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Leaching of copper(I) sulphide by sulphuric acid solution with addition of sodium nitrate

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Abstract

Finely grained samples of copper(I) sulphide were leached by H₂SO₄ solution with added NaNO₃. The occurrence probability of chemical reactions was analysed based on literature data and products which were formed during the process and the overall leaching reaction was defined. The effect of temperature, concentration of NaNO₃ and H₂SO₄, stirring speed, phase ratio and time, on the leaching degree of copper was studied. The quantity of copper dissolved increases with growth of the values of all the parameters. Kinetic analysis shows that the leaching mechanism is very complex. By using appropriate mathematical kinetic models, it is found that the leaching rate is chemically controlled. It was concluded that the leaching reaction is first order with respect to the concentration of NaNO₃ and second order with respect to the concentration of H₂SO₄.

Keywords: Copper(I) sulphide; Sulphuric acid; Sodium nitrate; Leaching; Kinetics

1. Introduction

Hydrometallurgical processes provide an efficient method for processing of low-grade complex ores. In spite of the fact that in pyrometallurgical processes, the sulphide sulphur is used as fuel, hydrometallurgical processes are increasingly popular because of environmental protection (Warren, 1958; Thomas et al., 1967). Concerns over air pollution and the environmental problem of acid rain have made governments all over the world tighten their regulations regarding the emission of sulphur dioxide. The focus is on the production of elemental sulphur and soluble copper sulphate. Copper(I) sulphide is frequently found both as a common component of other copper sulphides (CuFeS₂, CuS) in their natural raw materials and as a basic component in the semi-products of existing technologies of copper and lead production. Leaching of copper(I) sulphide has been the subject of many investigations (Mulak and Niemiec, 1969; Fisher and Roman, 1971; King et al., 1975). Those investigations included leaching under high pressure and atmospheric pressure. The process of copper matte leaching under high pressure conditions, in both acidic and alkaline solutions, necessitates high capital and operation costs. Sullivan (1933) studied the leaching processes of copper sulphides by acidified ferric sulphate solutions. He showed that chalcolite (Cu₂S) dissolves in a two-stage process with covellite (CuS) as the solid...
product formed at the end of the first stage. In the second stage, the process occurs through the formation of elemental sulphur. Cheng and Lawson (1991) investigated the kinetics of leaching chalcocite in acidic oxygenated sulphate–chloride solutions and also found that the process occurred in two stages. Nitric acid and nitrates are very strong oxidants. The former investigations were mainly aimed at leaching sulphides by using nitric acid as an oxidant, while leaching processes with use of nitrates have not been investigated. Habashi (1999) considers that metal sulphide oxidation by nitric acid can be achieved in two ways. In one case, \( \text{NO}_3^- / \text{CO}_0 \) ion is oxidant and during the reaction it is reduced to \( \text{NO} \) or \( \text{NO}_2 \). In the other case, oxygen which arises from nitric acid decomposition is the oxidant. Some authors (Ackerman, 1990; Anderson et al., 1993) have come to the conclusion that the leaching process of metal sulphides by using nitric acid as oxidant is more efficient in the presence of \( \text{NO}^+ \) ions. This paper aims to investigate the leaching process of copper(I) sulphide by sulphuric acid solution in the presence of sodium nitrate as it has not been studied sufficiently either from the theoretical or practical point of view.

2. Chemical reaction and thermodynamics

On the basis of literature data of the copper(I) sulphide leaching in oxidized, acidic medium and the products in the solution, as well as in the solid residues of leaching, determined by X-ray analysis, the chemical reactions chosen for study in the \( \text{Cu}_2\text{S} – \text{H}_2\text{SO}_4 – \text{NaNO}_3 – \text{H}_2\text{O} \) system were the following. Reactions in the first leaching stage:

\[
\text{Cu}_2\text{S} + 2/3\text{NaNO}_3 + 4/3\text{H}_2\text{SO}_4 \\
= \text{CuS} + \text{CuSO}_4 + 1/3\text{Na}_2\text{SO}_4 + 2/3\text{NO}(g) + 4/3\text{H}_2\text{O} \tag{1}
\]

\[
\text{Cu}_2\text{S} + 2\text{NaNO}_3 + 2\text{H}_2\text{SO}_4 \\
= \text{CuS} + \text{CuSO}_4 + \text{Na}_2\text{SO}_4 + 2\text{NO}_2(g) + 2\text{H}_2\text{O} \tag{2}
\]

Reactions in the second leaching stage:

\[
\text{CuS} + 2/3\text{NaNO}_3 + 4/3\text{H}_2\text{SO}_4 \\
= \text{CuSO}_4 + 1/3\text{Na}_2\text{SO}_4 + \text{S}^0 + 2/3\text{NO}(g) + 4/3\text{H}_2\text{O} \tag{3}
\]

\[
\text{CuS} + 2\text{NaNO}_3 + 2\text{H}_2\text{SO}_4 \\
= \text{CuSO}_4 + \text{Na}_2\text{SO}_4 + \text{S}^0 + 2\text{NO}_2(g) + 2\text{H}_2\text{O} \tag{4}
\]

The overall reactions for the first and the second stage are derived from the above reactions:

\[
\text{Cu}_2\text{S} + 4/3\text{NaNO}_3 + 8/3\text{H}_2\text{SO}_4 \\
= 2\text{CuSO}_4 + 2/3\text{Na}_2\text{SO}_4 + \text{S}^0 + 4/3\text{NO}(g) + 8/3\text{H}_2\text{O} \tag{5}
\]

\[
\text{Cu}_2\text{S} + 4\text{NaNO}_3 + 4\text{H}_2\text{SO}_4 \\
= 2\text{CuSO}_4 + 2\text{Na}_2\text{SO}_4 + \text{S}^0 + 4\text{NO}_2(g) + 4\text{H}_2\text{O} \tag{6}
\]

The other reactions in the system:

\[
\text{S}^0 + 3\text{NO}_2(g) + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 3\text{NO}(g) \tag{7}
\]

\[
3\text{NO}_2(g) + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}(g) \tag{8}
\]

\[
\text{NO}(g) + 2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \\
= 3\text{NO}_2(g) + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \tag{9}
\]

Table 1

<table>
<thead>
<tr>
<th>Eq. no.</th>
<th>( \Delta G^\circ_{298} ) (kJ/mol)</th>
<th>( \Delta G^\circ_363 (kJ/mol) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>- 146.317</td>
<td>- 149.854</td>
</tr>
<tr>
<td>(2)</td>
<td>- 156.922</td>
<td>- 174.959</td>
</tr>
<tr>
<td>(3)</td>
<td>- 125.841</td>
<td>- 130.411</td>
</tr>
<tr>
<td>(4)</td>
<td>- 136.446</td>
<td>- 155.517</td>
</tr>
<tr>
<td>(5)</td>
<td>- 272.157</td>
<td>- 280.266</td>
</tr>
<tr>
<td>(6)</td>
<td>- 293.369</td>
<td>- 330.476</td>
</tr>
<tr>
<td>(7)</td>
<td>- 346.727</td>
<td>- 344.715</td>
</tr>
<tr>
<td>(8)</td>
<td>8.449</td>
<td>25.469</td>
</tr>
<tr>
<td>(9)</td>
<td>- 15.909</td>
<td>- 37.658</td>
</tr>
</tbody>
</table>
Thermodynamic analysis included calculation of standard Gibbs energy change and $E-pH$ diagrams.

In order to clarify the occurrence probability and priority of quoted reactions (1)–(9), Gibbs energy change was calculated within a temperature range from 25 to 90 °C and values are shown in Table 1. HSC Chemistry software and its database of thermodynamic values of reaction participants were used in calculations.

The negative values of Gibbs energy change $\Delta G_T$ for reactions (1)–(9) but not reaction (8) show that they are all thermodynamically feasible except reaction (8).

The more negative $\Delta G_T$ value of reaction (6) suggests that it occurs with higher thermodynamic probability than reaction (5). Therefore, reaction (6) is taken as possibly the overall reaction in the Cu$_2$S–H$_2$SO$_4$–NaNO$_3$–H$_2$O system.

$E-pH$ diagrams show the thermodynamic stability of water solution components and dependence on pH values and electrochemical potential (Pacović, 1980).

$E-pH$ diagrams for systems S–H$_2$O, Cu–S–H$_2$O and Cu–N–S–H$_2$O are presented in Fig. 1. They were obtained by using HSC Chemistry software.

Fig. 1. $E-pH$ diagrams in systems (a) S–H$_2$O at 25 °C, (b) Cu–S–H$_2$O at 25 °C, (c) Cu–N–S–H$_2$O at 25 °C and (d) Cu–N–S–H$_2$O at 90 °C.
From Fig. 1, it can be concluded that acid medium favours the formation of elemental sulphur, $S^2$– ions which exist only under very high pH values and strong reduction condition; copper leaching from Cu$_2$S and CuS necessitates oxidation conditions. At higher pH values and under oxidation conditions, Cu$_2$O and CuO exist in water solutions.

3. Experiments

Cu(I) sulphide, from RTB Bor mine, Serbia, with 80.4% of Cu and 18.6% of S and density of 5.04 kg/dm$^3$ was used in the investigation. The average particle diameter of Cu(I) sulphide was 8 $\mu$m. Sodium nitrate and sulphuric acid of pa purity were used. All leaching experiments were carried out in a glass reactor equipped with a Teflon stirrer, condenser, thermometer, glass funnel for adding the solid sample and a sampling device. This apparatus provides hermetic conditions and heating at constant temperature. The calculated volumes of H$_2$SO$_4$ and NaNO$_3$ solutions were put into the glass reactor and heated to the selected temperature. When the temperature was reached, the solid sulphide was added and that moment is taken for beginning of reaction. After definite leaching intervals, the solution samples were taken for chemical analysis, which was carried out with AAS (Perkin Elmer). The solid residues were carefully filtered out, washed with distilled water, dried and their phase content was determined by X-ray analysis (SIEMENS D500).

The following parameters were studied: temperature ($^\circ$C): 40, 60, 80 and 90; concentration of NaNO$_3$ (mol dm$^{-3}$): 0.15, 0.25, 0.40 and 0.60; concentration of H$_2$SO$_4$ (mol dm$^{-3}$):0.3, 0.5, 1.0 and 1.5; stirring speed (min$^{-1}$): 200, 300 and 450; and phase ratio (S/L): 10, 20 and 30 g Cu$_2$S in 1.2 dm$^3$ of the solution. Leaching times were: 3, 5, 10, 15, 20 and 30 min.

4. Experimental results and discussion

4.1. Temperature dependence

Fig. 2 shows the temperature dependence of copper sulphide leaching degree in an oxidized, acidic solution under the following conditions: 0.4 mol dm$^{-3}$ NaNO$_3$, 1.0 mol dm$^{-3}$ H$_2$SO$_4$, stirring speed 300 min$^{-1}$ and phase ratio 20 g Cu$_2$S/1.2 dm$^3$.

The temperature has very strong influence on the copper leaching degree. It suggests that the process is chemically controlled, which has been confirmed in further kinetic analysis. The quantity of leached copper increases when the temperature is increased from 40 to 90 $^\circ$C. This is probably due to the molecules in the reaction system not possessing enough energy which is needed for the successful reaction (activation energy) at those temperatures. A remarkable jump in leaching degree is noticeable between 60 and 80 $^\circ$C. The maximum leaching degree is 97.8% at 90 $^\circ$C and after 30 min.

4.2. Effect of NaNO$_3$

The influence of NaNO$_3$ concentration on the copper leaching degree was determined in a NaNO$_3$ concentration range from 0.15 to 0.60 mol dm$^{-3}$ and a time frame from 3 to 30 min. The other experimental conditions were constant (80 $^\circ$C, 1.0 mol dm$^{-3}$ H$_2$SO$_4$, stirring speed 300 min$^{-1}$ and phase ratio 20 g Cu$_2$S/1.2 dm$^3$). The effect of changing the initial concentration of NaNO$_3$ is shown in Fig. 3, from where it can be seen that the reaction rate increases with NaNO$_3$ concentration increase. The experimental results confirm the fact that sulphuric acid without oxidants does not react with chalcocite (Cu$_2$S) because the copper sulphides are stable in water solutions up to electrochemical potential +0.337 V (Pacović, 1980) (see E–pH diagrams).
4.3. Effect of H$_2$SO$_4$

The influence of H$_2$SO$_4$ concentration on the leaching degree was studied by the variance of the initial solution acidity and under constant following conditions: 80 °C, 0.4 mol dm$^{-3}$ NaNO$_3$, stirring speed 300 min$^{-1}$ and phase ratio 20 g Cu$_2$S/1.2 dm$^3$. Experimental results are represented in Fig. 4.

The quantity of leached copper depends strongly on the solution acidity and it increases with the growth of H$_2$SO$_4$ concentration from 0.3 to 1.5 mol dm$^{-3}$. The formation of elementary sulphur in acid solution is favoured instead of H$_2$S. Cu$^{2+}$ ions are also more stable in more acid solutions, which is important from the viewpoint of Cu$_2$S solubility. Also, the oxidizing potential of NO$_3$ ions increases with the increase of solution acidity, which contributes to the leaching of copper.

4.4. Effect of stirring speed

The influence of stirring speed on leaching degree was studied by changing of stirring speed from 200 to 450 min$^{-1}$ and under the following conditions: 80 °C, 0.4 mol dm$^{-3}$ NaNO$_3$, 1.0 mol dm$^{-3}$ H$_2$SO$_4$ and phase ratio 20 g Cu$_2$S/1.2 dm$^3$. The leaching degree dependence on the stirring speed is shown in Fig. 5.

Stirring conditions are very important from the standpoint of reactants’ transportation in a solid–liquid system. The thickness of the diffusion layer surrounding Cu$_2$S particles decreases with the increase of stirring speed (Zelikman et al., 1983) and that is
why the reaction rate increases with the increase of stirring speed (Fig. 5). However, from Fig. 5, it can be seen that the stirring speed influence on the copper leaching degree is not too strong, which also indicates that the leaching process is chemically controlled.

4.5. Effect of solid–liquid ratio

The influence of solid–liquid ratio (S/L) on the leaching degree was studied under the following conditions: 80 °C, 0.4 mol dm$^{-3}$ NaNO$_3$, 1.0 mol dm$^{-3}$ H$_2$SO$_4$ and stirring speed 300 min$^{-1}$. Experimental results are shown in Fig. 6, from where it can be seen that the higher S/L ratio, the higher is the copper leaching degree.

4.6. X-ray diffraction analysis

In order to investigate the leaching process mechanism, the solid products were exposed to the X-ray
analysis and in this way, their phase content was determined. The solid residues obtained at 60 and 90 °C under the following conditions: stirring speed 300 min⁻¹, 0.4 mol dm⁻³ NaNO₃, 1.0 mol dm⁻³ H₂SO₄, 20 g Cu₂S/1.2 dm³ and 30 min, were chosen for the X-ray analysis (Figs. 7 and 8). From Fig. 7, it can be seen that at 60 °C, the solid residue consists of digenite (Cu₉S₅), chalcocite (Cu₂S) and covellite (CuS). The phase content of the solid product obtained at 90 °C (Fig. 8) is elementary sulphur and covellite (CuS). These X-ray results confirm the assumption that the leaching process of copper(I) sulphide in an oxidized, acidic solution has two stages: in the first stage CuS is formed, while the elementary sulphur is formed in the second stage.

5. Process kinetics

The process of copper(I) sulphide leaching in H₂SO₄ solution in the presence of NaNO₃ is a complex heterogenous process. Kinetic analysis was made on the basis of experimental results (Figs. 2–4).

5.1. Activation energy

Activation energy for the process of copper(I) sulphide leaching was determined by using the kinetic equations of Ginstling-Brounshtein, Spenser-Topley and Wadsworth (Sohn and Wadsworth, 1979). By applying these equations, it can be concluded that experimental results of the temperature influence on leaching degree (Fig. 2) are best fitted by Spenser-Topley equation (Eq. (10)) as shown in Fig. 9.

\[ 1 - (1 - \alpha)^{1/3} = kt \]  

(10)

where \( k \) is a rate constant with unit of reciprocal time.
The activation energy of 60 ± 0.7 kJ/mol for the Cu$_2$S leaching according to Eq. (5) was calculated from the slope of the plot using Arrhenius equation (Fig. 10).

5.2. Dependence of reaction rate on leaching reagents concentration—reaction order

Reaction order for NaNO$_3$ and H$_2$SO$_4$ was determined from results in Figs. 3 and 4 by applying the Spenser-Topley equation. Rate constants $k_{Na}$ and $k_{H}$ were calculated from the plots’ slopes as shown in Figs. 11 and 12. This analysis demonstrated the following:

- The copper(I) sulphide leaching is a first-order reaction with respect to the concentration of NaNO$_3$ (Fig. 13) and its rate equation is:

$$- \frac{d[Cu_2S]}{dt} = k_{Na}[NaO_3]$$

(11)

- The copper(I) sulphide leaching is a second-order reaction with respect to the concentration of H$_2$SO$_4$ (Fig. 14) and its rate equation is:

$$- \frac{d[Cu_2S]}{dt} = k_{H}[H_2SO_4]^2$$

(12)

where: $k_{Na}$ and $k_{H}$ are rate constants; [NaNO$_3$] and [H$_2$SO$_4$] are the leaching reagent concentrations.

6. Conclusion

From the results obtained in the study of copper(I) sulphide leaching by H$_2$SO$_4$ solution with the addition of NaNO$_3$, the following conclusions can be made.

(1) On the basis of experimental data, thermodynamic calculations and the products in the solution, as well as in the solid residues, determined by X-ray analysis, the chemistry mechanism is determined by the following reactions: the first leaching stage
(Eq. (2)), the second leaching stage (Eq. (4)), overall leaching reaction for both first and second leaching stage (Eq. (6)).

(2) The influence of working parameters on the leaching degree shows that the increase in values of all working parameters affects the increase in the quantity of the dissolved copper. The temperature influence on the reaction rate is especially great: the temperature increase from 40 to 90 °C is followed by an increase in leaching degree from 10% to 98%.

(3) The value of activation energy, $60 \pm 0.7$ kJ/mol, calculated by applying the Spenser-Topley equation, proves that the leaching process is chemically controlled.

(4) The copper(I) sulphide leaching is a first-order reaction with respect to the concentration of NaNO$_3$.

(5) The copper(I) sulphide leaching is a second-order reaction with respect to the concentration of H$_2$SO$_4$.

References


