SUSTAINABLE EXTRACTION AND PROCESSING OF RAW MATERIALS, 2024

ACID AND AMMONIA LEACHING OF SECONDARY COPPER SULFIDES

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ABSTRACT. The study focuses on understanding the efficiency and kinetics of copper recovery from secondary sulphide ores, which are increasingly becoming a significant source of copper. An experimental investigation was undertaken to assess the leaching behaviour of secondary copper sulphides in acid and ammonia media. The test work consisted of ore sample characterisation, including physico-mechanical properties determination, chemical assay, whole rock analysis, mineralogy, and copper distributions, followed by acid consumption tests, agglomeration, and agitation leach tests. Leaching tests were conducted in a lab-scale agitated reactor using 100 g of the ore sample, 0.3 l of leach solution, a stirring rate of 420 rpm and a leach time of up to 200 hours. The effect of the reaction time and oxidant (Fe^{3+}, NO^{+}) concentration on the copper recovery was evaluated. The maximum copper extraction was obtained in the test performed using acid media with the addition of NO^{+} as an oxidant. Further, a potential hydrometallurgical process option for recovering copper from secondary sulphide sources is proposed.

Key words: copper, leaching, secondary sulphides, oxidant

Introduction

Copper is a critical industrial metal that drives advancements in technology today. Historically, copper processing relied on pyrometallurgical method, consisting of froth flotation, smelting and electrorefining, which involve high energy consumption and environmental impacts. However, the depletion of high-grade copper ores, coupled with stricter environmental regulations, has prompted a shift towards hydrometallurgical approaches (Habashi, 2018). Hydrometallurgy offers several advantages, including lower energy requirements, reduced emissions, and the ability to process low-grade and complex ore deposits. With the increasing demand for sustainable resource management, the focus has shifted towards secondary sulphide copper ores due to their abundant presence and potential economic viability. Secondary sulphides, on the other hand, present challenge to conventional hydrometallurgical techniques since they require oxidation and leach at a slower rate (Fisher and Roman, 1971; Walsh and Rimstidt, 1986; Ferron, 2003).

The success and efficiency of copper extraction from secondary minerals are largely determined by the leaching media used. Currently, the leaching process that uses sulphuric acid in the presence of oxidants as a leaching medium stands out as a prevalent method of recovering copper from secondary sulphides. Oxidants such as ferric iron, chlorides, and oxygen are frequently used to improve leaching kinetics and enhance copper recovery (Bartlett, 2007; Nicolle et al., 2015; Toro et al., 2021).

Furthermore, ammonia-based leaching solutions have gained significant attention due to their unique properties and advantages (Radmehr et al., 2012; Radmehr et al., 2013; Conejeros et al., 2020). Ammonia, in its various forms such as ammonium sulphate or ammonium carbonate, serves not only as a complexing agent for copper ions but also as a pH modifier, contributing to the optimisation of leaching conditions. The use of ammonia offers the potential for selective leaching, thereby minimizing the co-dissolution of impurities and enhancing the purity of the obtained copper solutions.

This paper presents an investigation into the characterisation and leaching kinetics of secondary sulphide copper ores, aiming to identify their response to various leaching conditions. This study used an integrated strategy involving physico-mechanical, chemical, and mineralogical analyses as well as leaching tests to provide necessary information for the development of an efficient and environmentally friendly hydrometallurgical process for copper recovery from secondary sulphides.

Materials and methods

Sample preparation

Around 200 kg of run-of-mine copper ore containing mainly secondary sulphides, provided by a large mining company, was crushed to -19 mm and blended to produce a 50 kg representative sample. The sample was then crushed to 100% passing 2.0 mm and split into representative sub-samples for characterisation and testing. Some sub-samples were further pulverised to -150 µm.

Sample characterisation

The ore samples characterisation process includes physical-mechanical properties determination, X-ray diffraction (XRD) analysis, ICP multi-element analysis, whole rock analysis, copper phase analysis, and mineralogical analysis. The chemical composition of the ore was determined using whole rock analysis and four-acid digestion, followed by an ICP-OES scan. Copper phase analysis was used to determine the distribution of copper minerals within the ore, and the ore mineralogy was examined employing quantitative X-ray diffraction (XRD) and optical microscopy.

Metallurgical testing

To preliminary evaluate the acid consumption of the ore early in the test work, an "empirical" acid consumption test at a constant pH of 1.5 for 1 hour was performed following Scheffel (2014). The amount of acid added during the test was recorded and used to calculate both gross and net acid consumption in kilos per ton of ore. An agglomeration testing to estimate the acid addition required to agglomerate and cure the ore was conducted. Acid dosages of 50, 100, and 150% of the calculated net acid consumption were applied to agglomerate a 1-kilogram sample. The agglomerated samples were then

cured for 24 hours before being leached for 2 hours on a laboratory bottle roller following Scheffel et al. (2016).

Agitation leach tests were performed on a 100-gram sample pulped with a 300-ml leaching solution in a 1-liter glass reactor with a stirring rate of 420 rpm at 25-30 °C.

The leach testing comprised two alternative approaches to copper recovery. The first approach included acid leaching alone and with ferric (Fe^{3+}) and nitrosonium (NO^{+}) ions as oxidants. Ferric sulphate and sodium nitrite were used as sources of Fe^{3+} and NO^{+} ions, respectively. The tests were set to run for 200 hours, with solution samples taken at 24, 100, and 200 hours.

The second approach used alkaline leaching with ammonium chloride and ammonium sulphate solutions containing 5 g/l free ammonia. During the testing, sodium hypochlorite was added as an oxidizing agent. The leach was allowed to run for 20 hours, with solution samples collected at 4, 8, 12, and at the end of the tests.

Results and Discussion

Table 1 shows the physical and mechanical properties of the ore sample.

Table 1. *Physical and mechanical properties*

Parameter	Unit	Value
Bulk density	g/cm^3	1.75
Specific gravity	-	2.81
Porosity	%	2.06
Water saturation	%	0.22

Results of elemental ICP-OES and whole rock analyses are shown in Tables 2 and 3, respectively.

Table 2. *ICP-OES analysis*

Parameter	Unit	Value
Cu	%	0.3150
Co	%	0.0015
Ni	%	0.0076
Zn	%	0.0824
As	%	0.0009
Mo	%	0.0005
Ag	%	0.0009
Cd	%	0.0002
Sb	%	0.0011
Pb	%	0.0140
Bi	%	0.0006

According to the ICP-OES analysis results in Table 2, copper is the major element in the ore sample with a concentration of 0.315 %. Lead and zinc are also identified at moderately substantial levels: 0.014 % and 0.0824 %, respectively. The whole rock analysis results (Table 3) demonstrate that the sample contains a substantial amount of silica, indicating the presence of silicate minerals. When combined with the relatively high aluminum content, this suggests an abundance of aluminosilicate minerals.

The distribution of copper minerals within the ore is presented in Table 4.

Table 3. *Whole rock analysis*

Parameter	Unit	Value
Fe_2O_3	%	4.54
MnO	%	0.37
TiO_2	%	0.48
CaO	%	6.76
K_2O	%	1.79
P_2O_5	%	0.12
SiO_2	%	66.74
Al_2O_3	%	11.38
MgO	%	1.68
Na_2O	%	1.38
LOI	%	4.76

Table 4. *Copper phase analysis*

Cu, %			Total Cu, %
Cu in oxide minerals	Cu in secondary sulphides	Cu in primary sulphides	
0.008	0.281	0.026	0.315

The results of the copper phase analysis in Table 4 reveal that secondary sulphides account for 89.2 % of copper, primary sulphides for 8.3 %, and oxide minerals for just 2.5 %.

The X-ray diffraction pattern of the sample is presented in Figure 1.

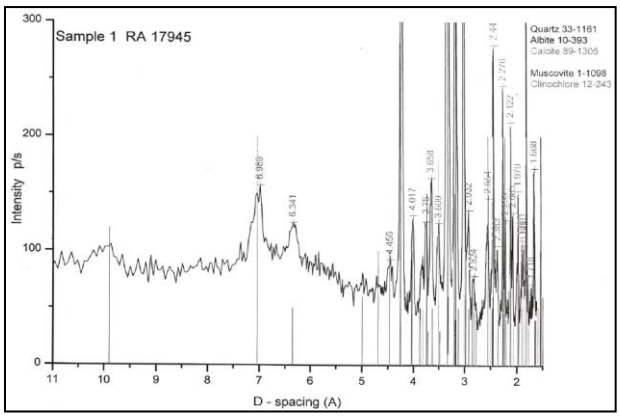


Fig. 1. XRD pattern of the studied material

As can be seen from Figure 1, the sample comprises 40 % quartz, 27 % albite (Na-Ca), 12 % clinochlore (Mg-Fe), 9% calcite, 7 % muscovite and 4 % microcline. The copper minerals were below the XRD detection limit, however optical microscopy verified their presence.

The optical microscope results show that copper mainly occurs as chalcocite, digenite, and diurleite, with minor amounts of covellite and bornite. In addition to copper mineralogy, optical microscopy revealed that the gangue minerals are primarily quartz and feldspar, with lesser amounts of chamosite, muscovite, and calcite.

Figure 2 depicts chalcocite (yellow) with bornite and digenite (grey blue) inclusions in a quartz mass (dark grey).

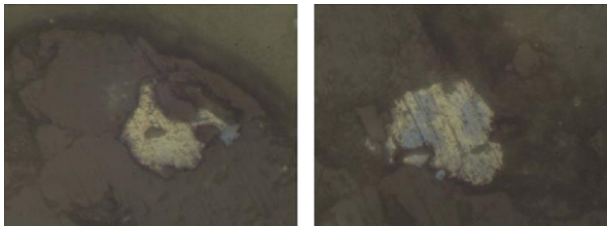


Fig. 2. Photomicrographs of the –12+6 mm fraction of the crushed ores (field width 205 μm)

Acid consumption is an essential characteristic of the leaching process, associated with both copper dissolution and gangue minerals reactions (Thomas, 2021). "Empirical" acid consumption test was used for preliminary determination of the acid consuming character of the ore. The gross acid consumption was 40.9 kg H_2SO_4/t ore with corresponding net acid consumption of 39.8 kg H_2SO_4/t ore.

The results of the agglomeration testing are presented in Table 5.

Table 5. *Ore agglomeration test results*

H_2SO_4, kg/t	H_2SO_4, g/l	Cu, g/l	pH
19.9	2.93	0.0	5.8
39.8	5.87	0.13	3.8
59.7	8.80	0.14	1.2

Based on the results in Table 5, an addition of about 40 kg of H_2SO_4 per ton of ore in agglomeration appears feasible.

Acid leaching was conducted using various solutions, such as sulphuric acid alone (Test 1), sulphuric acid with 3 g/l Fe^{3+} (Test 2), and sulphuric acid with 2 g/l NO^+ (Test 3). The effect of leach time on the copper dissolution was investigated at a solid/liquid ratio of 1:3 and 50 g/l H_2SO_4. During the tests, samples were taken from the solution, and the values of copper and ferric iron concentrations were determined. The results are shown in Table 6 and Figure 3.

Table 6. *Acid leaching test results*

N	Leach time, h					
	24		100		200	
	Cu, mg/l	Fe^{3+}, g/l	Cu, mg/l	Fe^{3+}, g/l	Cu, mg/l	Fe^{3+}, g/l
1	116	0.23	140	0.45	160	0.63
2	133	2.33	638	3.53	835	3.35
3	298	0.55	695	1.63	893	1.57

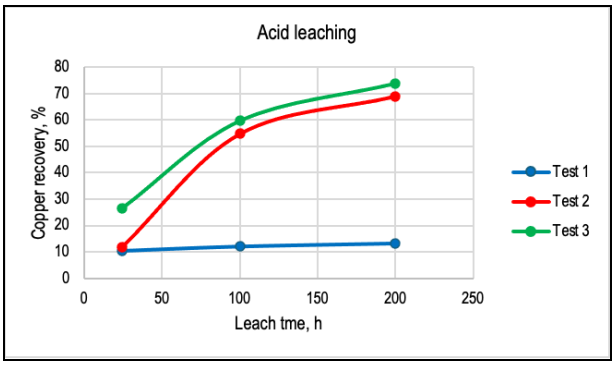


Fig. 3. Acid leaching: copper recovery vs. time

As listed in Table 6, the recovery of copper increased with leach time. A comparison of leach results without and with the addition of Fe^{3+} and NO^+ ions indicated that the presence of an oxidant in the solution increased copper recovery (68.9 % and 73.7 % with oxidants versus 13.2 % without). The highest recovery was achieved using the NO^+ ions. This is thought to be a result of the significantly higher redox potential of NO^+ ions (1.45 V) compared to that of Fe^{3+} (0.77 V) (Anderson, 2003).

According to Anderson (2003), adding sodium nitrite to the sulphuric acid solution, induces the following reactions:

Formation of nitrous acid:

$$NaNO_2 + H^+ \rightarrow HNO_2 + Na^+ \quad (1)$$

Generation of NO^+ ions from nitrous acid:

$$HNO_2 + H^+ \rightarrow NO^+ + H_2O \quad (2)$$

Oxidation of copper sulphides by NO^+ ions:

$$2CuS + 4NO^+ \rightarrow 2Cu^{+2} + 2S^0 + 4NO \quad (3)$$

To assess the effect of leach time on copper dissolution, alkaline leaching was performed using 1 g/l ammonium chloride (Test 1) and 1 g/l ammonium sulphate solutions (Test 2) containing 5 g/l free ammonia and sodium hypochlorite as an oxidant. During the leach period only copper concentrations were monitored. Table 7 and Figure 4 show the obtained results.

Table 7. *Ammonia leaching test results*

N	Leach time, h			
	4	8	12	20
	Cu, mg/l	Cu, mg/l	Cu, mg/l	Cu, mg/l
1	195	303	456	530
2	134	348	494	564

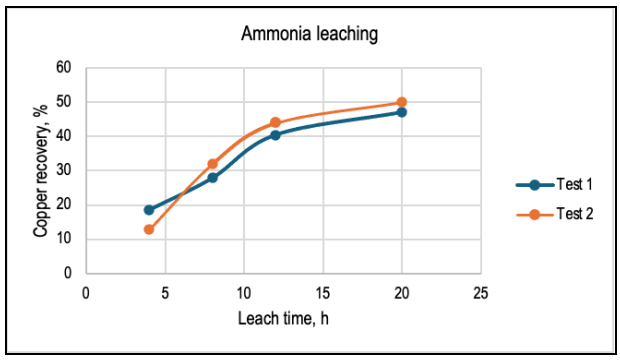


Fig. 4. Ammonia leaching: copper recovery vs. time

As can be seen in Table 7 and Figure 4, the copper recoveries obtained in both tests did not vary significantly during the 20-hour leach time. However, Test 2 showed a slightly higher copper recovery rate.

The findings show that among the acid and ammonia leach media that were examined, sulphuric acid leaching with oxidants is the most effective and feasible way to extract copper from the ore. The highest copper recovery was observed using NO^+-assisted acid leaching, whereas ammonia leaching yielded around 50 % copper recovery.

As a result of this experimental study, a flowsheet for the recovery of copper from the copper secondary sulphide ore has been proposed. Figure 5 outlines a hydrometallurgical

process for copper recovery including leaching, counter current decantation (CCD), ion exchange, and solvent extraction followed by electrowinning. Copper ore with a particle size of P80 200 µm is first leached in 50 g/l sulphuric acid at a slurry density of 25–30 % and ambient temperature with the addition of sodium nitrite as a source of NO^+ ions. After acid leaching, the leach residue is separated from the copper pregnant leach solution (PLS) by counter-current decantation circuit. The washed residue is neutralized with lime in several stages before disposal. The clarified PLS is transferred to ion exchange unit to concentrate the copper and this is followed by the subsequent extraction of the copper as a high purity cathode product by solvent extraction and electrowinning.

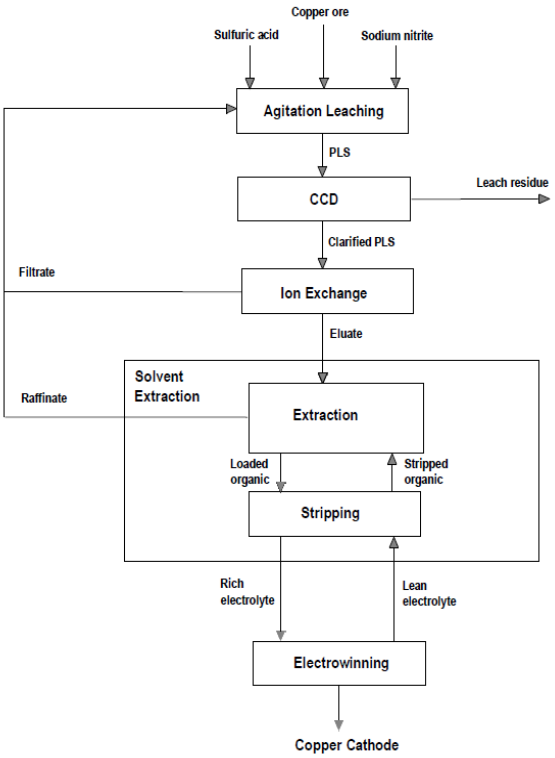


Fig. 5. Proposed flow sheet for recovery of copper from secondary sulphide ore

Conclusions

Characterisation and metallurgical testing on a representative sample were conducted with the aim of assessing the copper recovery potential from secondary copper sulphide ore by acid and ammonia leaching. The major conclusions drawn from the study include:

- Copper assays showed that the grade of the ore sample was 0.315 % as total copper.
- According to the phase analysis, 89.2 % of the copper is associated with secondary sulphides, 8.3 % with primary sulphides, and 2.5 % with oxide minerals.
- X-ray diffraction analysis indicated 40 % quartz, 27 % albite, 12 % clinochlore, 9 % calcite, 7 % muscovite, 4 % microcline and 1 % other minerals.
- The main copper minerals detected by the optical microscopy are chalcocite, digenite, and diurleite.
- The examined secondary copper sulphide ore is not suitable for leaching by sulphuric acid, as evidenced by the 13.2 % copper recovery obtained from the testing.
- The highest copper recovery from oxidative acid leaching tests achieved 73.7 % after 200 hours in the presence of NO^+ as an oxidant.
- Leach extraction profiles suggest that greater copper recoveries might be achieved with further optimisation of acid leaching.
- Oxidative acid leaching is more effective than ammonia leaching at extracting copper from the ore. Ammonia leaching produced unsatisfactory results, indicating that this approach is not favourable for the ore. The ammonia leach tests yielded a copper recovery of approximately 50 %. This figure is lower than the 73.7 % copper recovery obtained for acid leaching using NO^+ as an oxidant.
- The NO^+-catalyzed acid agitation leaching operating in closed circuit with ion exchange, solvent extraction, and electrowinning copper recovery plant seems to be a potentially viable process option for the treatment of secondary copper sulphide ore. However, additional research is required to optimise the leaching process and define the operating parameters of the ion exchange and solvent extraction for the concentration and recovery of copper from the pregnant leach solution, as well as the conditions for copper electrowinning.

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