Abstract

In a response to the recent growth in the global demand for copper products, mining industries have intensified in their mining operations. Unfortunately, the grade of copper ore mined today is declining due to the intensive mining of the relatively high grade copper resources. Therefore, future copper ore deposits to be mined are likely to be richer in impurity elements like antimony and arsenic which attract smelter’s penalty if the content of these impurities is too high. It is however imperative to selectively eliminate and recover the antimony impurity of the copper concentrates in an environmentally friendly process with a view of upgrading the concentrates for pyrometallurgical processing.

This paper discusses the alkaline sulphide hydrometallurgical technology to selectively solubilize antimony impurity from a copper concentrate. The effect of sodium sulphide and sodium hydroxide concentrations, leaching time and leaching temperature on antimony dissolution will be examined. Furthermore, antimony recovery as a marketable product from simulated pregnant leach liquor through electrodeposition will be discussed. Various experimental factors that influence antimony deposition from alkaline sulphide electrolyte are reported.

1. Introduction

Due to the recent growth in the global demand for copper products, mining industries have increased in their mining operations. Fig.1 illustrates an increasing growth in global copper consumption as a consequence of overall economic growth. To meet-up with the increase in the world copper demand, the grade of copper ore mined today is declining (Fig. 2) due to the intensive mining of the relatively high grade copper resources. Therefore, future copper ore deposits to be mined are likely to be richer in impurity elements like antimony and arsenic which attract smelter’s penalty if the content of these impurities is too high. Removal of antimony in copper metallurgy is one of the major problems encountered today since copper ore reserves free of antimony are becoming exhausted and the resources of unexploited ores often contain relatively high amounts of this element, which need to be eliminated. It is however imperative to selectively eliminate and recover the antimony impurity of the copper concentrates in an environmentally friendly process with a view of purifying the concentrates for pyrometallurgical processing.

The main antimony-bearing minerals in copper sulphide deposits are sulphosalts and sulphides such as tetrahedrite (Cu$_2$Sb$_4$S$_{13}$), jamesonite (Pb$_3$FeSb$_6$S$_{14}$), bournonite (PbCuSb$_3$S$_6$) and stibnite (Sb$_2$S$_3$)[1-4]. Unfortunately, these copper-antimony minerals exhibit similar flotation properties to copper sulphides and are easily floated to copper concentrates [5]. Due to high penalties imposed by smelters on copper concentrates containing antimony greater
than 0.3% [6], alternative hydrometallurgical processing routes for the treatment of such resources need to be developed.

![Fig. 1: World copper demand (kilo-tonnes refined copper) [7]](image)

![Fig. 2: Average grades for copper industry [7]](image)

However, a promising alkaline sulphide hydrometallurgical technology of selectively dissolving antimony from copper concentrates has been studied extensively and reported in the literature [1-4, 8-12]. The pregnant leach solution has been purified to recover antimony as a metal or solid sodium thioantimonate [13].

This paper therefore discusses the alkaline sulphide hydrometallurgical technology to selectively solubilize antimony impurity from a copper concentrate. The effect of sodium sulphide and sodium hydroxide concentrations, leaching time and leaching temperature on antimony dissolution is examined. Furthermore, antimony recovery as a marketable product from simulated pregnant leach liquor through electrodeposition is discussed. The various experimental factors that influence antimony deposition from alkaline sulphide electrolyte are reported.

2. Experimental methods

The copper concentrate used in this investigation was a flotation concentrate obtained from Boliden Mineral AB, Sweden. More than 80% of the mineral particles were less than 40 µm. The major mineralogical compositions of the concentrate were chalcopyrite, sphalerite, galena, pyrite, tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$), bournonite (PbCuSbS$_3$), stannite (Cu$_2$FeSnS$_4$) and arsenopyrite [3]. Table 1 presents the elemental analysis of the concentrate.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental analysis (%) of the complex copper concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>17.8</td>
</tr>
<tr>
<td>Fe</td>
<td>27.1</td>
</tr>
<tr>
<td>Pb</td>
<td>7.1</td>
</tr>
<tr>
<td>Zn</td>
<td>5.7</td>
</tr>
<tr>
<td>Sb</td>
<td>1.69</td>
</tr>
<tr>
<td>Sn</td>
<td>0.14</td>
</tr>
<tr>
<td>As</td>
<td>0.42</td>
</tr>
<tr>
<td>Se</td>
<td>0.06</td>
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<tr>
<td>Hg</td>
<td>0.03</td>
</tr>
<tr>
<td>Ag</td>
<td>0.08</td>
</tr>
</tbody>
</table>
The leaching experiments were conducted in a batch mode using a 1 L four-necked round bottomed glass reactor (Fig. 3a). The leaching solution was prepared by dissolving sodium sulphide (Na$_2$S·3H$_2$O) in sodium hydroxide (NaOH) solution. The concentration of sodium hydroxide used at each run of the test was 20 wt% of the sodium sulphide concentration used. The lixiviant was first added to the reactor and when the desired temperature was reached, 200 g/L of the concentrate was added except where otherwise stated. The contents of the reactor were mechanically homogenized using a paddle stirrer at a constant stirring rate of 300 rpm and heated on an auto-regulated device. All the leaching experiments lasted for 6 h. At predetermined time intervals, a slurry sample was taken from the reactor for the analysis of dissolved metals. All reagents used for leaching and chemical analysis were of analytical grade and used without further purification. Leaching results were evaluated by means of elemental determinations on the leach products using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) / Sector Field Mass Spectrometry (ICP-SFMS).

![Fig. 3: Leaching (a) and electrowinning (b) experimental set-up](image)

The electrowinning tests were performed in a 1 L rectangular stainless steel (EN-1.4436) cell (Fig. 3b). The cathode was a 7.1 cm x 6.8 cm x 0.2 cm stainless steel (EN-1.4436) plate with a total of 101 cm$^2$ exposed plating area on both side of the plate. The cathode plate was placed between two anodes. The anode was made from nickel wire (Ø = 0.38 mm, 99.8% Ni) which was vertically wound around the anode plastic frame. The total anode working area was one-tenth of the cathode area and the gap between anode and cathode was 4 cm. A stock solution of the electrolyte was prepared by dissolving analytical grade antimony sulphide (Sb$_2$S$_3$), sodium sulphide (Na$_2$S·3H$_2$O) and sodium hydroxide (NaOH) in deionized water.

The influence of cathodic current density, electrolyte temperature, the concentration of sodium sulphide and sodium hydroxide on the current efficiency of antimony deposition and specific energy consumption was investigated. The cathodic current density was varied between 50 and 250 A/m$^2$, while the concentration of sodium hydroxide was varied between 100 and 400 g/L. The electrolyte temperature used was 45, 60, 75 and 90°C. The hydrated water in Na$_2$S·3H$_2$O was compensated for during the preparation of the various concentration of Na$_2$S (60, 100 and 150 g/L) used in the tests. Each experiment was run for 9 h and the
cathode was changed at time intervals of 1, 2, 4, 6 and 9 h. Deposited antimony was washed thoroughly in warm tap water, dried and weighed.

3. Results and discussion

3.1 Leaching of antimony

3.1.1 Influence of Na₂S concentration on antimony leaching

The influence of sodium sulphide concentration on the recovery of antimony from a copper concentrate containing antimony is shown in Fig. 4. The applied leaching conditions were as follows - solid concentration: 100 g/L, temperature: 90°C and time: 6 h. The concentration of Na₂S used was 100, 150 and 200 g/L. The result described in Fig. 4 reveals that the concentration of sodium sulphide has a significant influence on antimony dissolution from the concentrate. At 200 g/L Na₂S addition, about 97% antimony is removed within 6 h, however, the recovery decreases when sodium sulphide concentration is reduced to 150 and 100 g/L, reaching up to 92% and 63% in 6 h, respectively. Therefore, it can be concluded that the higher the concentration of sodium sulphide, the higher the recovery of antimony from the concentrate.

Since antimony is present in the concentrate as tetrahedrite (Cu₁₂Sb₄S₁₃) and bournonite (PbCuSbS₃), the result shows that the leaching of antimony from these minerals strongly depends on the concentration of Na₂S. This is because during leaching of these antimony minerals, they decompose and the various elements in the minerals react with sulphide ions to form either soluble (Na₃SbS₃) or insoluble (CuS, Cu₂S, PbS) sulphide compounds. This implies that for an effective and efficient leaching process, more than the stoichiometric requirement of sulphide ions needed to dissolve the antimony content of the material should be used. This result is consistent with the earliest investigation by the authors [1, 10, 14] when antimony was leached from a tetrahedrite rich complex sulphide concentrate.
3.1.2 Influence of leaching temperature

The dependence of antimony leaching from an antimony-containing copper concentrate on temperature is shown in Fig. 5. The leaching experiments were investigated by conducting tests at: 40°C to 100°C while keeping the concentrations of sodium sulphide and solid material constant at 150 g/L and 100 g/L, respectively. Each experiment was run for 6 h. It is apparent from Fig. 5 that leaching of antimony from the concentrate is strongly influenced by temperature. At 40°C, 38% of antimony was extracted, and when the leaching temperature was raised to 80°C, about 87% of antimony was leached. The maximum antimony recovery of 92% was obtained when the reaction temperatures were increased further to 90°C and 100°C, respectively. This indicates that it is unnecessary to perform antimony leaching from the concentrate at a temperature greater than 90°C. The strong dependence of the leaching process on temperature suggests that the process is chemically-controlled through the reaction taking place on the surface of the mineral particles [4, 10].

![Fig. 5: Influence of temperature on antimony leaching](image)

3.1.3 Influence of leaching time

The influence of leaching time on antimony dissolution from the copper sulphide concentrate was investigated. Leaching experiments were conducted under the following conditions: 200 g/L solid concentration, 90°C reaction temperature, 150 g/L Na₂S and NaOH concentration was 20%w/w of Na₂S concentration. The experimental results are presented in Fig. 6. Increasing the leaching time resulted in increased antimony extraction. From the plots in Fig. 6, it can be seen that the leaching kinetic was faster in the first 60 minutes, and thereafter, the rate of antimony leaching was observed to be slowly decreasing with increasing time. This is probably attributed to the leaching of the fine mineral particles before the coarse ones since more than 80% of the mineral grains were less than 40µm. After 60 minutes of leaching, approximately 68% of antimony was extracted, and when the leaching time was increased to 360 minutes, antimony extraction was 92%.
3.1.4 Analysis of leach residue

At the end of the leaching tests, four of the leach residues (purified concentrate) at which the antimony recovery was greater than 95% were selected for elemental analysis. The average content of the elements analysed from these residues is plotted in Fig. 7. The result indicates that the alkaline sulphide lixiviant is strongly selective in dissolving antimony from the concentrate. About 96% of the antimony content of the concentrate has been removed into solution. This confirms the previous findings reported in the literature \[1, 2, 10, 11\]. It is noticeable from the figure that only about 10% of arsenic is removed during the leaching. This is because arsenic is present mainly as arsenopyrite in the concentrate, and arsenopyrite mineral has been reported to be unreactive to alkaline sulphide solution \[3, 13\]. The antimony content (0.07%) in the purified concentrate is far less than the concentration of antimony that should be present in the smelter’s feedstock under which no penalty will be charged \[6\].
3.2 Electrodeposition of antimony

3.2.1 The effect of sodium sulphide concentration

The effect of sodium sulphide concentration on the current efficiency and specific energy was studied by using the following electrolytic conditions - initial antimony concentration: 35 g/L, NaOH concentration: 350 g/L, cathode current density: 200 A/m² and electrolyte temperature: 75°C. The concentrations of initial sodium sulphide used in these tests were 60, 100 and 150 g/L. The result obtained from this experiment is described in Fig. 8. The figure indicates that the current efficiency decreases with increasing free sodium sulphide concentration. After 9 h of electrodeposition, current efficiency decreased from 88% to 87% and 77% for 60, 100 and 150 g/L of sodium sulphide, respectively. This implies that by increasing the free sodium sulphide concentration in the electrolyte, it will promote the oxidation of sulphide sulphur to undesirable sulphur species like $\text{S}_2^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ in the solution (Eqs. 1-2) and the oxidized sulphur species will further get reduced when they are in contact with the cathode (Eqs. 4-7) or other constituents of the solution (Eq. 9). These oxidation and reduction processes consume energy to no purpose, and consequently decreases the current efficiency of the electrolytic process.

![Fig. 8: Influence of Na$_2$S concentration of current efficiency and specific energy](image)

In addition, oxidation and reduction of antimony complex ions as shown in equations 3 and 8 will also contribute to the lowering of current efficiency. Fig. 8 also shows the effect of sodium sulphide concentration on the specific energy for depositing one kilogram of antimony. It was observed during the experiments that the average cell voltage decreased with increasing Na$_2$S concentration. At 60 g/L Na$_2$S, the cell voltage was 2.48 V but when the concentration of Na$_2$S increased to 150 g/L, the average cell voltage was 2.13 V. The specific energy of the electrolytic process is directly related to the average cell voltage, the plot shown in Fig. 8 illustrates that the specific energy is not much influenced. The increase in sulphide concentration might have increased the electrolyte conductivity.

At the anode:

\[
\begin{align*}
2\text{S}^{2-} &\rightarrow \text{S}_2^{2-} + 2e^- & (1) \\
\text{S}_2^{2-} + 1.5\text{O}_2 &\rightarrow \text{S}_2\text{O}_3^{2-} & (2) \\
\text{SbS}_3^{3-} + \text{S}^{2-} &\rightarrow \text{SbS}_4^{3-} + 2e^- & (3)
\end{align*}
\]
At the cathode:

\[ \text{S}_2\text{O}_3^{2-} + 2e^- \rightarrow \text{S}^{2-} + \text{SO}_3^{2-} \]  
(4)

\[ \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + 8e^- \rightarrow 2\text{S}^{2-} + 6\text{OH}^- \]  
(5)

\[ 3\text{S}_2^{2-} + 2\text{Sb}^0 \rightarrow 2\text{SbS}_3^{3-} \]  
(6)

\[ \text{S}_n^{2-} + 2(n-1)e^- \rightarrow n\text{S}^{2-}, n = 2, 3, \ldots \]  
(7)

\[ \text{SbS}_4^{3+} + 2e^- \rightarrow \text{SbS}_3^{3-} + \text{S}^{2-} \]  
(8)

In the electrolyte:

\[ \text{S}_n^{2-} + (n-1)\text{SbS}_3^{3-} \rightarrow \text{S}^{2-} + (n-1)\text{SbS}_4^{3-} \]  
(9)

3.2.2 The effect of current density

Fig. 9 illustrates the effect of cathodic current density on antimony electrodeposition. The tests were conducted under the following electrowinning conditions: 100 g/L Na\textsubscript{2}S, 350 g/L NaOH, 35 g/L initial Sb concentration, 75\textdegree C electrolyte temperature and 9 h electrodeposition time. It can be seen from the figure that the current efficiency was steadily increasing with increasing cathodic current density up to 150 A/m\textsuperscript{2}, but after this, current efficiency started decreasing. The antimony left in solution after 6 h at 200 and 250 A/m\textsuperscript{2} cathode current density was 17.8 and 16.0 g/L Sb, respectively. This implies that hydrogen evolution might be the reason for the reduced current efficiency experienced after 6 h for the tests conducted at 200 and 250 A/m\textsuperscript{2} cathodic current density. A similar observation has been reported when the antimony content of the electrolyte was lower than 15 g/L [13, 15, 16]. Another reason could be that since thiosulphate and polysulphide concentrations increase with electrowinning time due to the continuous formation at the anode, the part of current used for the reduction of thiosulphates and polysulphides at the cathode (according to Eqs. 4, 5, 7) increases when the antimony concentration decreases.

![Fig. 9: Influence of current density on current efficiency and specific energy](image_url)

The influence of the current density on the specific energy consumption is shown in Fig. 9. It is apparent from the figure that increase in the cathodic current density resulted in a
steady increase in the specific energy consumed during the process. After 9 h of electrodeposition, the specific energy for depositing 1 kg of antimony was 0.61 kWh at 50 A/m² but when the current density was raised to 250 A/m², the specific energy was increased to 2.32 kWh. It has been reported that higher current density leads to larger cell capacity and productivity, but will concomitantly increase the cell voltage and power consumption [16]. It was noticed during the electrowinning tests that increase in cathode current density influences the morphology of the deposit. At 50 A/m², antimony deposition was smooth, silvery whitish in colour and strongly adherent to the cathode while at 250 A/m², the deposit was rough and greyish-green with loose adherence to the cathode material.

3.2.3 The effect of NaOH concentration

To verify the effect of increase in NaOH concentration on the electrowinning of antimony from alkaline sulphide solutions, the experiments were performed using 35 g/L initial antimony concentration, 100 g/L Na₂S, 200 A/m² current density, 75°C electrolyte temperature and 9 h electrolysis time. The results contained in Fig. 10 demonstrate that increase in NaOH concentration enhances the current efficiency of antimony deposition significantly. This observation is attributed to the preferential discharge of hydroxide ions at the anode (Eq. 10) over sulphide (Eq. 1) due to the concentration difference between anions.

$$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \quad (10)$$

As a result, the formation of the harmful sulphur species which can hinder antimony deposition at the cathode is restricted. The current efficiency increased from 60% to 90% when the concentration of sodium hydroxide was raised from 100 g/L to 400 g/L, respectively. The specific energy was noticed to decrease with increasing sodium hydroxide concentration. This observation is due to the increase in sodium hydroxide concentration which enhances antimony deposition. The specific energy of an electrolytic process is inversely proportional to the mass of the metal deposited at the cathode. This suggests that an increase in the amount of antimony deposited due to the increase in NaOH concentration will lead to a decrease in the specific energy. The physical appearance of the antimony cathode was observed to be smooth and adherent to the cathode when 100 g/L NaOH was used, but when the concentration of NaOH was increased to 400 g/L, the deposit was rough and darkened.
3.2.4 The effect of electrolyte temperature

Studies to observe the influence of the electrolyte temperature on antimony electrodeposition from alkaline sulphide solutions were conducted under the following conditions: 35 g/L initial Sb concentration, 100 g/L Na₂S, 350 g/L NaOH and cathode current density of 200 A/m². The results of the experiments are reported in Fig. 11, which indicates that the temperature of the electrolyte has a significant influence on the current efficiency of the electrolytic process. The figure displays that, after 9 h, current efficiency increases from 81% at 45°C to 90% and 93% when the temperature was raised to 60°C and 90°C, respectively. The reason for the increment is that, at 45°C, the viscosity of the electrolyte was higher than at the other temperatures due to the decreased solubility of the electrolyte components, and consequently increases the solution resistance and electrode polarization [16]. It is apparent from the figure that increase in electrolyte temperature decreases the solution resistance which consequently increases the ionic diffusion coefficient, and thereby correspondingly reduces the specific energy consumption.

![Fig. 11: Influence of temperature on current efficiency and specific energy](image)

**Conclusions**

This investigation determines the technical practicality, on a bench-scale, of the combined sulphide leaching and electrodeposition processes to recover antimony as a metal from a copper concentrate containing antimony. The results from the leaching step showed that antimony dissolution strongly depends on the concentration of the leaching reagent as well as the leaching temperature and time. The antimony content in the concentrate was reduced from 1.7% to less than 0.1%, which is desirable for copper metallurgy. Current efficiency is one of the important parameters to evaluate the performance of an electrolytic process. The study revealed that current efficiency of antimony deposition from sulphide electrolytes is highly dependent on the concentration of sodium hydroxide and the current density used. It was illustrated in this test that the combined effect of increasing anode current density (which was 10 times higher than the cathode current density) and NaOH concentration enhanced the current efficiency of the electrolytic process. It was demonstrated that excess free sulphide ions influences the current efficiency of the process detrimentally.
Increase in the electrolyte temperature as well as the concentration of NaOH tends to decrease the specific energy of the electrolytic process.

References


