HYDROMETALLURGICAL UPGRADE OF A TETRAHEDRITE RICH COPPER CONCENTRATE

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December 2010
ABSTRACT

Removal of impurity elements in copper metallurgy is one of the major problems encountered today since pure copper ore reserves are becoming exhausted and the resources of unexploited ores often contain relatively high amounts of antimony, arsenic, mercury and bismuth, which need to be eliminated. The present work aims at pre-treating a tetrahedrite rich complex copper sulphide concentrate by selective dissolution of the impurities, therefore, upgrading it for pyrometallurgical processing. Characterisation of the complex concentrate was performed and the result shows that antimony and part of arsenic were present as tetrahedrite and bournonite. Dissolution kinetics of tetrahedrite in aqueous alkaline sodium sulphide solutions was investigated. It was found that the rate of dissolving tetrahedrite by the lixiviant increases with increase in reaction temperature, sodium sulphide concentration, sodium hydroxide concentration, and with decrease in mineral particle size. The kinetic study indicates that the rate of leaching tetrahedrite in the lixiviant under the selected conditions is chemically controlled through the particle surface reaction. The activation energies of the process were estimated as 81 kJ/mol and 75 kJ/mol, respectively, for antimony and arsenic dissolution from tetrahedrite. The estimated activation energies were within the range reported for a chemically controlled reaction process.

Besides, the alkaline sulphide lixiviant proves selective and effective to dissolve these impurity elements from the concentrate with good recoveries. Further investigations on the factors influencing the leaching efficiency of the lixiviant were studied. Analysis of the leach residue indicates that copper content of the tetrahedrite has transformed into copper sulphides with the average chemical formula Cu_{1.64}S. The grade and economic value of the concentrate were improved greatly after sulphide treatment, and therefore, suitable as a feedstock for smelting. The impurities in the concentrate were found to have reduced to a level satisfactory for smelting operation.

Furthermore, modelling and optimisation of alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn were conducted. Response surface methodology, in combination with central composite face-centred design (RSM-CCF), was used to optimise the operating parameters. The leaching temperature, sulphide ion concentration and solid concentration were chosen as the variables, and the response parameters were antimony and tin recoveries, and the time required to achieve 90% Sb dissolution. It was seen that the leaching process was strongly dependent on the reaction temperature as well as the sulphide ion concentration without any significant dependence on the solid concentration. Additionally, a mathematical model was constructed to characterise the leaching behaviour within the experimental range studied. The results from the model allow identification of the most favourable leaching conditions. The model was validated experimentally, and the results show that the model is reliable and accurate in predicting the leaching process.
ACKNOWLEDGEMENTS

Firstly, I give thanks to God Almighty for His divine favour, protection, wisdom, love and mercy that endureth for ever.

Secondly, I would like to express my sincere gratitude to my supervisor, Professor Åke Sandström for his guidance and valuable suggestions/contributions during the course of this work. More power to your elbow. I am also indebted to Dr. Caisa Samuelsson for her valuable comments and role as co-supervisor of my programme.

Most importantly, I would like to give my profound appreciation to the following organisations: VINNOVA, Boliden Minerals AB, LKAB and the Adolf H. Lundin Charitable Foundation for their financial supports to carry out this research.

A special thank you goes to all the employees and colleagues at the Division of Extractive Metallurgy for their valuable supports and helps. A special recognition is deserving of Birgitta Nyberg for giving me some technical clues during my experimental work. I must sincerely thank the following people from Boliden Mineral AB: Dr. Nils-Johan Bolin, Jan-Eric Sundkvist, Paul Kruger and Andreas Berggren for their contributions and suggestions to the success of this research.

Further thanks to all my friends who in one way or the other have contributed meaningfully to my stay and study at LTU. May God bless you all.

Finally, my heartfelt gratitude is extended to my loving wife, Patricia, and my wonderful children for their understanding and perseverance when I returned home late in the night. I love you all.
LIST OF APPENDED PAPERS

PAPER I
Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media

Samuel A. Awe, Caisa Samuelsson and Åke Sandström
Hydrometallurgy 103 (2010) 167-172

PAPER II
Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution

Samuel A. Awe and Åke Sandström
Minerals Engineering 23 (2010) 1227-1236

PAPER III
Separation of antimony from a complex copper concentrate: Process optimization by response surface methodology

Samuel A. Awe, Mohammad Khoshkhoo, Paul Kruger and Åke Sandström
Manuscript under review in Separation and Purification Technology Journal

Other contribution not included
Leaching mechanism of tetrahedrite in alkaline sulfide solution

Samuel A. Awe and Åke Sandström
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1. INTRODUCTION

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. Copper’s chemical, electrical, physical and aesthetic properties make it a material of choice in a wide range of domestic, industrial and high technology applications. Its ductility, corrosion resistance, malleability and excellent conductivity of heat and electricity make it to have diverse application potentials in modern material development and engineering [1]. The industrialization of developing economies in Asia, and the drive to improve standards of living in the region, fuelled the demand for copper over the last 10 years. Economic, technological and societal factors have influenced the demand and supply of copper in 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 [2].

Naturally, copper occurs in the Earth’s crust in a variety of forms. It can be found in sulphide deposits as chalcopyrite CuFeS₂, bornite Cu₉FeS₈, chalcocite Cu₂S & covellite CuS; in carbonate deposits as azurite Cu₃(CO₃)₂(OH)₂ & malachite Cu₂(CO₃)(OH)₂; in silicate deposits (as chrysocolla (Cu₃Al₂)(OH)₄·nH₂O & dioptase CuSiO₃(OH)₂) and as pure native copper. Copper is extracted from its ore by either smelting with refining [3, 4] or leaching with electrowinning [4]. Copper extraction through pyrometallurgical processing of concentrate relies heavily on copper sulphides and to a lesser degree on copper oxides, which are processed hydrometallurgically. Today, most of the new copper sulphide mineral deposits found are complex in nature and often found in association with minerals like tetrahedrite, enargite and tennantite [5] which render the concentrate unsuitable as a feedstock for smelting due to its antimony, arsenic and mercury contents which create serious environmental problems [6-8] and even affect the quality of the copper product [9]. Many of such complex sulphide mineral deposits are largely found in Sweden. Due to their association with the impurity elements (Sb, As and Hg) that make it difficult to produce clean and high grade concentrate, the deposits have been discovered for quite long time but have so far not been possible to mine economically. As a result of the global increase in demand for base metals, the mining companies are now giving more attention to these low grade and complex ore deposits to economically process them.
Arsenic and antimony have been considered as undesirable elements that cause serious toxicological and environmental problems [7, 10] which have forced the smelter to be conscious of the type of concentrate to be processed due to the stringent environmental law. Apart from this, it is reported that the presence of these noxious elements will significantly affect both the quality and the physical properties of the copper product [9-11]. However, as the global demand for copper continues to grow resulting in a decline in copper deposits with low antimony and arsenic impurities, the focus is now directed on the processing of copper ores with high tetrahedrite, tennantite and enargite contents. The high contents of the impurities in this type of copper resources would significantly reduce their economic values. Therefore, it is highly desirable to reduce the impurity from the ore concentrates to acceptable level prior to shipping to the smelter in order to eliminate smelter penalties and to reduce shipping weight. Furthermore, it is essential that the antimony and arsenic should be removed by a technique which minimises pollution control problems and produces arsenic as a waste product suitable for landfill while antimony is recovered as a marketable products; and consequently upgrades the ore concentrates for pyrometallurgical treatment.

1.1 Impurity minerals in copper concentrate

The common impurity minerals usually found in association with copper ores include tetrahedrite (Cu₅Sb₂S₁₃), jamesonite (Pb₃FeSb₆S₁₄), bournonite (PbCuSbS₃), tennantite (Cu₁₂As₄S₁₃) and enargite (Cu₅AsS₄). These minerals are economically attractive; however, the content of antimony and arsenic reduces their economic values effectively due to the additional requirements for treatment options for the containment of hazardous emissions from pyrometallurgical processing [12]. Tetrahedrite is a complex sulphide of copper and antimony which can be an interesting and important resource of copper (40-46%), antimony (27-29%) [13] and or other non-ferrous metals as is evident from its general chemical formula (Cu,Ag)₁₀(Cu,Zn,Hg,Cd,Fe)₂(Sb,As,Bi)₄S₁₃ [14]. Tetrahedrite belongs to a family of minerals usually called “fahlore” which is often described as the “sulphosalts”. This family indicates a certain type of un-oxidized sulphur mineral that is structurally distinct from a sulphide [15]. The tetrahedrite group is notable for the variety of elements which are stable in its structure. The formula may be written as A₁₂B₄C₁₃, where A = Ag, Cu, Fe, Hg, Zn; B = As, Sb, Bi; C = S, Se, Te. Naturally, it is very difficult to find pure tetrahedrite because its original constituents are always partially substituted by other elements. Thus, arsenic can substitute for antimony leading to tennantite, while copper can be substituted by silver, zinc, iron, mercury,
cadmium, lead etc, and some sulphur may be replaced by Se and Te [7, 15, 16]. Apart from the toxic elements (As, Hg) contained in tetrahedrite mineral, the substantial amount of copper, silver and gold usually present in the mineral makes its mining economically attractive.

1.2 Industrial applications of antimony and its compounds

Antimony is a brittle metal that is not readily fabricated and has no significant use in its unalloyed state. When alloyed with lead and other metals, it increases their hardness, mechanical strength, corrosion resistance, and electrochemical stability or decreases their coefficient of friction. Some antimony alloys expand slightly upon cooling, a valuable property for use in type metal and other castings. Besides, antimony and its compounds have a wide range of non-metallurgical industrial applications as shown in Fig. 1.

![Pie chart showing industrial applications of antimony](image)

**Fig. 1**: Applications of antimony [17]

The recent study report submitted by the Ad-hoc Working Group of the European Commission on defining the critical raw materials for the European Union (EU) has listed
antimony as one of the critical materials needed by the EU [18]. This implies that the price of antimony will continue to rise due to the risk of supply shortage of antimony to the EU economy. Based on this study, recovery of antimony as a marketable product will be of a paramount importance to the mining and metals industries. However, antimony which was regarded as a waste material from copper metallurgy will add values to the process economy.

1.3 The aim and scope of the work

In copper metallurgy, the pyrometallurgical processing route still accounts for almost 80% of copper production throughout the World. But this treatment method can only process relatively pure sulphide copper-concentrates efficiently and economically. As a result of the depletion of high-grade copper sulphide ore deposits, most of the copper ores mined today are complex in nature and even contain a number of impurity elements which attract smelter penalties. Besides, the high contents of the impurities usually accompanied with such ores significantly reduce their economic value. Therefore, the present research aims at improving the grade of the copper sulphide concentrate as a feedstock suitable for pyrometallurgical processing, by a selective removal of the impurities (As, Sb & Sn) in the concentrate via alkaline sulphide hydrometallurgical technology.

The scope of this research includes

- A mineralogical study of the various materials used
- Investigation of tetrahedrite dissolution kinetics and the factors influencing its dissolution in alkaline sulphide media
- Examining the effectiveness of the lixiviant to selectively solubilize the impurities from the concentrate and
- Modelling and optimization of the alkaline sulphide leach process
2. PROCESSING OF COPPER CONCENTRATES

There are two major ways of processing copper concentrates. These include pyrometallurgical and hydrometallurgical routes. Copper sulphide ores are desirable feedstock materials for pyrometallurgical production of copper while the oxide and lean sulphide copper ores are treated via hydrometallurgical routes. Further discussion about the copper production routes is explained in the following sections.

2.1 Pyrometallurgical treatment

Pyrometallurgical processing of copper concentrates involves high temperature reactions which include roasting, smelting and conversion. The prevalence of antimony/arsenic minerals among the copper-bearing minerals, and as a result, the relatively high impurity content in the concentrates substantially reduces their economic value, owing to the hazardous emissions generated from pyrometallurgical processing (Eqs. 1-3). The amount of impurity elements removed during the roasting of the concentrate is very high. These impurities, as well as their oxides (Eqs. 2 and 3), are highly volatile and leave the reactor as off-gas constituents. Thus, in unfavourable metal market conditions, direct roasting of such impurity-containing copper concentrate is uneconomical because gas cleaning facilities demands are too expensive [19]. In order to minimize the problems associated with the processing of such concentrate, the impurity content must be reduced to low levels acceptable in the smelting plant.

\[
\begin{align*}
2\text{CuFeS}_2 + \text{O}_2 & \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2 \quad (1) \\
4\text{Cu}_3\text{AsS}_4 + 7\text{O}_2 & \rightarrow 12\text{CuS} + 4\text{SO}_2 + 2\text{As}_2\text{O}_3 \quad (2) \\
\text{Cu}_2\text{S} + \text{Sb}_2\text{S}_3 + 9/2\text{O}_2 & \rightarrow \text{Cu}_2\text{S} + 3\text{SO}_2 + \text{Sb}_2\text{O}_3 \quad (3)
\end{align*}
\]

In addition, Wang [11] discussed that during copper smelting, some of the undesirable impurities like antimony, arsenic, bismuth and lead are only partially removed by oxidation. When white metal and blister copper are in equilibrium, these impurities are partly distributed into the copper phase, from which their removal is difficult.

In an attempt to reduce the impurity contents, alkaline sulphide hydrometallurgical technology has been explored and considered suitable for dissolving these impurities selectively from the concentrate prior to pyrometallurgical processing.
2.2 Hydrometallurgical processing

As the global demand for copper steadily increases and the need for environmentally sound processing also grows, successful hydrometallurgical treatment of antimony and arsenic containing concentrates has come to the forefront. The amphoteric nature of antimony allows the use of both acidic and basic media for its solubilization [20, 21]. But, in reality only two solvent systems are utilized in antimony hydrometallurgy: acidic chloride [22-27] and alkaline sulphide [21, 28-30].

2.2.1 Acidic chloride leaching of tetrahedrite

Extensive work has been performed by several researchers on acidic oxidative leaching of tetrahedrite minerals in chloride [14, 16, 22-25, 27], and even sulphate media [5, 7]. According to the stability of tetrahedrite, it is necessary to use a strong oxidizing agent. The most commonly oxidizing agents used are Cu^{2+}, Fe^{3+}, O_2, ozone and Cl_2 [16]. The atmospheric leaching of tetrahedrite in chloride media has been studied in detail by Correia et al. [23, 24]. They found that at temperatures 60–104 °C and ferric concentrations 0.001–1 mol/L, leaching of tetrahedrite in FeCl_3–NaCl–HCl solutions is controlled by a surface reaction. The process is extremely slow [23, 25]; it takes about 50 h to extract 90% of copper at 104 °C from tetrahedrite particles of size -100 + 63 μm [24]. Correia et al. [23] observed that tetrahedrites with high iron content dissolved faster than iron-poor tetrahedrites, a phenomenon that was interpreted in terms of the mineral semiconducting properties. The use of ozone (O_3) can improve the rate of tetrahedrite dissolution [14] but, even under the best conditions tested (tetrahedrite particle size -45 μm; 9.0 g/h O_3 per L of solution; ambient temperature), it takes about 6 h to reach 50% extraction of copper [7].

Havlik et al. [22] conducted a leaching investigation with native tetrahedrite concentrate in acidic ferric chloride in the temperature range of 40-90 °C. The results reveal slow leaching rate behaviour exhibiting apparent parabolic kinetics. It was observed that increasing the temperature improves the metal extraction and the apparent activation energy was 38 kJ/mol. This indicates that the process occurs in the mixed regime of both diffusion and chemical reaction. Riveros and Dutrizac [5] performed a series of leaching test on tetrahedrite (Cu_12Sb_4S_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 Fe₂(SO₄)₃ - H₂SO₄ 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 FeCl₃-HCl solutions proceeds according to the shrinking core model and both Cu and Ag 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 apparent activation energy was 116 kJ/mol.

By acidic oxidative leaching, e.g. in acidified ferric chloride solutions, copper and iron enter into solution, while antimony is partially precipitated as a compound with a composition similar to the mineral tripuhyite (FeSbO₄) and the overall leaching reaction proceeds slowly with complicated kinetics [31].

### 2.2.2 Alkaline sulphide treatment of tetrahedrite

Leaching of copper-antimony-arsenic sulphide minerals in alkaline sulphide media have been studied [2, 9, 13, 21, 28-30, 32-38] and even applied industrially [39-41]. Antimony solubilizes under basic sulphide conditions while other metals like copper, silver, zinc, lead and iron remain in the residue [2, 16]. Usually, leaching is conducted in alkaline solution with about 100% stoichiometric excess of sodium sulphide (Na₂S) for 4 -12 h at temperatures close to the solution boiling point. The lixiviant must contain enough sodium hydroxide (NaOH) to avoid the hydrolysis of sulphide ions (S²⁻) to hydrosulphide (HS⁻), which reduces the leaching efficiency [7, 42]. The tetrahedrite-tennantite mineral series are refractory to most common leaching processes [16, 22]. Consequently, Balaz et al. [13, 21, 28, 29, 34, 43, 44] carried out an intensive grinding on such mineral prior to its leaching in alkaline sulphide solution such that significant dissolution of antimony and arsenic can be obtained within a short period of leaching. However, this method is uneconomical due to the higher energy required for the grinding. Many arsenic-sulphur minerals solubilize in the lixiviant with the exception of arsenopyrite which is resistant to the reagent [7, 31, 41]. Filippou et al. [7] reported that the copper product obtained after sulphide leaching may be chalcocite (Cu₂S) or covellite (CuS), while arsenic and antimony are dissolved as thioanions: thioarsenate (AsS₄³⁻), thioantimonite (SbS₄³⁻), thioantimonate (SbS₅⁴⁻) etc., depending on the feed composition and the reaction conditions. The chemistry of the reactions taken place during alkaline sulphide leaching is briefly described as follow:
Cu$_2$Sb$_2$S$_{13}$ (s) + 2Na$_2$S (aq) $\rightarrow$ 5Cu$_2$S (s) + 2CuS (s) + 4NaSbS$_2$ (aq)  

(4)

NaSbS$_2$ (aq) + Na$_2$S (aq) $\rightarrow$ Na$_3$SbS$_3$ (aq)  

(5)

Sb$_2$S$_3$ (s) + 3Na$_2$S (aq) $\rightarrow$ 2Na$_3$SbS$_3$ (aq)  

(6)

2Cu$_3$AsS$_4$ (s) + 3Na$_2$S (aq) $\rightarrow$ 3Cu$_2$S (s) + 2Na$_3$AsS$_4$ (aq)  

(7)

As$_2$S$_3$ (s) + 3Na$_2$S (aq) $\rightarrow$ 2Na$_3$AsS$_3$ (aq)  

(8)

It is reported [7, 33] that when the lixiviant is made by dissolving elemental sulphur in sodium hydroxide solution, a solution containing a mixture of sodium sulphide, sodium thiosulphate and sodium polysulphides will be formed according to reactions 9 and 10.

$\text{4S}_0^0$ (s) + 6NaOH (aq) $\rightarrow$ 2Na$_2$S (aq) + Na$_2$S$_2$O$_3$ (aq) + 3H$_2$O  

(9)

(X-1)$\text{S}_0^0$ (s) + Na$_2$S (aq) $\rightarrow$ Na$_x$S$_x$, where x = 2 to 5  

(10)

The S/NaOH lixiviant was used by the Sunshine Mining and Refining Company to dissolve antimony from tetrahedrite. Anderson et al. [33] reported that the lixiviant can leach gold and silver associated with the mineral due to the thiosulphate and polysulphides in the reagent which are good oxidants and complexing agents. The flowsheet describing the process at the Sunshine Mining plant is presented in Fig. 2a.
Similarly, the alkaline sodium sulphide leach process (Fig. 2b) was used at Equity Silver Mines Ltd., British Columbia, Canada, to remove soluble antimony and arsenic from a copper-silver concentrate of average composition 17% Cu, 7% Sb, 4% As, 23.5% Fe, 7,000 g/t (0.7%) Ag and 20 g/t Au [41, 45]. The process employed at Equity Silver plant (Fig. 2b) had many similarities with the process adopted in the Sunshine refinery (Fig. 2a), but it also had some significant differences. At the Equity plant, antimony was entirely recovered as sodium hydroxyl antimonate and arsenic was converted to calcium arsenate to be impounded at a site far from the mine [7, 40, 41] whilst antimony was solely electrowon at the Sunshine plant [46].

Above all, literatures [13, 14, 20, 28] have shown that alkaline sulphide technology is by far the most utilized because of its inherent selectivity to dissolve antimony, arsenic, mercury, tin [7], and its ease of full-scale application due to minimal corrosion problems associated with the acidic leaching system. Conversely, acidic leaching has so far been limited to laboratory
applications due to low metal recoveries and complications with the accompanying elements [14].

Fig. 2b: The Equity Silver Mining Plant flowsheet [7].
3. MATERIALS AND METHODS

3.1 Material

The materials used in this investigation were a tetrahedrite-rich sulphide concentrate originated from Casapalca, Departamento Lima, Peru and Rockliden complex copper concentrate supplied by the Boliden Mineral AB, Sweden. The elemental analyses of the concentrates are shown in Tables 1 and 2. (For details see paper I, II and III).

| Table 1: Elemental analysis of a tetrahedrite-rich sulphide concentrate |
|-------------------------------------------------|--------|--------|--------|
| Size fraction | -106+75 μm | -75+53 μm | -53+38 μm |
| Cu% | 15.6 | 15.2 | 15.7 |
| Fe% | 11.1 | 14.2 | 13.3 |
| Zn% | 16.1 | 16.8 | 16.9 |
| Sb% | 5.78 | 5.43 | 5.71 |
| As% | 1.87 | 1.86 | 1.77 |

| Table 2: Elemental analysis of Rockliden complex copper concentrate |
|-------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Cu, % | Fe, % | Pb, % | Zn, % | Sb, % | Sn, % | As, % | Se, % | Hg, % | Ag, % | S, % |
| 17.8 | 27.1 | 7.1 | 5.7 | 1.69 | 0.14 | 0.42 | 0.06 | 0.03 | 0.08 | >15 |

3.2 Material characterization techniques

Mineralogical study is very important to the extractive metallurgist because it provides detailed information about the associated minerals in the material to be processed. Consequently, an appropriate processing route for the material can be designed. The various mineralogical techniques employed during this investigation are X-ray diffractometer (XRD), QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) analyses.
3.2.1 X-ray diffractometer (XRD)

A Siemens D5000 automatic X-ray diffractometer equipped with a continuous scanning device was employed to characterize the concentrate as well as the leach residue. XRD patterns were collected between 2θ angles of 10–90° (at Cu Kα radiation of 40 kV, 30 mA). Mineral phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

3.2.2 QEMSCAN and SEM-EDS analyses

A representative sample was taken from the tetrahedrite-bearing concentrate as well as its leach residue for QEMSCAN analysis. SEM-EDS technique was used to characterise the Rockliden complex copper concentrate. In both cases, the samples were embedded in epoxy and a diamond cutting wheel was used to cut the hardened blocks to size and expose the sample grains. The samples were polished and carbon coated before the analyses were performed on them. The mineralogy of particles was inferred from data obtained using the QEMSCAN® advanced mineral analysis system. The particles were examined using the Field Scan method, involving spot analyses over the surface of the block, collection of the resultant X-ray spectra and comparison with a spectral data base.

3.3 Leaching

Alkaline sulphide leaching tests were performed by dissolving the concentrate in the lixiviant, to determine the effect of the following parameters: sodium sulphide (Na2S·3H2O) concentration (0.76 M, 1.14 M and 1.89 M), sodium hydroxide (NaOH) concentration (0.75 M and 1.5 M), leaching temperature (357 K, 364 K, 371 K and 378 K) and particle size (-53 + 38 μm, -75 + 53 μm and -106 + 75 μm). All the leaching experiments, each lasting 6 h, were carried out with 0.5% solid, -75 + 53 μm particle size and 378 K reaction temperature (except where otherwise stated) in 500 mL leach solution containing 1.14 M Na2S·3H2O + 1.5 M NaOH. A 500 mL four-necked round bottomed glass reactor was used which was stirred mechanically with a paddle stirrer at a constant stirring rate of 600 rpm and heated in an auto-regulated system (Fig. 3). The lixiviant was first added to the reactor and when the desired temperature was reached, the solid sample was added. At predetermined time intervals, 5 mL sample slurry was taken from the reactor for the analysis of dissolved metals. All the reagents used for leaching and chemical analysis were of analytical grade and used without further
purification. The influence of each variable was determined by keeping all other variables constant.

Fig. 3: Leaching experimental set-up.

In an attempt to optimise the leaching process, MODDE 8.0 Umetrics software was used in the design of the experiment and analysis of the test results. Response surface methodology in combination with central composite face-centred design (RSM-CCF) was used for the experimental design and analysis. Leaching tests were conducted according to Table 3 (Details about the procedure is reported in paper III). Leaching results were evaluated by
means of chemical determinations on the leach products using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) / Sector Field Mass Spectrometry (ICP-SFMS).

**Table 3:** Central composite face-centred design arrangements and responses for the complex concentrate leaching by alkaline sulphide solution

<table>
<thead>
<tr>
<th>Exp.no.</th>
<th>Run order</th>
<th>Experimental factors</th>
<th>Response variables</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Temperature</td>
<td>S(^2) conc.</td>
<td>Solid conc.</td>
</tr>
<tr>
<td>N1 13</td>
<td>80</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>N2 2</td>
<td>100</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>N3 10</td>
<td>80</td>
<td>164</td>
<td>100</td>
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<td>N4 3</td>
<td>100</td>
<td>164</td>
<td>100</td>
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<tr>
<td>N5 1</td>
<td>80</td>
<td>41</td>
<td>300</td>
</tr>
<tr>
<td>N6 12</td>
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<td>41</td>
<td>300</td>
</tr>
<tr>
<td>N7 8</td>
<td>80</td>
<td>164</td>
<td>300</td>
</tr>
<tr>
<td>N8 4</td>
<td>100</td>
<td>164</td>
<td>300</td>
</tr>
<tr>
<td>N9 5</td>
<td>80</td>
<td>102.5</td>
<td>200</td>
</tr>
<tr>
<td>N10 16</td>
<td>100</td>
<td>102.5</td>
<td>200</td>
</tr>
<tr>
<td>N11 9</td>
<td>90</td>
<td>41</td>
<td>200</td>
</tr>
<tr>
<td>N12 6</td>
<td>90</td>
<td>164</td>
<td>200</td>
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<tr>
<td>N13 15</td>
<td>90</td>
<td>102.5</td>
<td>100</td>
</tr>
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<td>N14 14</td>
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<td>N16 17</td>
<td>90</td>
<td>102.5</td>
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<tr>
<td>N17 7</td>
<td>90</td>
<td>102.5</td>
<td>200</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

4.1 Mineralogical study

The two concentrates used in the study were characterised by XRD, QEMSCAN and SEM-EDS analyses in order to understand the major mineral constituents of each concentrate. The major mineralogical phases identified in the diffractograms of both concentrates (Fig. 4) were tetrahedrite, sphalerite, galena, chalcopyrite, pyrite and iron sulphide (check papers II and III for further detail).

![XRD patterns of Rockliden and a tetrahedrite-rich concentrates](image)

**Fig. 4:** XRD patterns of Rockliden and a tetrahedrite-rich concentrates

QEMSCAN analysis was conducted on the tetrahedrite-rich concentrate to confirm the mineralogy previously determined by the XRD technique. The result from this method is shown in Fig. 5 and Table 4. This result compares well with the XRD identification of the major phases present in the concentrate, but the method identifies a much wider range of minor minerals (Table 4) that were below the detection limit for XRD. This confirms that QEMSCAN analysis can provide much more mineralogical information than the XRD method for trace mineralogy [47]. No arsenic mineral was detected by the two techniques meaning that the arsenic in the mineral is hosted in the tetrahedrite structure. Also, the QEMSCAN result shows that the concentrate is rich in tetrahedrite (Table 4) and silver is
found bonded in the tetrahedrite (Fig. 5). This confirms the presence of silver and arsenic as a solid solution in the tetrahedrite crystal structure as widely reported in the literature [7].

**Table 4:** Mineralogy of a tetrahedrite-rich concentrate defined by QEMSCAN

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass fraction (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedrite</td>
<td>30.2</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>20.6</td>
</tr>
<tr>
<td>Galena</td>
<td>19.0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>15.7</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>13.4</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.4</td>
</tr>
<tr>
<td>Tetrahedrite with Ag</td>
<td>0.1</td>
</tr>
<tr>
<td>Andalusite (Al₂SiO₅)</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.5</strong></td>
</tr>
</tbody>
</table>

**Fig. 5:** QEMSCAN micrograph of a tetrahedrite-rich concentrate.

SEM-EDS technique was used to verify the mineralogical constituents of Rockliden concentrate. The result, as shown in Fig. 6, corroborates the one obtained from the XRD analysis, but the method further identifies the minor minerals (Table 5) that were not detected by XRD technique. The minerals recorded in Table 5 were estimated from the atomic weight percent obtained from the SEM-EDS analysis. Apart from tetrahedrite, SEM result (Fig. 6) shows that antimony was also found as bournonite (PbCuSbS₃) while tin and arsenic was present as stannite (Cu₂FeSnS₄) and arsenopyrite, respectively. It is apparent from Table 5
that silver is bound in the tetrahedrite structure which may enhance the processing economy of the concentrate.

Fig. 6: SEM micrograph of Rockliden copper concentrate. A- tetrahedrite, B- bournonite, C-stannite, D- chalcopyrite, E- galena, F- sphalerite, G- pyrite, H- arsenopyrite and I- pyrrhotite.

Table 5: Mineralogy and atomic proportions of selected microanalyses of Rockliden copper concentrate defined by SEM-EDS analysis

<table>
<thead>
<tr>
<th></th>
<th>Cu %</th>
<th>Fe %</th>
<th>Zn %</th>
<th>Pb %</th>
<th>Sb %</th>
<th>As %</th>
<th>Sn %</th>
<th>Ag %</th>
<th>S %</th>
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<td>1.31</td>
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<td></td>
<td></td>
<td>26.99</td>
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<tr>
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<td>5.77</td>
<td>1.62</td>
<td>31.34</td>
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<td>25.55</td>
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<td>1.06</td>
<td>38.81</td>
<td>27.11</td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td>0.84</td>
<td>39.01</td>
<td>26.10</td>
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<tr>
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<td>12.57</td>
<td></td>
<td>29.11</td>
<td>31.09</td>
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<td>9</td>
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<td></td>
<td>27.96</td>
<td>30.92</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>0.99</td>
<td>32.89</td>
<td>44.79</td>
<td></td>
<td>21.32</td>
<td></td>
<td></td>
<td></td>
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<td>46.07</td>
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<td></td>
<td></td>
<td></td>
<td>Arsenopyrite</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>33.15</td>
<td>30.17</td>
<td></td>
<td>36.84</td>
<td>30.17</td>
<td></td>
<td></td>
<td></td>
<td>Chalcopyrite</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>32.72</td>
<td>30.17</td>
<td></td>
<td>37.11</td>
<td>30.17</td>
<td></td>
<td></td>
<td></td>
<td>Chalcopyrite</td>
<td></td>
</tr>
<tr>
<td>14</td>
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<td>83.07</td>
<td></td>
<td>15.59</td>
<td>30.17</td>
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<td></td>
<td></td>
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<tr>
<td>15</td>
<td>8.14</td>
<td>55.58</td>
<td></td>
<td>36.28</td>
<td>30.17</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>16</td>
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<td></td>
<td></td>
<td>55.83</td>
<td>30.17</td>
<td></td>
<td></td>
<td></td>
<td>Pyrite</td>
<td></td>
</tr>
</tbody>
</table>
4.2 Factors affecting tetrahedrite leaching (*Papers I & II*)

4.2.1 Sulphide ion and hydroxide ion concentrations

During sulphide leaching, sodium sulphide dissociates according to reaction 11. The protonation of sulphide ions occur according to the equilibrium reactions 12 and 13 [36] which take place simultaneously during the leaching process.

\[
\begin{align*}
\text{Na}_2\text{S} & \leftrightarrow 2\text{Na}^+ + \text{S}^{2-} \quad (11) \\
\text{S}^{2-} + \text{H}^+ & \leftrightarrow \text{HS}^- \quad \log K_1 = 11.96 \quad (12) \\
\text{HS}^- + \text{H}^+ & \leftrightarrow \text{H}_2\text{S} \quad \log K_2 = 7.04 \quad (13)
\end{align*}
\]

Fig. 7 shows a plot of the molar concentrations of \(\text{S}^{2-}\), \(\text{HS}^-\) and \(\text{H}_2\text{S}\) in the leach liquor as a function of the solution pH at a total sulphide concentration of 1.14 M. It can be inferred from Fig. 7 that sulphide ion concentration increases rapidly when pH is increased from 10 and upwards, therefore, pH is an important factor. This is because, at a pH > 12, the protonation of sulphide ions will be prevented and therefore available to solubilize antimony according to reactions 4 and 5. Also, a strong alkaline environment is needed to reduce the consumption of more expensive sodium sulphide due to the hydrolysis of sulphide ions (Eq. 14).

\[
\text{S}^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + \text{OH}^- \quad (14)
\]

*Fig. 7: Equilibrium diagram of sulphide species as a function of pH at a total sulphide ion concentration of 1.14 M at 298 K.*
According to Fig. 8, it is apparent that Na₂S concentration has a significant effect on the extraction of antimony and arsenic from the complex sulphide concentrate. After 6 h leaching, approximately 21% of antimony and arsenic was extracted at a concentration of 0.76 M Na₂S and when the Na₂S concentration was increased to 1.14 M, the extraction increased with almost a factor of 3. Further increase in the concentration to 1.89 M Na₂S resulted in an extraction of antimony and arsenic of 87% and 92%, respectively (Fig. 8).

![Graph showing the effect of Na₂S concentration on metal extraction]

**Fig. 8:** Effect of sodium sulphide concentration on As/Sb leaching.

In addition, it is indicated from Fig. 9 that the natural logarithm of the rate constant (lnk_r) is a linear function of ln[Na₂S] when the kinetic data obtained from the study were plotted. The kinetic equations about the effect of the initial concentration of Na₂S on the leaching rate of antimony and arsenic can be written as shown in Eqs. 15 and 16, respectively.

\[
\ln k_r = 2.2 \ln[Na_2S] - 7.77 \tag{15}
\]

\[
\ln k_r = 2.3 \ln[Na_2S] - 7.76 \tag{16}
\]

The apparent reaction order for dissolving antimony and arsenic from tetrahedrite by the lixiviant was estimated to be approximately equal to 2, which implies that both elements reacted similarly with the lixiviant as should be expected since they were present in the same mineral.
Fig. 9: Determination of the reaction order with respect to [Na$_2$S].

Furthermore, the effect of hydroxide ion concentration on the extraction of antimony and arsenic was investigated and plotted in Fig. 10. It is illustrated in the figure that when a low concentration (0.75 M) of NaOH was used, the rate of extracting antimony and arsenic was slower and about 25% and 24% of antimony and arsenic were dissolved after 6 h leaching, respectively. As the concentration of NaOH increased to 1.5 M, the rate of metal extraction was accelerated and the percentage of metal extracted was enhanced. About 57% antimony and 60% arsenic was leached by the lixiviant after 6 h. The observed increase in metal extraction at high concentration of NaOH is due to the higher availability of $S^{2-}$ ion for dissolution action (as described in Paper II), which is promoted by the increase in the pH of the leach liquor. Consequently, the hydrolysis of sulphide ion is prevented which otherwise would reduce its leaching efficiency.
4.2.2 Leaching time

The effect of leaching time on antimony and arsenic dissolution from the complex sulphide concentrate was investigated. The experimental results are presented in Fig. 11. It is obvious from the figure that, by increasing the leaching time, antimony and arsenic extraction would be improved. Due to the narrow size fraction used in this investigation, the metal extraction by the lixiviant is linearly dependent on the leaching time. After 1 h of leaching, approximately 13% of both antimony and arsenic was extracted, and when the leaching time was increased to 6 h, antimony and arsenic extraction was 57% and 60%, respectively. By examining the extraction trend shown in Fig. 11, it can be assumed that higher extraction would be achieved if the leaching time was extended beyond 6 h.
4.2.3 Mineral particle size

The influence of particle size on antimony and arsenic leaching from the tetrahedrite-rich concentrate was studied using three particle sizes (-53 + 38, -75 + 53 and -106 + 75 μm) at 105 °C in leach solutions containing 150 g/L Na₂S·3H₂O + 60 g/L NaOH. A 2.5 g of the concentrate was leached in 500 mL of the solution. It is observed from Fig. 12 that the rate of dissolving antimony and arsenic decreases with increase in particle size. However, it can be concluded that the smaller the particle size, the faster was antimony and arsenic leaching by the lixiviant.

Fig. 11: Effect of leaching time on As/Sb leaching.
4.2.4 Reaction temperature

In order to investigate the effect of reaction temperature on antimony and arsenic dissolution from a tetrahedrite-rich concentrate, the experiments were performed under the following leaching conditions: mineral particle size of -75 + 53 μm, 150 g/L Na₂S, 60 g/L NaOH and temperatures ranging from 84 ºC to 105 ºC. The amount of the concentrate leached was kept constant at 5 g/L. Fig. 13 illustrates the results obtained from the tests. It could be inferred from the figure that the reaction temperatures have a significant effect on the rate of antimony and arsenic dissolution. One can infer from Fig. 13 that the leaching rate increases rapidly with increasing time and temperature. After 360 minutes of leaching, about 57% and 60% of antimony and arsenic were dissolved, respectively, at a reaction temperature of 105 ºC.
4.3 Leaching kinetics and activation energy (Paper I)

The important parameters of the leaching process are the overall rate and the variation in rate with leaching time. Since, these will determine the size of the reactors needed for a design criterion of plant capacity, and the degree of extraction that would be experienced in the plant when it is operated at a selected capacity, above or below, the design capacity. Leaching rates are usually investigated on a laboratory-scale, and the kinetic data obtained from the study are used in the scaling-up of the process [48]. Besides, a careful kinetic study is required to accurately establish the impact of variations in operating rate on metal’s extraction, so as to make wise choices of operating rates for variations in market conditions.

When surface chemical reaction is rate controlling, the kinetics may be correlated graphically using Eq. 17.

\[
1 - (1 - X)^{1/3} = \frac{k_s M_s C_A}{\rho_s \rho_0} t = k_s t
\]

where \(X\) is the fraction reacted, \(k_s\) 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, \(\rho_s\)
density of the concentrate, $\beta$ 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 and $k_r$ is the rate constant. Application of Eq. 17 to the experimental data obtained, at different temperatures, resulted in linear plots presented in Fig. 14.

![Graph](image)

**Fig. 14:** A plot of $1-(1-X)^{1/3}$ vs. time at various reaction temperatures for antimony and arsenic dissolution in alkaline sulphide solution.

It is observed, from this plot, during the whole reaction time that the data in the figure are linear, which indicate that the rate of the reaction is chemically controlled through the particle surface reaction. The slopes of the straight lines from each plot in Fig. 14 were estimated which is equivalent to the rate constants, $k_r$.

The temperature dependence of the chemical reactions can be given by the Arrhenius equation [49, 50] as follows:

$$k_r = A \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (18)

Where $A$ is the frequency factor and $E_a$ is the apparent activation energy. The Arrhenius plot shown in Fig. 15 was made by plotting the natural logarithm of the rate constant ($\ln k_r$) against the reciprocal of the temperature ($1/T$). Hence, the activation energies of antimony and arsenic
were calculated from the slopes of the Arrhenius plots presented in Fig. 15 as 81 kJ/mol and 75 kJ/mol, respectively, which is in agreement with the reported activation energy for a chemically controlled process [49]. Since the calculated activation energies are high, it can be concluded that the dissolution rate of antimony and arsenic from tetrahedrite by alkaline sulphide solution is very sensitive to the reaction temperature.

Fig. 15: Arrhenius plot for tetrahedrite leaching in alkaline sulphide solution.

### 4.4 Selectivity of sulphide lixiviant to dissolve Sb and As (Paper II)

In order to identify the mineralogical changes brought about by leaching, the solid residue obtained after leaching was characterized by XRD and QEMSCAN analyses. The results were compared with the mineralogy of the original concentrate. The XRD pattern shown in Fig. 16 indicates that a new mineralogical phase, spionkopite (Cu$_{39}$S$_{28}$) is observed together with other major phases identified in the original material (Fig. 4). The XRD pattern in Fig. 16 shows that the tetrahedrite peaks found in the concentrate have disappeared completely implying that copper content of the tetrahedrite had been transformed to the new copper sulphide phase observed in the residue.
Fig. 16: XRD analysis of the leach residue after alkaline sulphide leaching (Paper II).

In addition, QEMSCAN analysis results on the leach residue are presented in Figs. 17 and 18. The major mineral phases observed in the residue were sphalerite, galena, pyrite and chalcopyrite, with the newly formed copper sulphide phase. In particular, observation of the polished sections of the leach residue (Fig. 17) showed a micro-porous structure of the new solid phase often enclosing a nucleus of untransformed tetrahedrite. The average crystal chemical formulae of the solid residue determined by QEMSCAN analysis on the transformed phase proves the conversion of tetrahedrite into a copper sulphide having stoichiometry of Cu$_{1.64}$S, which is close to the stoichiometry of the spionkopite observed by XRD but can also be a mixture of chalcocite and covellite. This observation confirms the expectation that tetrahedrite would decompose to either covellite or chalcocite in alkaline sulphide media [7]. However, if the leaching time had been prolonged further, the untransformed tetrahedrite would have been converted completely into the new copper sulphide phase observed in the residue.
Furthermore, QEMSCAN analysis provides more interesting information about the selectivity of the lixiviant to solubilize antimony and arsenic from the concentrate containing them. Comparing the information given in Fig. 18 concerning the concentrate and the residue, one can see that the major phases found in the concentrate were upgraded and not leached with the exception of tetrahedrite phase which was reduced from 30.2% to 1.1% in the residue. This result confirms that other metal sulphides in the concentrate remains insoluble in the sulphide solution with the exception of antimony and arsenic that form soluble sulphide complexes. This analysis shows that the Na₂S/NaOH lixiviant is suitable for pre-treating, difficult to treat, complex antimony-arsenic-containing sulphide ores prior to their smelting and thereby avoiding the difficulty experienced when such ores are directly treated in smelting plant.
In this section, the study conducted on the modelling and optimisation of the alkaline sulphide leach process to selectively dissolve antimony and tin from the copper concentrate containing them is discussed. Tin removal from the concentrate was considered as one of the response variables because the concentrate under consideration contains about 0.14% Sn, which may be interesting to remove prior to smelting. Moreover, arsenic was present as arsenopyrite in the concentrate which is very refractory to the alkaline sulphide lixiviant.

### 4.5.1 Data evaluation and response surface methodology (RSM) model analysis

MODDE 8.0 software was used for the design and analysis of the experimental results. The experimental factors investigated were leaching temperature ($X_1$), sulphide ion concentration ($X_2$) and solid concentration ($X_3$), while the output variables were antimony recovery (Sb), tin recovery (Sn) and $T_{90}$ (i.e. time required to leach out 90% Sb from the concentrate).

The distributions of the data for all the responses were inspected for normality, and it was observed that the responses needed to be transformed in order to obtain improved models.
Negative logarithmic transformation was carried out for Sb recovery, and power transformation was performed for both Sn recovery and T90 as shown in Table 6.

**Table 6: Response transformation**

<table>
<thead>
<tr>
<th>Response</th>
<th>Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (%)</td>
<td>-10Log(100-Y)</td>
</tr>
<tr>
<td>Sn (%)</td>
<td>Y^-1</td>
</tr>
<tr>
<td>T90 (h)</td>
<td>Y^-0.5</td>
</tr>
</tbody>
</table>

Evaluation of the raw data revealed that the replicate errors were satisfactorily small for all of the output responses. The model was fitted using multiple linear regression (MLR) method, and the overall result of the model fitting is displayed in Fig. 19.

![Fig. 19: Summary of fit plot of the initial modelling.](image)

Moreover, a model can be judged as good, if $R^2 - Q^2 < 0.2$, $Q^2 > 0.5$, model validity $>0.25$ and reproducibility is greater than 0.5 [51]. It is observed that the predictive power ($Q^2$) of the models ranges from excellent to good. The $Q^2$ values for the responses Sb, T90 and Sn are 0.93, 0.91 and 0.55, respectively. All models also show high model validity, which is an
indication of no lack of fit. Fig. 19 shows that Sb recovery and T\textsubscript{90} models satisfied the model performance indicator conditions while the Sn recovery model did not. The lower Q\textsuperscript{2} value of Sn recovery model could be due to the presence of irrelevant terms contained in the regression model. The regression coefficients plots of the models were examined and the statistically non-significant terms were eliminated. Thus, the models were refined and simplified. The summary of fit plot of the refined models is presented in Fig. 20. It can be seen from Fig. 20 that all three Q\textsuperscript{2} values have increased, and now amount to 0.97, 0.97 and 0.74 for Sb recovery, T\textsubscript{90} and Sn recovery, respectively. The refined models show improved model validity.

![Fig. 20: Summary of fit plot of the refined modelling.](image)

The outcome of the normal probability plot of the residuals after refinement (Fig. 21) reveals that the models are satisfactory, except for the deviating behaviour of experiment 2 in Sn recovery model. Subsequently, experiment 2 was critically scrutinized for any possible error, but was found to be well fitted into the other models; therefore, the experiment cannot be removed from the model. Due to the satisfactory values of R\textsuperscript{2} and Q\textsuperscript{2} for Sn recovery model, it may be assumed that experiment 2 is a weak outlier which does not influence the model decisively.
In order to obtain information concerning how the input variables affect the responses, regression coefficient plots of the refined models were made and interpreted (Fig. 22). Inspection of these plots shows that reaction temperature and sulphide ion concentration have a strong effect on all the three responses [52, 53]. It seems that solid concentration has insignificant effect on all the three responses within the selected range of solid concentration.
Furthermore, examination of the analysis of variance (ANOVA) of the refined models for the responses Sb recovery, Sn recovery and T90 as shown in Table 7, reveal that all the regression models are statistically significant with a 95% confidence level in the range studied. For all the response variables, F₀ values are greater than F_critical values, and P-values are smaller than 0.05. According to the results displayed in Table 7, one can infer that the model error of the original model is of the same magnitude as the replicate error for all the responses, because their P-values are greater than 0.05 and F₀<F_critical at 95% confidence level. Hence, the models have small error and good fitting power, meaning that the models show no lack of fit.
Table 7: ANOVA for the quadratic models predicted for each response variable

<table>
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<tr>
<th>Response variable</th>
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<th>SS</th>
<th>MS (variance)</th>
<th>F₀</th>
<th>F_critical α = 0.05</th>
<th>P-value</th>
<th>SD</th>
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<td></td>
<td>0.0609</td>
<td></td>
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<td></td>
<td>Lack of fit (model error)</td>
<td>9</td>
<td>0.0347</td>
<td>0.0039</td>
<td>1.28</td>
<td>19.37</td>
<td>0.514</td>
<td>0.0621</td>
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<td>2</td>
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<td>0.0030</td>
<td></td>
<td></td>
<td>0.0550</td>
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<tr>
<td>Sn recovery</td>
<td>Total corrected</td>
<td>16</td>
<td>0.0005</td>
<td>3.37e-5</td>
<td></td>
<td></td>
<td>0.0058</td>
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<td></td>
<td>Regression</td>
<td>5</td>
<td>0.0005</td>
<td>1.01e-4</td>
<td>30.61</td>
<td>3.20</td>
<td>0.000</td>
<td>0.0100</td>
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<tr>
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<td>Residual</td>
<td>11</td>
<td>3.61e-5</td>
<td>3.29e-6</td>
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<td></td>
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<td></td>
<td>Lack of fit (model error)</td>
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<td>3.39e-5</td>
<td>3.77e-6</td>
<td>3.36</td>
<td>19.37</td>
<td>0.251</td>
<td>0.0019</td>
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<td>Pure error (replicate error)</td>
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<td>2.24e-6</td>
<td>1.12e-6</td>
<td></td>
<td></td>
<td>0.0010</td>
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</tr>
<tr>
<td>T90</td>
<td>Total corrected</td>
<td>16</td>
<td>0.1823</td>
<td>0.0114</td>
<td></td>
<td></td>
<td>0.1068</td>
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<td>0.0001</td>
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<td>0.0109</td>
<td></td>
</tr>
</tbody>
</table>

DF-degree of freedom, SS-sum of squares, MS-mean square, SD-standard deviation

The illustration from Fig. 23 shows that the observed responses correlated very well with the predicted values. Hence, the models can be considered adequate for the predictions and for the optimisation process. The regression models describing the correlation between the transformed response variables and the parameters investigated were as written in Eqs. 19-21.

\[
Sb = -1.002 + 0.168X_1 + 0.485X_2 - 0.079X_2^2 \tag{19}
\]
\[
Sn = 0.030 - 0.003X_1 - 0.004X_2 - 0.005X_2^2 - 0.003X_1X_2 \tag{20}
\]
\[
T_{90} = 0.422 + 0.044X_1 + 0.123X_2 - 0.039X_2^2 - 0.020X_1X_2 \tag{21}
\]

In the regression models shown in Eqs. 19-21, all the experimental parameters are in coded values, where \(X_1\) is the reaction temperature, \(X_2\) is sulphide ion concentration, \(X_3\) is solid concentration, and \((X_2)^2\) and \(X_1X_2\) are the square and interaction of the main factors. The presence of significant square and interaction terms in the regression equations confirms the existence of quadratic behaviour and non-linear combining effects of the variables.
Fig. 23: Relationship between observed and predicted values for the response variables Sb, Sn and T90.

4.5.2 Model validation and optimisation

The validity of the model with regards to the response variables Sb, Sn and T90 was investigated by performing a separate experiment at the conditions shown in Table 8 for 24 hours. The results as shown in Table 8 indicate a close agreement with the values predicted by the model. Consequently, the model from a response surface methodology is considered to be accurate and reliable, for predicting the leaching of antimony and tin from the complex copper concentrate, and also good at predicting the time needed to recover 90% of the antimony from the concentrate.

Table 8: Validation of model

<table>
<thead>
<tr>
<th>Temp. X1, °C</th>
<th>Sulphide conc. X2, g/L</th>
<th>Solid conc. X3, g/L</th>
<th>%Sb Predicted</th>
<th>Observed</th>
<th>%Sn Predicted</th>
<th>Observed</th>
<th>T90, h Predicted</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>45</td>
<td>290</td>
<td>36-58</td>
<td>52</td>
<td>30-37</td>
<td>26</td>
<td>19-30</td>
<td>20</td>
</tr>
</tbody>
</table>
Furthermore, optimisation of the factors affecting the leaching process can be carried out depending on what is expected from the process. If high recoveries of Sb and Sn are desirable in as short as possible leaching time and at a moderate cost, one might opt for leaching at maximum temperature and sulphide ion concentration as displayed in Figures 24 and 25.

**Fig. 24:** Contour plots of Sb recovery showing the interaction between sulphide concentration (g/L) and temperature (°C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.

**Fig. 25:** Contour plots of Sn recovery showing the interaction between sulphide concentration (g/L) and temperature (°C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.
If for practical and economic reasons, low production cost, less corrosion and electrowinning problems are desirable by the smelter. A lower temperature and less sulphide concentration can be used to set the factors in such a level to obtain high recovery of Sb (min 90%) by extending the leaching time as presented in Fig. 26.

**Fig. 26:** Contour plots for the response T₉₀ showing the interaction between sulphide concentration (g/L) and temperature (°C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.
5. CONCLUSIONS

Mineralogical investigation of the complex sulphide concentrate used in this investigation shows that the concentrate is rich in tetrahedrite. Antimony, arsenic and silver form a solid solution in the tetrahedrite crystal structure and other major minerals identified were sphalerite, galena, chalcopyrite and pyrite. Alkaline sulphide leaching of the concentrate shows that antimony and arsenic extraction from a tetrahedrite-rich concentrate strongly depends on the concentration of sulphide and hydroxide ions, reaction temperature, particle size and the leaching time.

The kinetic study indicates that the rate of tetrahedrite leaching by the lixiviant under the selected conditions is chemically controlled through the particle surface reaction. The activation energies were found to be 81 kJ/mol and 75 kJ/mol, respectively, for antimony and arsenic dissolution from tetrahedrite, which are consistent with the values of activation energies reported for the chemically controlled reaction process.

Due to the relative slow leaching kinetics of tetrahedrite, fine mineral particles are required in order to significantly improve antimony and arsenic extraction. Analysis of the leach residue indicates that the lixiviant is strongly selective to remove the impurity metals As and Sb. Tetrahedrite in the concentrate was found to be converted into a new species having the average chemical formula \( \text{Cu}_{1.64}\text{S} \) which could be a mixture of chalcocite, covellite or spionkopite. The study shows that alkaline sulphide leaching can be a suitable hydrometallurgical upgrading process from technological and environmental point of view, to selectively and effectively reduce the antimony and arsenic content from the complex sulphide concentrate, and therefore, upgrading it for further pyrometallurgical treatment.

Modelling and optimisation of alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn was conducted using response surface methodology-central composite face-centred design (RSM-CCF). Further, RSM was established to be effectual and reliable in formulating models for fitting the experimental data and predicting leaching behaviour of the copper concentrate in alkaline sulphide media. The experimental variables studied were reaction temperature, sulphide ion concentration and the concentration of solid leached. The response parameters include antimony recovery, tin recovery and the estimated time required to achieve 90% Sb dissolution. A strong model with no lack of fit was developed and the validity of the model was confirmed experimentally. The result shows that the model is reliable and accurate for predicting the leaching process.
FUTURE WORK

The following investigations are planned for the future work:

- Fundamental studies on antimony electrowinning from a modelled alkaline sulphide electrolyte with the factors affecting it
- Study the effect of arsenic, tin and mercury on the quality of the electrodeposited antimony
- Investigating the morphological and topographical structures of the electrodeposited antimony in order to ascertain its quality
REFERENCES

PAPER I

Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media

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Hydrometallurgy 103 (2010) 167-172
Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media

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A R T I C L E   I N F O

Article history:
Available online 30 March 2010
Received 16 February 2010
Received in revised form 16 March 2010
Accepted 17 March 2010

Keywords:
Dissolution kinetics
Alkaline sodium sulphide
Tetrahedrite
Leaching
Lixiviant

A B S T R A C T

The present study investigates the dissolution kinetics of tetrahedrite in aqueous alkaline sodium sulphide solutions. Effect of reaction temperature, mineral particle size, sodium sulphide and sodium hydroxide concentrations on antimony and arsenic dissolution rate from tetrahedrite were studied. It was found that the rate of reaction increases with increase in reaction temperature, sodium sulphide concentration, and sodium hydroxide concentration and with decrease in mineral particle size. The kinetic study indicates that the rate of tetrahedrite leaching in the lixiviant under selected conditions is chemically controlled through the particle surface reaction. The estimated activation energies were found to be 81 kJ/mol and 75 kJ/mol, respectively, for antimony and arsenic dissolution from tetrahedrite, which are in agreement with the values of activation energies reported for the chemically controlled reaction process.
fast, the solution would be governed by the rate of diffusion of the ions from the surface of the solid through the boundary layer. On the other hand, if the rate of reaction is slow, it will control the overall process and the process will be chemically controlled, thus, diffusion through the boundary layer will not play any critical role (Aydogan et al., 2005). It is reported that a diffusion-controlled heterogeneous process was characterised by being slightly dependent on temperature, while the chemically controlled process was strongly dependent on temperature which is attributed to linear dependency of diffusion coefficients and exponential dependency of chemical velocity constants on temperature. However, the activation energy of a diffusion-controlled process is characterised as being 4–12 kJ/mol, while it is usually greater than 42 kJ/mol for a chemically controlled process (Aydogan et al., 2005; Habashi, 1980).

Recently, Riveros and Dutrizac (2008) performed a series of leaching tests on tetrahedrite (Cu12Sb4S13) in acidic media using Fe2(SO4)3, FeCl3 or O2 as oxidizing agents. At temperatures <100 °C, the dissolution kinetics of disks of synthetic iron-bearing tetrahedrite in Fe2(SO4)3–H2SO4 media were linear; the leaching rates were slow but increased significantly with increasing temperature with an apparent activation energy of 120 kJ/mol. The dissolution of sized particles of natural Ag-bearing tetrahedrite in FeCl3–HCl solutions proceeds according to the shrinking core model and both Cu and Ag dissolve at about the same rate provided that the total chloride concentration of the solution is high enough to solubilize the AgCl reaction product. The leaching rates were slow and the apparent activation energy is 116 kJ/mol. The addition of sulphate ions to the FeCl3–HCl system reduces the tetrahedrite leaching rate to values similar to those realized in the Fe2(SO4)3–H2SO4 system.

Similarly, Anderson and Kryš (1993) leached an argentiferous tetrahedrite concentrate from the Sunshine mine in sodium sulphide lixiviant produced by dissolving elemental sulphur in sodium hydroxide at temperatures close to the solution boiling point for 4–12 h. The chosen variables investigated were agitation rate, concentrate regrind, temperature, percent solids, caustic concentration, carbonate concentration, and individual sulphur species concentration. Their findings show that the process is sensitive to the amount of regrind performed on the concentrate, reaction temperature and sulphide concentration. They also concluded that polysulphide, increased levels of thiosulphate and carbonate concentration.

In addition, alkaline sulphide leaching of copper–antimony–arsenic sulphide minerals has been extensively studied and documented in the literatures (Baláz et al., 1998, 1992; Awe, 2008; Baláz and Achimoviová, 2006a,b; Baláz et al., 2001; Delfino et al., 2003; Frohlich and Míkó, 2001; Yang et al., 2005; Tongamp et al., 2010; Ackerman et al., 1993; Coltrinari, 1977; Dayton, 1982) but no detailed study was found regarding the dissolution kinetics of natural tetrahedrite in alkaline sulphide solutions. However, in the present study, the dissolution kinetics of tetrahedrite in aqueous alkaline sodium sulphide solution was investigated. The effect of the reaction temperature, mineral particle size, and the concentration of sodium sulphide and sodium hydroxide on the dissolution rate have been evaluated. The dissolution kinetics of tetrahedrite was examined according to the heterogeneous reaction models. The activation energies of antimony and arsenic dissolution from tetrahedrite by alkaline sulphide solution were determined from the experimental data.

2. Material and methods

2.1. Material

The tetrahedrite used in this investigation was prepared from the tetrahedrite crystals bought from Gregory, Bottlely & Lloyd Company, United Kingdom, which originated from Casapalca, Huarochirí, 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: −150 + 106, −106 + 75, −75 + 53, −53 + 38 and −38 + 20 μm. The particle size fractions of −106 + 75, −75 + 53 and −53 + 38 μm were used in this study.

2.2. Analytical and instrumentation techniques

X-ray powder diffraction (XRD) was used to characterise the tetrahedrite mineral using a Siemens D5000 automatic diffractometer equipped with a continuous scanning device. CuKα radiation of 40 kV and 30 mA with a sample rotation of 30 rpm was used. Diffraction patterns (Fig. 1) for the sample were measured in the 2-theta range from 5 °C to 90 °C and crystalline phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument. The tetrahedrite mineral and the leach solutions were chemically analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Sector Field Mass Spectrometry (ICP-SFMS).

2.3. Experimental procedure

The leaching experiments were conducted in batch-wise mode in a four-necked round bottomed glass reactor which was stirred mechanically with a paddle stirrer at 600 rpm and heated with an autoregulated device. The leaching solution (500 mL) was added to the reactor and when the desired temperature was reached, 2.5 g of solid sample was added in all the leaching experiments. At appropriate time intervals, 5 mL sample of the leach solution was collected for the analysis of the metals dissolved in the leach liquor. All reagents used for leaching and chemical analysis were of analytical grade and used without purification. The experimental leaching conditions used were: sodium sulphide (Na2S·3H2O) 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 °C, 91 °C, 98 °C and 105 °C), mineral particle size (−53 + 38 μm, −75 + 53 μm and −106 + 75 μm) and reaction time of 360 min in all cases.

<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>−106 + 75 μm</td>
<td>15.6</td>
<td>11.1</td>
<td>16.1</td>
<td>5.8</td>
<td>1.9</td>
<td>28.0</td>
</tr>
<tr>
<td>−75 + 53 μm</td>
<td>15.2</td>
<td>14.2</td>
<td>16.8</td>
<td>5.4</td>
<td>1.9</td>
<td>31.5</td>
</tr>
<tr>
<td>−53 + 38 μm</td>
<td>15.7</td>
<td>15.3</td>
<td>16.9</td>
<td>5.7</td>
<td>1.8</td>
<td>26.5</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of the mineral sample.
3. Results and discussion

3.1. Effect of temperature

The effect of reaction temperature on the rate of antimony and arsenic dissolution from tetrahedrite at different reaction times are plotted in Fig. 2 using mineral particle size fraction of −75 + 53 μm, and concentration of sodium sulphide and sodium hydroxide of 150 g/L and 60 g/L respectively at temperatures ranging from 84 °C to 105 °C. The amount of solid leached was kept constant at 5 g/L. The obtained results reveal that the reaction temperatures studied have a significant effect on the rate of antimony and arsenic dissolution from tetrahedrite. It can be seen from Fig. 2 that the leaching rate increases rapidly with increasing time and temperature. After 360 min of leaching, about 57% and 60% of antimony and arsenic were dissolved respectively at a reaction temperature of 105 °C.

3.2. Kinetic model

3.2.1. Rate control by diffusion through the product layer

If the rate of the reaction is controlled by diffusion through the product layer, the integrated rate equation is described as follows:

\[ 1 - \left(1 - X\right)^{\frac{2}{3}} = \frac{2M_S C_A}{\rho S \beta r_0^2} t = k_d t \]  

(1)

where \( X \) is the fraction reacted, \( k_d \) 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, \( \rho S \) 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, \( k_c \) and \( k_r \) are the rate constants which are calculated from Eqs. (1) and (2), respectively. An attempt was made to fit the obtained experimental data to the model equation described in Eq. (1), and this is presented in Fig. 3 for both antimony and arsenic dissolution from tetrahedrite. It is observed that the data do not correlate to this model, since neither a straight line nor a zero point intercept was obtained in both figures.

3.2.2. Rate control by chemical reaction

When surface chemical reaction is rate controlling, the kinetics may be correlated graphically using Eq. (2).

\[ 1 - (1 - X)^{\frac{1}{3}} = \frac{k_r M_S C_A}{\rho S \beta r_0} t = k_r t \]  

(2)

Application of Eq. (2) to the experimental data obtained, at different temperatures, resulted in linear plots presented in Fig. 4. It is observed, from both plots, during the whole reaction time that the data in these figures are linear, which indicate that the rate of the reaction is chemically controlled through the particle surface reaction. The slopes of the straight lines from each figure were estimated which is equivalent to the rate constants, \( k_r \).

3.2.3. Calculation of the activation energy

A process may be regarded either as diffusion rate controlled through the porous layer when the activation energy of the process is from 4 to 12 kJ/mol or chemical rate controlled through the particle surface reaction when its activation energy is greater than 42 kJ/mol.

![Fig. 2. Effect of leaching temperature on tetrahedrite dissolution rate.](image)

![Fig. 3. A plot of $1 - 2(1 - X)^{2/3}$ vs. time at various reaction temperatures for tetrahedrite dissolution in alkaline sulphide solution.](image)

![Fig. 4. A plot of $1 - (1 - X)^{1/3}$ vs. time at various reaction temperatures for antimony and arsenic dissolution from tetrahedrite in alkaline sulphide solution.](image)

![Fig. 5. Arrhenius plot for tetrahedrite leaching in alkaline sulphide solution.](image)
The temperature dependence of the chemical reactions can be given by the Arrhenius equation (Ray, 1993; Habashi, 1980) as follows:

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

where \( A \) is the frequency factor and \( E_a \) is the apparent activation energy. The Arrhenius plot shown in Fig. 5 was made by plotting the natural logarithm of the rate constant (\( \ln k_r \)) against the reciprocal of the temperature (\( \frac{1}{T} \)). Hence, the activation energies of antimony and arsenic were calculated from the slopes of the Arrhenius plots presented in Fig. 5 as 81 kJ/mol and 75 kJ/mol respectively, which is in agreement with the reported activation energy for a chemically controlled process (Habashi, 1980). Since the calculated activation energies are high, it can be concluded that the dissolution rate of antimony and arsenic from tetrahedrite by alkaline sulphide solution is very sensitive to temperature.

3.3. Effect of particle size

The effect of particle size on the leaching of antimony and arsenic from tetrahedrite mineral was studied using three particle sizes (\( -53+38, -75+53 \) and \( -106+75 \) μm) at 105 °C in leach solutions containing 150 g/L Na₂S·3H₂O and 60 g/L NaOH. 2.5 g of tetrahedrite was leached in 500 mL of the solution and maintained throughout the tests. It was observed from Fig. 6 that the rate of antimony and arsenic dissolution increases with increase in time and decreases with increase in particle size. The smaller the particle size, the faster was tetrahedrite leaching by the lixiviant. Linearization of the kinetic curves for antimony and arsenic dissolution from tetrahedrite was performed by means of Eq. (2) and presented in Fig. 7. The rate constant values increased with the decrease in the particle size, which may be attributed to the increase in surface area with the decrease in particle size. The values of the rate constants were plotted against the reciprocal of the mineral particle radius yielding a linear relationship with correlation coefficients of 0.99 and 0.98 (Fig. 8) respectively for antimony and arsenic dissolution from the tetrahedrite. In addition, the linear dependence of the rate constant on the inverse particle radius, Fig. 8, is further evidence in support of the surface reaction shrinking particle model proposed for this process.

3.4. Effect of sodium sulphide concentration

Antimony and arsenic form complex compounds with sulphide ions, therefore, the influence of sodium sulphide concentration on tetrahedrite leaching is an important parameter to investigate. When tetrahedrite is leached in alkaline sulphide solution, a variety of reaction products may result. This includes chalcocite (\( \text{Cu}_2\text{S} \)) or covellite (\( \text{CuS} \)), while arsenic and antimony are dissolved as thioanions: thioarsenate (\( \text{AsS}_4^{3-} \)), thiantimonite (\( \text{SbS}_3^{3-} \)), thiantimonate (\( \text{SbS}_4^{3-} \)) etc depending on the feed composition, sulphide ion concentration and the reaction conditions (Filippou et al., 2007). The dissolution reaction of tetrahedrite in alkaline sulphide solutions is expressed as follows:

\[
\text{Cu}_3\text{Sb}_4\text{S}_{13}(s) + 2\text{Na}_2\text{S}(aq) \rightarrow 5\text{CuS}(s) + 2\text{CuS}_2^-(aq) + 4\text{NaSbS}_2(aq) \\
\text{NaSbS}_2(aq) + \text{Na}_2\text{S}(aq) \rightarrow \text{Na}_3\text{SbS}_3(aq)
\]  

Leaching tests were conducted to investigate the effect of varying the initial concentration of sodium sulphide in the range of 100–250 g/L at
105 °C in solutions containing 60 g/L sodium hydroxide. During the tests, the amount of solid leached was kept constant at 5 g/L taking from −75 + 53 μm mineral particle size fraction. It is apparent that the rate of dissolving antimony and arsenic from tetrahedrite (Fig. 9) by the lixiviant increases steadily with increasing sodium sulphide concentration, and the dissolution rate at Na₂S concentration of 250 g/L is much higher than that at 150 and 100 g/L Na₂S·3H₂O. The results show that tetrahedrite leaching depends strongly on the concentration of sodium sulphide in the leach liquor. When the data from the experiment was substituted into Eq. (2), Fig. 10 was constructed. By plotting the natural logarithm of the slope of each line (lnkr) in Fig. 10 against the natural logarithm of initial concentration of sodium sulphide (ln[Na₂S]), Fig. 11 can be drawn. It is indicated from Fig. 11 that lnkr is a linear function of ln [Na₂S]. The kinetic equations about the effect of the initial concentration of Na₂S on the leaching rate of antimony and arsenic can be written as Eqs. (6) and (7), respectively.

\[
\ln kr = 2.231[Na_2S] - 7.77
\]  

\[
\ln kr = 2.383[Na_2S] - 7.76
\]  

Therefore, the apparent reaction order for dissolving antimony and arsenic from tetrahedrite by the lixiviant was estimated to be approximately equal to 2, which implies that both elements reacted similarly with the lixiviant as should be expected since they were present in the same mineral.

3.5. Effect of sodium hydroxide concentration

Fig. 12 presents the influence of sodium hydroxide concentration on the leaching of tetrahedrite mineral. The tests were carried out under the following leaching conditions: 150 g/L Na₂S·3H₂O; particle size of −75 + 53 μm; 2.5 g of tetrahedrite leached in 500 mL of the lixiviant; reaction temperature and time of 105 °C and 360 min respectively. It is evident from this figure that tetrahedrite dissolution in the lixiviant is strongly dependent on the concentration of NaOH. This can be observed from the plot that the percentage of antimony and arsenic (Fig. 12) reported into the leach liquor after 360 min at a concentration of 60 g/L NaOH is greater than that obtained at sodium hydroxide concentration of 30 g/L. It is also found that increase in NaOH concentration accelerates the rate at which antimony and arsenic solubilise in the leach solution. The kinetic data obtained from the tests are plotted in Fig. 13. This plot shows a linear relationship and therefore supports that tetrahedrite leaching by the lixiviant is controlled by the shrinking particle model for reaction-controlled process.

4. Conclusions

The dissolution kinetics of tetrahedrite in aqueous alkaline sulphide solution was investigated. It was found that the rate of reaction increases with increase in reaction temperature, sodium sulphide concentration, and sodium hydroxide concentration and with decrease in mineral particle size. The kinetic study indicates that the rate of tetrahedrite leaching in the lixiviant under selected conditions is chemically controlled through the particle surface reaction. The activation energies were found to be 81 kJ/mol and...
75 kJ/mol, respectively, for antimony and arsenic dissolution from tetrahedrite, which are consistent with the values of activation energies reported for the chemically controlled reaction process.

Acknowledgements

The authors would like to thankfully acknowledge the financial support from VINNOVA, Boliden Mineral AB, LKAB and the Adolf H. Lundin Charitable Foundation.

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Selective leaching of arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution

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Minerals Engineering 23 (2010) 1227-1236
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ABSTRACT

Removal of impurity elements in copper metallurgy is one of the major problems encountered today since pure copper ore reserves are becoming exhausted and the resources of unexploited ores often contain relatively high amounts of impurity elements like antimony, arsenic, mercury and bismuth, which need to be eliminated. The present work is aimed at pre-treating a tetrahedrite rich complex sulphide concentrate by selective dissolution of the impurities, therefore, upgrading it for pyrometallurgical processing. To accomplish this, dissolution of antimony and arsenic by an alkaline sulphide lixiviant from the concentrate were investigated. The lixiviant proved selective and effective to dissolve these impurity elements from the concentrate with good recoveries. Further investigations on the factors influencing the leaching efficiency of the lixiviant were studied. The parameters considered were sulphide ion and hydroxide ion concentrations, mineral particle size, reaction temperature and leaching time. Analysis of the leach residue indicates that copper content of tetrahedrite has transformed into copper sulphides with the average chemical formula Cu$_{1.6}$S. The grade and economic value of the concentrate were improved greatly after sulphide treatment, and therefore, suitable as a feedstock for smelting. The impurities have been reduced to low levels which are tolerable in the smelting furnace and consequently reduce both the treatment and environmental problem encountered when such concentrate is processed pyrometallurgically.

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1. Introduction

Copper extraction through pyrometallurgical processing of concentrate relies heavily on copper sulphides; and to a lesser degree on copper oxides, which are processed hydrometallurgically. The majority of copper sulphide mineral deposits mined today are complex in nature. These minerals are often found in association with tetrahedrite (Cu$_2$Sb$_4$S$_{13}$), enargite (Cu$_3$AsS$_4$) and tennanite (Cu$_2$AsS$_4$) minerals (Riveros and Dutrizac, 2008), which render them less appropriate as a feed material for smelting due to their noxious elements which can create serious toxicological and environmental problems (Filippou et al., 2007; Lattanzi et al., 2008). These minerals are eco-

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doi:10.1016/j.mineng.2010.08.018
handling, energy consumption, possibility of toxic arsine gas for-
maton, and loss of high copper in a low value recycle product (Navarro and Alpicac, 2002).

As a result of the global increase in demand for base metals, mining companies are now paying more attention to the low grade and complex sulphide ore deposits to economically process them. However, this necessitates pre-treatment operations to be con-
ducted to selectively remove the impurities prior to the smelting of the copper concentrates. Therefore, this paper reports and dis-
cusses the studies carried out on the selective leaching of antimony and arsenic under various experimental conditions from a tetrahe-
drite rich complex sulphide concentrate in alkaline sulphide media.

2. Methods of pre-treating As/Sb rich sulphide ores/
concentrates

In an attempt to upgrade sulphide concentrates rich in arsenic and antimony for pyrometallurgical processing, selective flotation of enargite, tetrabehrite and tennantite from other copper sulph-
hides such as covellite (CuS), chalcocite (CuFeS2), chalcocite (CuS) and bornite (CuFeS2) has been studied (Curreli et al., 2005; Filippou et al., 2007). The outcome showed that these miner-
als are difficult to separate from other sulphide minerals (Filippou et al., 2007) because they exhibit similar flotation properties as cop-
per sulphides and therefore report to copper concentrates.

Apart from this, a more cost effective and environmentally friendly process for the removal of antimony and arsenic from the so called "dirty concentrates" prior to pyrometallurgical pro-
cessing has been considered to be achieved through hydrometall-
lurgical process (Baláž and Achimovicová, 2006b; Baláž et al., 1998; Nadkarni et al., 1975). The discussions about the possibility of leaching antimony-arsenic bearing minerals in copper resources are available in literature. It is reported that the amphoteric nature of antimony allows the use of both acidic and basic media for its solubilization (Anderson, 2001; Baláž et al., 2001). In reality, only two lixiviant systems are utilized in antimony hydrometallurgy: acidic chloride (Correia et al., 2001; Correia et al., 2000; Goy et al., 1983; Havlík et al., 1999; Havlík and Kammel, 2000; Padilla et al., 2005) and alkaline sulphide (Awe, 2008; Baláž and Achimovicová, 2006a; Baláž et al., 2001; Frohlich and Mikloš, 2001). Previous studies have shown that arsenic and antimony containing minerals dissolve slowly in acidic media below 100 °C (Correia et al., 2001; Padilla et al., 2005). Significantly faster leaching rates have been obtained in alkaline media containing sulphide (Awe et al., 2010; Awe and Sandström, 2010; Baláž et al., 2000; Baláž et al., 2001) or sodium hypochlorite (Viñals et al., 2003) as well as in acid media at ele-
vated temperatures (Nevia Correia et al., 1993; Riveros and Duttri-
zac, 2008). Due to the refractoriness of tetrabehrite, enargite and tennantite to most lixiviants; concentrated leaching agents, high reac-
tion temperatures and long leaching times are required to effi-
ciently dissolve antimony and arsenic (Baláž, 2000). In a recent study conducted by the authors, it was shown that the rate of leaching tetrabehrite in alkaline sulphide lixiviant was chemically controlled through the particle surface reaction (Awe et al., 2010). Filippou et al. (2007) reported that alkaline sulphide solution is selective in dissolving antimony and arsenic; and the copper prod-
uct obtained after sulphide leaching may be chalcocite or covellite, while arsenic and antimony are dissolved as thioarsenite (AsS3(4-)), thioarsenate (AsS5(3-)), thiosalmonite (SbS5(3-)), thio-
vanadinite (SbV5(3-)), etc. depending on the feed composition and the reaction conditions. The chemical reactions occurring during sul-
phide leaching are briefly described as follow (Filippou et al., 2007):

\[
\begin{align*}
\text{Cu}_2\text{Sb}_2\text{S}_7(s) + 2\text{Na}_2\text{S}(aq) & \rightarrow 5\text{Cu}_2\text{S}(s) + 2\text{CuS}(s) \\
& \quad + 4\text{NaSbS}_3(aq) \\
\text{NaSbS}_3(aq) + \text{Na}_2\text{S}(aq) & \rightarrow \text{Na}_2\text{SbS}_3(aq) \\
\text{Sb}_2\text{S}_3(s) + 3\text{Na}_2\text{S}(aq) & \rightarrow 2\text{Na}_2\text{SbS}_3(aq) \\
2\text{Cu}_2\text{AsS}_4(s) + 3\text{Na}_2\text{S}(aq) & \rightarrow 3\text{Cu}_2\text{S}(s) + 2\text{Na}_2\text{AsS}_3(aq) \\
\text{As}_2\text{S}_3(s) + 3\text{Na}_2\text{S}(aq) & \rightarrow 2\text{Na}_2\text{AsS}_3(aq)
\end{align*}
\]

Baláž et al. (1998) disclosed that sulphide lixiviant reacts with mercury to form a soluble salt complex which could easily be hydrolyzed if the alkali concentration is very low.

Furthermore, alkaline sulphide leaching processes have been utilized industrially at operations in Russia, China, the Sunshine antimony refinery, Idaho, USA (Anderson and Krys, 1993), and also at Equity Silver Mines Ltd., British Columbia, Canada (Dayton, 1982; Filippou et al., 2007). At Sunshine, the lixiviant was pro-
duced on site by dissolving elemental sulphur, a major product of the silver refinery, in sodium hydroxide and the resulting solu-
tion contains the following chemical species: sodium sulphide, thiosulphate and polysulphides according to reactions (6) and (7) (Ackerman et al., 1993).

\[
\begin{align*}
4\text{S}^-(s) + 6\text{NaOH}(aq) & \rightarrow 2\text{Na}_2\text{S}(aq) + 2\text{Na}_2\text{S}_2\text{O}_3(aq) + 3\text{H}_2\text{O} \\
(\text{X} - 1)\text{S}^-(s) + \text{Na}_2\text{S}(aq) & \rightarrow \text{Na}_x\text{S}_y,
\end{align*}
\]

In addition, the leach processes at Sunshine Mining and Equity Silver Mines are somehow similar while the solution purification processes are different. Antimony was electromonel from the leach solution at Sunshine Mining (Nordwick and Anderson, 1993) whereas Equity Silver Mines entirely recovered antimony in auto-
claves as sodium hydroxyl antimonate and arsenic was converted to calcium arsenate to be impounded at a site far from the mine (Dayton, 1982; Filippou et al., 2007).

Due to the widespread occurrence of antimony and arsenic con-
taining minerals in copper concentrates, a suitable pre-treatment process to selectively remove antimony and arsenic from such con-
centrates is a necessity. If the impurity content is reduced to an acceptable limit the penalties charged by the smelters would be alleviated. Thus, antimony can be recovered as marketable prod-
ucts while arsenic can be precipitated as a stable material (e.g. fer-
ric arsenate) suitable for landfills. By so doing, pyrometallurgical treatment of the so called "dirty ore/concentrate" will be made possible with more economical viability and environmental friendliness.

3. Materials and methods

3.1. Material characterization

The antimony-bearing sulphide material used in this investiga-
tion was bought from Gregory, Bottleby & Lloyd Company, United Kingdom and originated from Casapalca, Departamento Lima, Peru.

The coarse material was first crushed and part of its associated

<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finished Size</td>
<td>Size</td>
</tr>
<tr>
<td>Fine Material</td>
<td>Material</td>
</tr>
</tbody>
</table>
Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

A representative sample was taken from the antimony-bearing sulphide concentrate and also from the leach residue, at which the highest recovery of antimony was obtained, for QEMSCAN (a scanning electron microscope with four energy dispersive X-ray detectors and a microanalyser) analysis. The samples were mounted in epoxy and a diamond cutting wheel was used to cut the hardened blocks to size and expose the sample grains. The samples were polished and carbon coated prior to QEMSCAN analysis. The mineralogy of particles was inferred from data obtained using the QEMSCAN/C210 advanced mineral analysis system. The particles were examined using the Field Scan method, involving spot analyses over the surface of the block, collection of the resultant X-ray spectra and comparison with a spectral data base.

3.2. Leaching

Antimony and arsenic selective removal tests were performed by dissolving the antimony-bearing sulphide concentrate in alkaline sulphide solutions, to determine the effect of the following parameters: sodium sulphide (Na₂S·3H₂O) concentration (0.76 M, 1.14 M and 1.89 M), sodium hydroxide (NaOH) concentration (0.75 M and 1.5 M), leaching temperature (357 K, 364 K, 371 K and 378 K) and mineral particle size (≤53 + 38 μm, ≤75 + 53 μm and ≤106 + 75 μm). All experiments, each lasting 6 h, were carried out with 0.5% solids, ≤75 + 53 μm particle size and 378 K reaction temperature (except where otherwise stated) in 500 mL leach solution containing 1.14 M Na₂S·3H₂O + 1.5 M NaOH. A 500 mL four-necked round bottomed glass reactor was used which was stirred mechanically with a paddle stirrer at a constant stirring rate of 600 rpm and heated in an auto-regulated system. The lixiviant was first added to the reactor and when the desired temperature was reached, the solid sample was added. At predetermined time intervals, 5 mL sample solution 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. The influence of each variable was determined by keeping all other variables constant. Leaching results were evaluated by means of chemical determinations on the leach products using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)/Sector Field Mass Spectrometry (ICP-SFMS).

4. Results and discussion

4.1. Mineralogical composition

The mineralogical composition of the antimony-bearing sulphide concentrate was investigated using XRD and QEMSCAN methods of analysis. Fig. 1 shows the result obtained from XRD analysis performed on the concentrate. The major mineralogical phases identified in the diffractogram were tetrahedrite, sphalerite, galena, chalcopyrite, pyrite and iron sulphide.

QEMSCAN analysis was conducted on the concentrate sample to confirm the mineralogy previously determined by the XRD technique. The result from this method is shown in Fig. 2 and Table 2. This result compares well with the XRD identification of the major phases present in the concentrate, but the method identifies a much wider range of minor minerals (Table 2) that were below the detection limit for XRD. This confirms that QEMSCAN analysis can provide much more mineralogical information than the XRD method for trace mineralogy (Goodall et al., 2005). No arsenic mineral was detected by the two techniques meaning that the arsenic in the mineral is hosted in the tetrahedrite structure. Also, QEMSCAN result shows that the concentrate is rich in tetrahedrite (Table 2) and silver is found bonded in the tetrahedrite structure.

![Fig. 1. XRD diffractogram of antimony-bearing sulphide concentrate.](image-url)
This confirms the presence of silver and arsenic as a solid solution in the tetrahedrite crystal structure as widely reported in the literature (Filippou et al., 2007).

### 4.2. Eh–pH and speciation diagrams

In order to study the behaviour of sulphide ions during leaching in relation to the solution pH, an equilibrium Eh–pH diagram for S–H2O system was constructed using FactSage 6.1 computer software at the temperatures of 298 K and 378 K (Fig. 3a and b), respectively. The equilibrium diagram (Fig. 3) obtained shows that at lower redox potential, S²⁻ ion is the dominant ion in the solution at pH > 13 at 298 K (Fig. 3a) and at pH > 11 at 378 K (Fig. 3b). This implies that higher concentration of sodium hydroxide will be required at 298 K than at 378 K in order to prevent the protonation of S²⁻ to HS⁻ in the solution and therefore, making it available to solubilize antimony by forming soluble sulphide complexes. During sulphide leaching of tetrahedrite, sodium sulphide dissociates according to reaction (8) and antimony forms the complexes thioantimonite and thioantimonate (Filippou et al., 2007) with sulphide ions as shown in reactions (1) and (2). Many other species such as polysulphides, thiosulphates and sulphates (Fig. 3) may form if the leaching is performed under an oxidising environment.

### Table 2

Material mineralogy defined by QEMSCAN.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass fraction (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedrite</td>
<td>30.2</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>20.6</td>
</tr>
<tr>
<td>Galena</td>
<td>19.0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>15.7</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>13.4</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.4</td>
</tr>
<tr>
<td>Tetrahedrite with Ag</td>
<td>0.1</td>
</tr>
<tr>
<td>Andalusite (Al₂SO₄)</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>99.5</td>
</tr>
</tbody>
</table>

(Fig. 2). This confirms the presence of silver and arsenic as a solid solution in the tetrahedrite crystal structure as widely reported in the literature (Filippou et al., 2007).

(Fig. 3). Eh–pH diagram of the S–H₂O system at (a) 298 K and (b) 378 K. The dashed line represents H₂(g)/H₂O.
Protonation of sulphide ions occur according to the equilibria (9) and (10) (Delfini et al., 2003) which take place simultaneously during the leaching process.

\[ \text{Na}_2\text{S} \rightarrow 2\text{Na}^+ + \text{S}^{2-} \quad (8) \]

\[ \text{S}^{2-} + \text{H}^+ \rightarrow \text{HS}^- \quad \log K_1 = -11.96 \quad (9) \]

\[ \text{HS}^- + \text{H}^+ \rightarrow \text{H}_2\text{S} \quad \log K_2 = 7.04 \quad (10) \]

Fig. 4 shows a plot of the molar concentrations of \( \text{S}^{2-} / \text{C}_0 \), \( \text{HS}^- / \text{C}_0 \) and \( \text{H}_2\text{S} \) in the leach liquor as a function of the solution pH at a total sulphide ion concentration of 1.14 M. It can be seen from Fig. 4 that sulphide ion concentration increases rapidly when pH is increased from 10 and upwards, therefore, pH is an important factor. This is because, at a pH > 12, the protonation of sulphide ions will be prevented and therefore available to solubilize antimony according to reactions (1) and (2). Also, a strong alkaline environment is needed to reduce the consumption of more expensive sodium sulphide due to the hydrolysis of sulphide ions (Eq. (11)).

\[ \text{S}^{2-} + \text{H}_2\text{O} \rightarrow \text{HS}^- + \text{OH}^- \quad (11) \]

4.3. Influence of temperature on antimony and arsenic dissolution

The plot shown in Fig. 5 describes the dependency of antimony and arsenic extraction from a tetrahedrite rich sulphide concentrates on the reaction temperature which was varied in the range between 357 K and 378 K. It is evident from Fig. 5 that, after 6 h, the extraction of antimony and arsenic from the mineral is highly influenced by the reaction temperature. At 357 K, 15% and 16% of antimony and arsenic were extracted respectively, and when the reaction temperature was increased to 378 K, about 57% and 60% of antimony and arsenic were extracted, respectively. This observation supports the conclusion made by (Baláž and Achimovičová, 2006a) that temperature accelerates and enhances the extraction of metals into the leach liquor.

4.4. Effect of leaching time on extraction

The effect of leaching time on antimony and arsenic dissolution from the complex sulphide concentrate were investigated and the experimental results are presented in Fig. 6. Increasing the leaching time resulted in increased antimony and arsenic extraction. Due to the narrow size fraction used in this investigation, the metal extraction by the lixiviant is linearly dependent on the leaching time. After 1 h of leaching, approximately 13% of both antimony and arsenic was extracted, and when the leaching time was increased to 6 h, antimony and arsenic extraction was 57% and 60%, respectively. Examination of metal extraction trend shown in Fig. 6 reveals that higher extraction could be achieved if the leaching time was extended beyond 6 h.

4.5. Influence of sulphide ion and hydroxide ion concentrations

In the experiments to study the influence of \( \text{Na}_2\text{S} \) concentration on antimony and arsenic dissolution, \( \text{Na}_2\text{S} \) concentration was varied in the range of 0.76–1.89 M while the \( \text{NaOH} \) concentration was kept constant at 1.5 M. The result is described in Fig. 7. It is apparent from the figure that \( \text{Na}_2\text{S} \) concentration has a significant effect on the extraction of antimony and arsenic from the mineral. After 6 h leaching, approximately 21% of antimony and arsenic was extracted at a concentration of 0.76 M \( \text{Na}_2\text{S} \) and when the \( \text{Na}_2\text{S} \) concentration was increased to 1.14 M, the extraction increased with almost a factor of 3. Further increase in the concentration to 1.89 M \( \text{Na}_2\text{S} \) resulted in an extraction of antimony and arsenic of 87% and 92%, respectively (Fig. 7).
Fig. 6. Effect of leaching time on As/Sb leaching.

Fig. 7. Effect of sodium sulphide concentration on As/Sb leaching.

Fig. 8. Effect of sodium hydroxide concentration on As/Sb leaching.
In order to study the effect of hydroxide ion concentration on the extraction, the leaching conditions were maintained the same as described above except that the concentration of Na$_2$S was constant at 1.14 M while the concentration of NaOH were 0.75 M and 1.5 M.

Fig. 8 illustrates that when a low concentration (0.75 M) of NaOH was used, the rate of extracting antimony and arsenic was slower and about 25% and 24% of antimony and arsenic were dissolved respectively. As the concentration of NaOH increased to 1.5 M, the metal extraction rate is accelerated and the percentage of metal extracted was enhanced. About 57% antimony and 60% arsenic was leached by the lixiviant after 6 h. The observed increase in metal extraction at high concentration of NaOH is due to the higher availability of S$^{2-}$/C$_{0}$ ion for dissolution action (as described in Section 4.2 above), which is promoted by the increase in the pH of the leach liquor and consequently, prevents the hydrolysis of sulphide ion which otherwise would reduce its leaching efficiency.

4.6. Particle size dependence on antimony and arsenic dissolution

The influence of particle size on the extraction of antimony and arsenic from the complex sulphide concentrate was examined for three different size fractions ($\leq 75\mu m$, $75\mu m < 53\mu m$, and $53\mu m < 38\mu m$) at 378 $K$ using solutions containing 1.14 M Na$_2$S and 1.5 M NaOH. It is illustrated in Fig. 9 that extraction of both metals increases with decreasing particle size. After 6 h leaching of the $\leq 75\mu m$ particle size fraction, about 43% and 49% of antimony and arsenic were extracted, respectively. When the same leaching conditions were applied to the size fraction $53\mu m < 38\mu m$, antimony and arsenic extraction were 68% and 75%, respectively. Since the leaching kinetics of tetrahedrite is relatively slow.
there is much to gain by grinding the material thereby creating a larger surface area which is advantageous for the leaching efficiency.

4.7. Selective removal of the impurity elements

In order to identify the mineralogical changes brought about by leaching, solid residue from the leaching test at which the highest antimony extraction was obtained, was characterized by XRD and QEMSCAN analyses. The results were compared with the mineralogy of the original concentrate. The residue used was obtained under the following leaching conditions: 1.89 M Na$_2$S + 1.5 M NaOH, 0.5% solids, 378 K reaction temperature and 6 h leach time where antimony recovery of 87% was obtained. The XRD pattern shown in Fig. 10 indicates that a new mineralogical phase, spionkopite ([Cu$_{2.9}$S$_{2.8}$]) is observed together with other major phases identified in the original concentrate (Fig. 1). Similarly, a non-stoichiometric copper sulphide ([Cu$_{3.9}$S$_{2.8}$]) phase was observed when the residues from enargite leached in alkaline sulphide solutions were analyzed (Filippou et al., 2007). The XRD pattern in Fig. 10 shows that the tetrahedrite peaks found in the concentrate (Fig. 1) have disappeared completely meaning that copper content of the tetrahedrite had been transformed to the new copper sulphide phase observed in the residue.
The results of the QEMSCAN analysis on the leach residue are presented in Figs. 11 and 12. The major mineral phases observed in the residue were sphalerite, galena, pyrite and chalcopyrite, with the newly formed copper sulphide phase. In particular, observation of the polished sections of the leach residue (Fig. 12) showed a micro-porous structure of the new solid phase often enclosing a nucleus of untransformed tetrahedrite. The average crystal chemical formulae of the solid residue determined by QEMSCAN analysis on the transformed phase proves the conversion of tetrahedrite into a copper sulphide having stoichiometry of Cu1.64S which is close to the stoichiometry of the sphalerite observed by XRD but can also be a mixture of chalcocite and covellite. This observation confirms the expectation that tetrahedrite would decompose to either covellite or chalocite in alkaline sulphide solution (Filippou et al., 2007). However, if the leaching time had been prolonged further, the untransformed tetrahedrite would have been converted completely into the new copper sulphide phase observed in the residue. Additionally, QEMSCAN analysis provides more interesting information about the selectivity of the lixiviant to solubilize the impurity elements from the concentrate. Comparing the information given in Fig. 11 concerning the concentrate and the residue, one can see that the major phases found in the concentrate were upgraded and not leached (Fig. 12) with the only exception of the tetrahedrite phase which was reduced from 30.2% to 1.1% in the residue. This result confirms that other metal sulphides in the concentrate remains insoluble in the sulphide solution with the exception of antimony and arsenic sulphides which form soluble complexes in sulphide media. This analysis shows that the Na2S/NaOH lixiviant is suitable for pre-leaching of the concentrate and the residue, one can see that the major phases identified were sphalerite, galena, chalcopyrite and pyrite. Alkaline sulphide leaching of the concentrate reveals that the concentrate is rich in tetrahedrite. Antimony and arsenic contamination of complex sulphides flotation concentrate. MSc Thesis, Luleå. University of Technology, Luleå, 42 pp.


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PAPER III

Separation of antimony from a complex copper concentrate: Process optimization by response surface methodology

Samuel A. Awe, Mohammad Khoshkhoo, Paul Kruger and Åke Sandström

Manuscript under review in the Journal of Separation and Purification Technology
Separation of antimony from a complex copper concentrate: process optimisation by response surface methodology

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ABSTRACT

This paper reports the modelling and optimisation results for the alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn. Response surface methodology, in combination with central composite face-centred design (RSM-CCF), was used to optimise the operating parameters. The leaching temperature, sulphide ion concentration and solid concentration were chosen as the variables, and the response parameters were antimony and tin recovery, and the time required to achieve 90% Sb dissolution. It was confirmed that the leaching process was strongly dependent on the reaction temperature as well as the sulphide ion concentration without any significant dependence on the solid concentration. Additionally, a mathematical model was constructed to characterise the leaching behaviour. The results from the model allow identification of the most favourable leaching conditions. The model was validated experimentally, and the results show that the model is reliable and accurate in predicting the leaching process.

Keywords: Alkaline sodium sulphide, Antimony, Leaching optimisation, Response surface methodology, Central composite face-centred design
1. Introduction

Antimony / arsenic-bearing minerals are commonly found in minor concentrations in many sulphide ore deposits. The tetrahedrite \((\text{Cu}_2\text{Sb}_4\text{S}_{13})\) mineral is often found in association with copper sulphide ores, and though it is an important source of copper, but it is more significant as a source of silver and antimony. Enargite \((\text{Cu}_3\text{As}_3\text{S}_8)\) and tennantite \((\text{Cu}_1\text{As}_4\text{S}_{13})\) are minor sources of copper, and they result in arsenic reporting to the processing circuit. These antimony and arsenic minerals contain significant concentrations of minor elements such as mercury, zinc, bismuth, selenium, etc., which result in penalties for copper concentrates sold to smelters [1]. However, processing of future copper ores and concentrates will most likely involve the treatment of more complex, fine-grained minerals containing increased levels of penalty elements, which are detrimental to the smelting process. Unfortunately, the prevalence of tetrahedrite, tennantite and enargite among the copper-bearing minerals will reduce their economic value due to their minor element content which generates hazardous emissions during pyrometallurgical processing [2].

In copper metallurgy, the removal of impurities is crucial to the production of high-quality copper. The ability to efficiently remove impurities will become even more important in the future, because copper ores show a decreasing ore grade and increasing levels of impurities. Consequently, the penalties charged by smelters for treating minor elements in copper concentrates will increase because the copper smelters are forced to improve their technology for the efficient removal and disposal of the penalty elements, which are difficult and costly to handle [3].

In Sweden, many of the complex sulphide mineral deposits found in the Boliden mining area are found in association with impurities like arsenic, antimony, bismuth and mercury which make it difficult to produce clean and high grade concentrates [4]. During the pyrometallurgical treatment of the complex sulphide concentrate at the smelting plant, arsenic
and mercury in the concentrate end up in the roaster flue dust which is therefore regarded as hazardous metallurgical waste. The arsenic oxide generated in the waste material is highly soluble and consequently, creates a serious environmental problem, which needs to comply with the stringent legislation for its disposal as landfill. As a result of more stringent environmental legislation, the allowable amount of arsenic in the processing waste generated is progressively decreasing. Consequently, high financial penalties are imposed by smelters to treat copper ores containing more than 0.2 wt.% arsenic [3]. Besides, the antimony, arsenic and bismuth contents of the complex sulphide mineral renders it undesirable as pyrometallurgical smelter feed because these impurities affect the conductivity and ductility of the refined copper and also form a scum on electrolytic cells which allow the impurities to be carried over to the cathodes [5, 6]. These impurities are deleterious from the standpoint of metal quality. It is known that small amounts of bismuth and antimony in the copper cathode makes it brittle and renders it unsuitable for producing electric wires. Therefore, it is desirable to remove these impurities at an early stage of processing, since they are difficult to remove from metallic copper. However, in order to increase the economic value and metal grade of the copper concentrates, as well as decreasing the cost of the environmental measures needed when complex sulphide concentrates are processed pyrometallurgically, it is therefore imperative to choose a pre-treatment processing route which can selectively remove these impurities from the complex sulphide concentrates prior to their smelting. In view of this, the hydrometallurgical processing route using alkaline sulphide lixiviant has been proven to be the best alternative route to remove these impurity elements selectively from such concentrates [4, 7-10] and consequently, produce a suitable feed for pyrometallurgical operations.
The efficiency of the process strongly depends on factors such as reaction temperature, concentration of sulphide ion, leaching time, particle size, the amount of solid leached and so forth.

Conventionally, the study of the effects of aforementioned factors, on sulphide leaching of impurity-bearing copper concentrates, has been conducted using an approach with one variable at a time [4, 7, 11]. The effect of each experimental factor was investigated in this method by altering the level of one factor at a time while keeping the levels of the other factors constant. But, if the aim of conducting a study is to determine the optimum operating conditions, response surface methodology (RSM) will be the appropriate method of performing the task. Conversely, RSM is an efficient methodology where all the experimental factors are varied simultaneously over a set of experimental runs. RSM is one of the relevant multivariate techniques that can deal with multivariate experimental design strategy, statistical modelling and process optimisation [12, 13]. It is employed to study the relationship between one or more response variables and a set of quantitative or qualitative experimental factors. RSM is often used after the vital controllable factors are identified and to find the factor settings that optimise the response [14]. This type of experimental design is usually chosen when non-linear interactions between the experimental parameters and the response variables are suspected. Furthermore, application of RSM reduces the number of experiments required for the analysis of the main effects and interactions between factors [14-16]. The objectives of the current research were to evaluate the influence of these experimental factors reaction temperature, sulphide ion concentration and solid concentration on the response variables and also model the behaviour of a complex copper concentrate in alkaline sulphide solution in order to determine the most favourable operating conditions.
2. Materials and methods

2.1 Material and characterisation techniques

Rockliden copper concentrate used in this investigation was a flotation concentrate obtained from Boliden Mineral AB, Sweden. Particle size distribution analysis performed on the concentrate shows that more than 80% of the mineral particles is smaller than 40 μm (Fig. 1).

Chemical analysis of the concentrate is presented in Table 1.

Table 1: Elemental analysis of the complex copper concentrate

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu, %</th>
<th>Fe, %</th>
<th>Pb, %</th>
<th>Zn, %</th>
<th>Sb, %</th>
<th>Sn, %</th>
<th>As, %</th>
<th>Se, %</th>
<th>Hg, %</th>
<th>Ag, %</th>
<th>S, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.8</td>
<td>27.1</td>
<td>7.1</td>
<td>5.7</td>
<td>1.69</td>
<td>0.14</td>
<td>0.42</td>
<td>0.06</td>
<td>0.03</td>
<td>0.08</td>
<td>&gt;15</td>
</tr>
</tbody>
</table>

Fig. 1. Particle size distribution of the concentrate.

A representative sample was taken from Rockliden complex sulphide concentrate for the scanning electron microscope (SEM) using a SEM JEOL JSM5900LV equipped with an EDS-analyser. The sample was embedded in epoxy and the harden block was polished and coated with carbon prior to the analysis. X-ray powder diffraction (XRD) was used to characterize the complex copper concentrate using a Siemens D5000 automatic diffractometer.
equipped with a continuous scanning device. Patterns were collected between 20 angles of 10–90° (at Cu Kα radiation of 40 kV, 30 mA). Mineral phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

2.2 Leaching procedure
Leaching experiments were performed by dissolving the Rockliden complex sulphide copper concentrate samples in 800 mL of lixiviant solutions. The lixiviant solution was prepared by dissolving sodium sulphide (Na₂S·3H₂O) in sodium hydroxide (NaOH) solution. The concentration of sodium hydroxide used at each run of the test was 20 wt% of sodium sulphide concentration used. A total of 17 experiments were conducted in a batch mode using a 1 L five-necked round bottomed glass reactor. The contents of the reactor were mechanically homogenized using a paddle stirrer at a constant stirring rate of 300 rpm and heated on auto-regulated device. All the leaching experiments lasted for 6 h. The lixiviant was first added to the reactor and when the desired temperature was reached, the solid sample was added. At predetermined time intervals, 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).

2.3 Experimental design
The experiment was designed using response surface methodology (RSM) approach. RSM is a particular set of mathematical and statistical methods that includes experimental design, model fitting and validation, and condition optimisation [16]. Experimental runs were designed in accordance with central composite face-centred design (CCF), which allows a full quadratic model for each response under investigation. A detailed discussion of CCF design is documented elsewhere [12, 13].
MODDE 8.0 Umetrics software was used in the design and analysis of the experiment. The effect of the following three factors on the efficiency of the leaching process was investigated: reaction temperature ($X_1$), sulphide ion concentration ($X_2$) and solid concentration ($X_3$). The interaction between the effects of the various variables was also examined. According to the previous work conducted by the authors [7, 17], the levels (low and high) of each of the factors were chosen as follow: temperature (80 and 100 °C), sulphide ion concentration (41 and 164 g/L) and solid concentration (100 and 300 g/L). The response variables were the recovery of antimony (Sb) and tin (Sn); and leaching time $T_{90}$, which is the time required to leach out 90% of antimony from the concentrate by alkaline sulphide lixiviant. Recovery of antimony and tin was computed based on solid residues analysis and it was calculated from equation 1 whilst $T_{90}$ was estimated from antimony leaching kinetic profiles which is fitted to the exponential equation (Eq.2).

\[
R = \frac{f - r}{f} \times 100\%
\]  

(1)

\[
C_t = C_0 e^{kt}
\]  

(2)

Where $R$ represents percent recovery of Sb or Sn, $f$ and $r$ are the amount (g) of Sb or Sn in the feed and residue, respectively, $C_0$ is the initial concentration of Sb in the feed material and $C_t$ is the concentration of antimony in the residue after time $t$ (h) of leaching while $k$ is the rate constant. Since the weight difference between the feed and leach residue was negligible, Eq. 2 was used to simplify the relationship between the leaching time and the amount of metal leached.

Table 2 shows the actual values of the independent variables at which the experiments were performed to estimate the response variables. The table contains the measured values of antimony and tin recoveries, as well as the calculated $T_{90}$ (h) from Eq. 2. The experiments were conducted in randomized order, to avoid any occurring systematic time trend which
could cause error in the model. The original design, that involved replicates of the reference mixture for estimating the pure error, was augmented with replicates of random runs so that the homogeneity of variance error could be checked. The model fitting was investigated by using multiple linear regression (MLR) method.

**Table 2** Central composite face-centred design arrangements and responses for the complex concentrate leaching by alkaline sulphide solution

<table>
<thead>
<tr>
<th>Exp.no.</th>
<th>Run order</th>
<th>Experimental factors</th>
<th>Response variables</th>
<th>Leaching time, (T&lt;sub&gt;90&lt;/sub&gt;) h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature X&lt;sub&gt;i&lt;/sub&gt; (°C)</td>
<td>S&lt;sup&gt;2&lt;/sup&gt; conc. X&lt;sub&gt;2&lt;/sub&gt; (g/L)</td>
<td>Solid conc. X&lt;sub&gt;3&lt;/sub&gt; (g/L)</td>
</tr>
<tr>
<td>N1</td>
<td>13</td>
<td>80</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>N2</td>
<td>2</td>
<td>100</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>N3</td>
<td>10</td>
<td>80</td>
<td>164</td>
<td>100</td>
</tr>
<tr>
<td>N4</td>
<td>3</td>
<td>100</td>
<td>164</td>
<td>100</td>
</tr>
<tr>
<td>N5</td>
<td>1</td>
<td>80</td>
<td>41</td>
<td>300</td>
</tr>
<tr>
<td>N6</td>
<td>12</td>
<td>100</td>
<td>41</td>
<td>300</td>
</tr>
<tr>
<td>N7</td>
<td>8</td>
<td>80</td>
<td>164</td>
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</tr>
<tr>
<td>N10</td>
<td>16</td>
<td>100</td>
<td>102.5</td>
<td>200</td>
</tr>
<tr>
<td>N11</td>
<td>9</td>
<td>90</td>
<td>41</td>
<td>200</td>
</tr>
<tr>
<td>N12</td>
<td>6</td>
<td>90</td>
<td>164</td>
<td>200</td>
</tr>
<tr>
<td>N13</td>
<td>15</td>
<td>90</td>
<td>102.5</td>
<td>100</td>
</tr>
<tr>
<td>N14</td>
<td>14</td>
<td>90</td>
<td>102.5</td>
<td>300</td>
</tr>
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<td>N15</td>
<td>11</td>
<td>90</td>
<td>102.5</td>
<td>200</td>
</tr>
<tr>
<td>N16</td>
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<tr>
<td>N17</td>
<td>7</td>
<td>90</td>
<td>102.5</td>
<td>200</td>
</tr>
</tbody>
</table>

The experimental results obtained from the CCF model were described in the form presented in Eq. 3,

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \]  

(3)

Where \( Y \) is the predicted response, \( \beta_0, \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are constant coefficients, linear coefficients, interaction coefficients and the quadratic coefficients, respectively, and \( X_i, X_j \) are the coded levels of the factors investigated. The model fitting was evaluated by checking the coefficients of determination \( R^2 \), \( R^2_{adj} \) and \( Q^2 \) values, which indicate the fraction of the variation of the response explained by the model, the fraction of variation of the response
described by the model adjusted for degrees of freedom and the fraction of the variation of the response predicted by the model, respectively. The validity of the model was examined at 95% confidence interval.

3. Results and discussion

3.1 Mineralogy of Rockliden copper concentrate

The mineralogical composition of the concentrate was investigated by XRD and SEM-EDS analytical techniques. Fig. 2 presents the result of XRD analysis performed on the concentrate. The main mineralogical phases identified in the XRD pattern were tetrahedrite, chalcopyrite, sphalerite, galena, iron sulphide and pyrite.

![Fig. 2. XRD pattern of the concentrate.](image)

The result from SEM-EDS analysis as shown in Fig. 3 corroborates the result obtained from the XRD analysis. This method identifies a much wider range of minor minerals (Table 3) that were below the detection limit for XRD. Apart from tetrahedrite, the SEM result (Fig. 3) shows that antimony was also found as bournonite (PbCuSbS$_3$) while tin and arsenic was present as stannite ($\text{Cu}_2\text{FeSnS}_4$) and arsenopyrite, respectively. It is apparent from Table 3...
that silver is bound in the tetrahedrite structure, which may enhance the value of the concentrate.

Fig. 3. SEM-EDS micrograph of the concentrate. A- tetrahedrite, B- bournonite, C- stannite, D- chalcopyrite, E- galena, F- sphalerite, G- pyrite, H- arsenopyrite and I- pyrrhotite.
Table 3: Mineralogy and atomic proportions of selected microanalyses of Rockliden copper concentrate defined by SEM-EDS analysis

<table>
<thead>
<tr>
<th></th>
<th>Cu %</th>
<th>Fe %</th>
<th>Zn %</th>
<th>Pb %</th>
<th>Sb %</th>
<th>As %</th>
<th>Sn %</th>
<th>Ag %</th>
<th>S %</th>
<th>Mineral</th>
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<tr>
<td>1</td>
<td>35.41</td>
<td>5.36</td>
<td></td>
<td></td>
<td>30.92</td>
<td>1.31</td>
<td></td>
<td>26.99</td>
<td></td>
<td>Tetrahedrite</td>
</tr>
<tr>
<td>2</td>
<td>34.43</td>
<td>5.55</td>
<td>2.51</td>
<td></td>
<td>30.64</td>
<td>1.29</td>
<td></td>
<td>25.58</td>
<td></td>
<td>Tetrahedrite</td>
</tr>
<tr>
<td>3</td>
<td>33.71</td>
<td>5.77</td>
<td>1.62</td>
<td></td>
<td>31.34</td>
<td>2.03</td>
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<td>25.55</td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>34.10</td>
<td>6.23</td>
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<td></td>
<td>30.14</td>
<td>1.34</td>
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</tr>
<tr>
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<td>34.41</td>
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<td></td>
<td>30.79</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>12.48</td>
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<td>38.81</td>
<td>27.11</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Bournonite</td>
</tr>
<tr>
<td>8</td>
<td>13.06</td>
<td>0.84</td>
<td>39.01</td>
<td>26.10</td>
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<td>Bournonite</td>
</tr>
<tr>
<td>9</td>
<td>12.54</td>
<td>1.37</td>
<td>38.35</td>
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<td>12</td>
<td>0.99</td>
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<td>15</td>
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<td>83.07</td>
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<td></td>
<td></td>
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</tr>
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<td>17</td>
<td>8.14</td>
<td>55.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sphalerite</td>
</tr>
<tr>
<td>18</td>
<td>44.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>19</td>
<td>58.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pyrrhotite</td>
</tr>
</tbody>
</table>

3.2 Data evaluation and RSM model analysis

The distributions of the data for all the responses were inspected for normality, and it was observed that the responses needed to be transformed in order to obtain improved models. Negative logarithmic transformation was carried out for Sb recovery, and power transformation was performed for both Sn recovery and T90 as detailed in Table 4. Evaluation of the raw data revealed that the replicate errors were satisfactorily small for all of the output responses.

Table 4: Transformation of responses

<table>
<thead>
<tr>
<th>Response</th>
<th>Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (%)</td>
<td>-10Log(100-Y)</td>
</tr>
<tr>
<td>Sn (%)</td>
<td>Y^1.1</td>
</tr>
<tr>
<td>T90 (h)</td>
<td>Y^0.5</td>
</tr>
</tbody>
</table>
The model was fitted using multiple linear regression (MLR) method, and the overall result of the model fitting is displayed in Fig. 4. A model can be judged as good, if $R^2 - Q^2 < 0.2 - 0.3$, $Q^2 > 0.5$, model validity $> 0.25$ and reproducibility is greater than 0.5 [13]. It is observed that the predictive power ($Q^2$) of the models ranges from excellent to good. The $Q^2$ values for the responses Sb, T$_{90}$ and Sn are 0.93, 0.91 and 0.55, respectively. All models also show high model validity, which indicates that, no lack of fit. Fig. 4 shows that Sb recovery and T$_{90}$ models satisfied the model performance indicator conditions while the Sn recovery model did not. The lower $Q^2$ value of Sn recovery model could be due to the presence of irrelevant terms contained in the regression model.

![Fig. 4. Summary of fit plot of the initial modelling.](image)

The regression coefficients plots of the models were examined and the statistically non-significant terms were eliminated. Thus, the models were refined and simplified. The summary of fit plot of the refined models is presented in Fig. 5. It can be seen from Fig. 5 that...
all three $Q^2$ values have increased, and now amount to 0.97, 0.97 and 0.74 for Sb recovery, $T_{90}$ and Sn recovery, respectively. The refined models show improved model validity.

**Fig. 5.** Summary of fit plot of the refined modelling.

The outcome of the normal probability plot of the residuals after refinement (Fig. 6) reveals that the models look satisfactory, except for the deviating behaviour of experiment 2 in Sn recovery model. Subsequently, experiment 2 was critically scrutinized for any possible error, but it was found to be well fitted into the other models; therefore, the experiment cannot be removed from the model. Due to satisfactory $R^2$ and $Q^2$ of Sn recovery model, it may be assumed that experiment 2 is a weak outlier which does not influence the model decisively. In order to obtain information concerning how the input variables affect the responses, regression coefficient plots of the refined models were made and interpreted (Fig. 7).

Inspection of these plots shows that reaction temperature and sulphide ion concentration have a strong effect on all the three responses. It seems that solid concentration has insignificant effect on all the three responses.
Fig. 6. Normal probability plots of residuals after model refinement.

Fig. 7. Regression coefficient plots for the responses Sb, Sn and T₉₀ after model refinement with confidence intervals.
Furthermore, examination of the analysis of variance (ANOVA) of the refined models for the responses Sb recovery, Sn recovery and T₉₀ as shown in Table 5, reveal that all the regression models are statistically significant with a 95% confidence level in the range studied. For all the response variables, F₀ values are greater than F_critical values, and P-values are smaller than 0.05. According to the results displayed in the ANOVA table (Table 5), it can be inferred that the model error of the original model is of the same magnitude as the replicate error for all the responses, because their P-values are greater than 0.05 and F₀<F_critical at 95% confidence level. Hence, the models have small error and good fitting power, meaning that the models show no lack of fit.

**Table 5** ANOVA for the quadratic models predicted for each response variable

<table>
<thead>
<tr>
<th>Response variable</th>
<th>Source</th>
<th>DF</th>
<th>SS (variance)</th>
<th>MS (variance)</th>
<th>F₀</th>
<th>F_critical α = 0.05</th>
<th>P-value</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb recovery</td>
<td>Total corrected</td>
<td>16</td>
<td>2.7026</td>
<td>0.1689</td>
<td>0.4109</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regression</td>
<td>5</td>
<td>2.6619</td>
<td>0.5324</td>
<td>143.58</td>
<td>3.20</td>
<td>0.000</td>
<td>0.7296</td>
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<tr>
<td></td>
<td>Residual</td>
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<td>0.0408</td>
<td>0.0037</td>
<td>0.0609</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lack of fit (model error)</td>
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<td>0.0347</td>
<td>0.0039</td>
<td>1.28</td>
<td>19.37</td>
<td>0.514</td>
<td>0.0621</td>
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<td>Pure error (replicate error)</td>
<td>2</td>
<td>0.0060</td>
<td>0.0030</td>
<td>0.0550</td>
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</tr>
<tr>
<td>Sn recovery</td>
<td>Total corrected</td>
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<td>0.0005</td>
<td>3.37e-5</td>
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<td>30.61</td>
<td>3.20</td>
<td>0.004</td>
<td>0.0100</td>
</tr>
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<td>Residual</td>
<td>11</td>
<td>3.61e-5</td>
<td>3.29e-6</td>
<td>0.0018</td>
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<td></td>
<td>Lack of fit (model error)</td>
<td>9</td>
<td>3.39e-5</td>
<td>3.77e-6</td>
<td>3.36</td>
<td>19.37</td>
<td>0.251</td>
<td>0.0019</td>
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<tr>
<td></td>
<td>Pure error (replicate error)</td>
<td>2</td>
<td>2.24e-6</td>
<td>1.12e-6</td>
<td>0.0010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₉₀</td>
<td>Total corrected</td>
<td>16</td>
<td>0.1823</td>
<td>0.0114</td>
<td>0.1068</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Regression</td>
<td>5</td>
<td>0.1798</td>
<td>0.0360</td>
<td>155.78</td>
<td>3.20</td>
<td>0.004</td>
<td>0.1896</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td>11</td>
<td>0.0025</td>
<td>0.0002</td>
<td>0.0152</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Lack of fit (model error)</td>
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<td>0.0023</td>
<td>0.0003</td>
<td>2.16</td>
<td>19.37</td>
<td>0.356</td>
<td>0.0160</td>
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<tr>
<td></td>
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<td>2</td>
<td>0.0002</td>
<td>0.0001</td>
<td>0.0109</td>
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<td></td>
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</table>

DF=degree of freedom, SS=sum of squares, MS=mean square, SD=standard deviation

Moreover, the observed responses correlated very well with the predicted values as illustrated in Fig. 8. Thereby, the models can be considered adequate for the predictions and for the
optimisation process. The regression models describing the correlation between the transformed response variables and the parameters investigated were as written in Eqs. 4-6.

\[
S_b = -1.002 + 0.168X_1 + 0.485X_2 - 0.079X_2^2
\]  
\[
Sn = 0.030 - 0.003X_1 - 0.004X_2 - 0.005X_2^2 - 0.003X_1X_2
\]  
\[
T_{90} = 0.422 + 0.044X_1 + 0.123X_2 - 0.039X_2^2 - 0.020X_1X_2
\]

In the regression models shown in Eqs. 4-6 all the experimental parameters are in coded values where \(X_1\) is the reaction temperature, \(X_2\) is sulphide ion concentration, \(X_3\) is solid concentration, and \((X_2)^2\) and \(X_1X_2\) are the square and interaction of the main factors. The presence of significant square and interaction terms in the regression equations confirms the existence of quadratic behaviour and non-linear combining effects of the variables.

**Fig. 8.** Relationship between observed and predicted values for the response variables \(S_b\), \(Sn\) and \(T_{90}\).
3.3 Interpretation of the data by response surface modelling

According to the empirical models explained in Eqs. 4-6, response surface plots were developed, which provide a better understanding of the effect of the experimental parameters on the response variables. Fig. 9 displays contour plots at various solid concentrations where antimony recovery is represented by varying simultaneously leaching temperature from 80 °C to 100 °C and sulphide concentration from 41 g/L to 164 g/L. The figure shows that antimony recovery increases with increase in both sulphide ion concentration and reaction temperature. The effect of both leaching temperature and sulphide concentration on antimony recovery can be explained by the fact that tetrahedrite, the antimony mineral, is refractory in nature. Therefore, high sulphide concentration and reaction temperature are needed to enhance antimony dissolution by the lixiviant. Besides, tetrahedrite dissolution in alkaline sulphide solution is controlled by chemical reaction with a relatively high activation energy [7], hence, higher lixiviant concentration as well as increasing leaching temperature would favour its dissolution.

![Fig. 9. Contour plots of Sb recovery showing the interaction between sulphide concentration (g/L) and temperature (°C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.](image-url)
Fig. 10 presents the effect of leaching temperature and sulphide concentration on tin recovery. It is seen that these independent variables have significant effects on tin dissolution. Like antimony, tin extraction is observed to increase with increasing temperature and sulphide concentration. The reason could be that the tin mineral, stannite (Cu₂FeSnS₄), may be refractory to the lixiviant, as is the case for the tetrahedrite mineral. Consequently, higher concentrations of sulphide and temperature would be needed to decompose the mineral for effective dissolution of tin. It is evident from Fig 10 that the concentration of the solid leached does not influence tin or antimony recovery (Fig. 9). For example, at 164 g/L sulphide concentration and 100 °C leaching temperature, tin recovery at 100 g/L, 200 g/L and 300 g/L solid concentrations were 64.7%, 69.5% and 68.5%, respectively.

Fig. 10. Contour plots of Sn recovery showing the interaction between sulphide concentration (g/L) and temperature (°C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.
Fig. 11 shows the influences of temperature and sulphide concentration on the time required to dissolve 90% Sb from the copper concentrate. It can be seen from the contour plots that the time needed to leach out 90% Sb decreases with increasing temperature and sulphide concentration, with an insignificant effect of solid concentration. The model reveals that it is possible to leach at lower sulphide concentration and temperature, which is beneficial to the process and still ensures high metal recovery over an extended leaching time. For instance, the lower left corners of the plots in Fig. 11 states the leaching conditions, at which 90% Sb can be obtained over 22 h duration of leaching, while the lixiviant concentration and temperature are at minimum levels.

Fig. 11. Contour plots for the response $T_{90}$ showing the interaction between sulphide concentration (g/L) and temperature ($^\circ$C) at various solid concentrations (a) 100 g/L (b) 200 g/L (c) 300 g/L.
3.4 Model validation

In order to test the validity of the model with regards to the response variables Sb, Sn and T_{90}, a separate experiment was performed at the conditions shown in Table 6 for 24 hours. The results, as shown in Table 6, indicate a close agreement with the values predicted by the model. Consequently, the model from a response surface methodology is considered to be accurate and reliable, for predicting the leaching of antimony and tin from the complex copper concentrate, and also good at predicting the time needed to recover 90% of the antimony from the concentrate.

Table 6 Validation of model

<table>
<thead>
<tr>
<th>Temp. X₁, °C</th>
<th>Sulphide conc. X₂, g/L</th>
<th>Solid conc. X₃, g/L</th>
<th>%Sb Predicted</th>
<th>%Sb Observed</th>
<th>%Sn Predicted</th>
<th>%Sn Observed</th>
<th>T_{90}, h Predicted</th>
<th>T_{90}, h Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>45</td>
<td>290</td>
<td>36-58</td>
<td>52</td>
<td>30-37</td>
<td>26</td>
<td>19-30</td>
<td>20</td>
</tr>
</tbody>
</table>

3.5 Process optimisation and economic implications

Furthermore, optimisation of the factors affecting the leaching process can be carried out depending on what is expected from the process. If high recoveries of Sb and Sn are desirable in as short as possible leaching time and at any cost, one might opt for leaching at maximum temperature and sulphide ion concentration as displayed in Figs. 9 and 10. On the other hand, if for practical and economic reasons, low production cost (due to heating energy and reagent costs); and less corrosion and electrowinning problems (due to high alkalinity and sulphide concentration respectively) are desirable. Consequently, lower temperature and sulphide concentration can be used (Fig. 11) to set the factors in such a level to obtain high recovery of Sb (min 90%) by extending the leaching time.

The three parameters considered in this study affect the economics of the process in various ways. Increasing the leaching temperature accelerates the leaching kinetics, resulting in a smaller volume for the leach tanks. However, for temperatures above 90° C, filtration will
have high maintenance costs due to material constraints, necessitating the use of additional cooling equipment prior to filtration. Therefore the economical optimum leaching temperature is likely to be around 90°C. There exists a strong correlation between the soluble sulphide (free ion) concentration and the leaching rate. However, raising the sulphide concentration could reduce the tank volumes at the expense of an increase in sulphide losses to the bleed stream. So any savings in capital expenditure is likely to be offset by an increase in operating cost. In practice, the process would have a large recycle stream and a small bleed stream, to minimise the loss of sulphide lixiviant. Another effective means of reducing the tank volumes is to increase the solids concentration. The result would be an increase in the solution metal concentrations reporting downstream, which would improve the recovery of antimony. Further work should therefore be undertaken to determine the maximum solids concentration that is technically feasible.

4. Conclusions

Modelling and optimisation of alkaline sulphide leaching of a complex copper concentrate containing 1.69% Sb and 0.14% Sn was conducted using response surface methodology-central composite face-centred design (RSM-CCF). It was demonstrated that the leaching process was strongly dependent on the reaction temperature as well as the sulphide ion concentration with insignificant dependence on solid concentration. A strong model with no lack of fit was developed and the validity of the model was confirmed experimentally. The result shows that the model is reliable and accurate for predicting the leaching process.

Acknowledgement

The authors would like to appreciate the following organisations VINNOVA, Boliden Mineral AB, LKAB and the Adolf H. Lundin Charitable Foundation, for their financial supports. The contribution from the Centre of Advanced Mining & Metallurgy (CAMM) is gratefully acknowledged.
References
