/L}]\]
\[ k_d \]  Apparent rate constant defined in Eq. (3)  \([\text{l/t}]\]
\[ k_r \]  Apparent rate constant defined in Eq. (4)  \([\text{l/t}]\]
\[ M_S \]  Molecular weight of the solid  \([\text{M/mol}]\]
\[ r_0 \]  Initial radius of the solid particles  \([\mu\text{m}]\]
\[ t \]  Reaction time  \([\text{minutes}]\]
\[ T \]  Reaction temperature  \([\text{K}]\]
\[ X \]  Fraction of metal extracted  \([0 \leq X \leq 1]\]
\[ \rho_S \]  Density of tetrahedrite  \([\text{g/cm}^3]\)

References