Atmospheric pressure leaching application for the recovery of copper and nickel from low-grade sources

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Challenges in the base metals industry include depletion of high-grade deposits, strict environmental controls governing mining operations, and high energy demands. Low-grade base metal ores and tailings have become alternative sources of metals such as copper and nickel, whose demand remains high. With strict regulatory and statutory laws governing the handling of mine dumps, tailings need to be processed. Processing of low-grade ores and tailings using traditional pyrometallurgical routes has proven to be uneconomic due to the very low metal values in the materials. It is therefore necessary to apply metallurgical technologies that are energy-efficient, cost-effective, and environmentally friendly for processing these materials. Hydrometallurgy has emerged as the most suitable processing method for low-grade ores and tailings as it requires low energy inputs and inexpensive construction materials compared to pyrometallurgy.

Copper tailings and a low-grade nickel ore were leached under atmospheric pressure using sulphuric acid as a lixiviant. To improve copper extraction, the tailings were upgraded on the Knelson centrifugal gravity concentrator prior to leaching. Copper extraction improved from 51% to 59% upon upgrading, with magnesium and iron extraction decreasing significantly. Reducing agents were added to the low-grade ore leaching system to improve nickel extraction. Addition of NaCl improved nickel extraction from 31% to 87%. Kinetic data for copper and nickel leaching fitted the equation, \( 1 - \frac{x}{2} (1 - x)^{\frac{3}{2}} = k_2 t \), indicating that the leaching reactions for both metals are diffusion-controlled.

Introduction

Low-grade ores and tailings are difficult to process through conventional methods because of their complex mineralogy and low metal content. A shortage of copper and nickel feedstock for sulphide refineries is another global challenge. With declining grades of copper and nickel deposits, there is a need for economical and environmentally responsible methods of metal extraction from alternative sources (Xie et al., 2005). These include low-grade ores and tailings, which may account for about 75% of the reserves of some important metals (Wen and Ruan, 2002).

Hydrometallurgical processes have become favourable for the processing of low-grade ores and tailings due to their generally lower capital costs as compared to pyrometallurgical processes, which are capital-intensive and demand stringent environmental controls (Dreisinger, 2009). Although high-pressure leaching presents lower energy demands as compared to pyrometallurgy, an effective process that can extract metals from low-grade ores and tailings at atmospheric pressure is required (Xie et al., 2005).

Copper commonly exists in the Earth’s crust as copper-iron-sulphide and copper sulphides. The metal also occurs in oxidized minerals such as carbonates, oxides, hydroxy-silicates, and sulphates (Davenport et al., 2002). Nickel ores include sulphides, arsenides, antimonides, arsenate, silicates, and oxides (Boldt and Queneau, 1967; Rosenberg, 1968). Sulphides and oxides are the most commonly exploited ores for economic purposes. Copper and nickel are extracted from sulphide ores by flotation followed by pyrometallurgical processing, while oxidized ores are processed through hydrometallurgy (Mudd, 2009).

Sulphide and oxide ores bearing important industrial metals are chemically stable and require excessive amounts of energy to break the bonds for metal liberation (Brooks and Subagyo, 2002). Gupta (2003) determined the theoretical energy required for smelting of copper and nickel to be 2.1 GJ/t and 3.6 GJ/t, respectively. About 80% of the world’s copper is produced by pyrometallurgical processes from sulphide ores, while the remainder is produced by hydrometallurgical processes. Nickel sulphide ores, as well as about 35% of nickel laterites, are processed pyrometallurgically, with the remainder being treated hydrometallurgically (Norgate and Jahanshahi, 2010).
Pyrometallurgical processing of sulphides normally involves roasting, smelting, and converting. Roasting removes sulphur and iron as sulphur dioxide (SO\textsubscript{2}) and iron oxide (FeO) respectively. The roasted charge is melted with a siliceous flux to produce liquid silicate and molten sulphide. Converting involves the removal of sulphur as the melt and the iron is removed as the silicate phase. Nickel laterite ores may be processed by direct smelting to produce ferronickel, without the concentration stage; however, this is not a commercial practice (Norgate and Jahanshahi, 2010).

Atmospheric pressure leaching has been suggested as a method of replacing high-pressure acid leaching, which entails high costs due to expensive materials required for the manufacturing of autoclaves (Büyükakinci, 2008). Whittington and Muir (2000) noted that significant amounts of nickel and cobalt could be extracted from laterite ores by atmospheric pressure leaching. It was found that sulphuric acid was the most efficient and widely used acid for leaching oxides, as compared to hydrochloric and nitric acid (Teir et al., 2007; Habashi, 1999; Habashi, 2003). In the leaching oxide ores and tailings, acid consumption can be escalated by the presence of gangue minerals such as silica, mica, calcite, pyroxene, feldspar, and iron-bearing minerals. To decrease acid consumption rates, gangue minerals may be rejected by physical separation techniques. Chemical treatment may also be applied to enhance the amenability of valuable minerals to acid leaching.

This study focused on atmospheric pressure acid leaching of a low-grade nickel laterite ore and copper tailings. The co-dissolution of cobalt, magnesium, and iron was observed as well as the reaction kinetics. Leaching was performed on upgraded copper tailings and low-grade nickel ore, with addition of reducing agents to investigate the effect of the less expensive auxiliary methods that can improve metal extraction with minimum impurity dissolution.

**Copper tailings upgrading using the Knelson concentrator**

Copper sulphide minerals co-exist with copper oxide minerals. Generally, copper oxide minerals do not respond well to traditional flotation as applied to sulphide minerals, (Lee et al., 2008), and are therefore rejected as tailings. Oxide minerals are traditionally processed by leaching. Leaching of tailings is accompanied by challenges in obtaining optimum metal extraction. Tailings have complex mineralogical compositions, and the presence of highly reactive gangue minerals (magnesium, iron, feldspar, and cupriferous mica) is associated with lower leaching efficiencies, high acid consumption, and high impurity carryover to solvent extraction and electrowinning. The removal of these gangue minerals can be accompanied by major benefits such as lower acid consumption, higher leaching efficiencies, and minimized impurity carry-over to the purification stages.

In this study, the copper tailings were upgraded using the Knelson concentrator (KC-MD3) prior to the leaching process, in an attempt to remove the gangue minerals such as iron, magnesium, and aluminium. Atmospheric leaching was conducted to determine the effect of the upgrading process on impurity co-extraction and copper recovery.

The Knelson centrifugal gravity concentrator is a gravity separation unit employed in the gold industry to recover both coarse and fine gold from primary and placer deposits, tailings, and pre-concentrates (Knelson and Jones, 1994). The Knelson concentrator was chosen for upgrading the copper tailings because of its unique benefits such as its ability to separate fine size fractions, low maintenance cost, and no reagent requirements (environmentally friendly). It can also be easily fitted to existing plant circuits without major plant modification. The concentrator utilizes a combination of fluidization water, centrifugal force, and shear-induced dispersive forces formed as a result of the upward movement of the slurry, which induces an interstitial trickling effect in the concentrating bed which simulates a percolation effect of fluidization water, centrifugal force, and shear-induced dispersive forces formed as a result of the upward movement of the slurry, which induces an interstitial trickling effect in the concentrating bed which simulates a percolation effect.

**Addition of reducing agents during laterite ore leaching**

The processing of some nickel laterite ore has been noted to improve upon addition of small amounts of sodium to the process water. In a study for processing nickel-rich nontronite ores using saline process water containing 5 g/l sodium (Na), acid consumption was seen to decrease compared to processing with fresh water (Johnson et al., 2005). It was also concluded that leaching with saline water seawater was ore- specific, because with blended ores the formation of alunite/jarosite occurred and acid consumption was high in saline leach solutions compared to fresh water (Whittington et al., 2003).

Reducing agents such as sodium chloride (NaCl) and sodium fluoride (NaF) are added to leaching processes to decompose refractory minerals containing nickel, thus promoting the dissolution of nickel (Hirasawa and Horita, 1987). It has also been noted that nickel laterite leaching can be improved by leaching in saline water rather than fresh water (Johnson et al., 2002; Whittington et al., 2003). Whittington and Johnson (2005) have indicated that in the absence of sodium in process water, great amounts of nickel adsorb onto amorphous silica in the leach residue. Thus sodium ions could lower the risk of nickel loss during leaching of laterites.
Material characterization

Copper tailings samples from Nchanga in the Zambian Copperbelt region and low-grade nickel ore from Waterval Boven in the Mpumalanga Province of South Africa were used in the test work. The samples were supplied by Konkola Copper Mine and Bohlaba Mines Ltd, respectively. Experiments for copper leaching were conducted on raw (as-received) tailings, with a second set of experiments conducted on tailings upgraded with the Knelson concentrator. For nickel, the experiments were conducted on the raw material only.

Copper tailings

The raw and upgraded copper tailings were analysed by X-ray diffraction (XRD) and the results are shown in Tables I and II. Mineralogical analysis showed that the copper tailings contained malachite, which is a copper-bearing carbonate hydroxide (Table I). Dominant phases in the tailings were found to be quartz and other gangue minerals: diopside, microcline, lizardite, muscovite, and the iron-bearing mineral haematite. Raw tailings contained up to 10.3% lizardite, and diopside phases which were successfully eliminated during the upgrading process (Table II). Copper is associated with malachite, and during the upgrading process the malachite content increased from 1.71% to 3.53% (Tables I and II).

Table I. Mineral composition of the raw copper tailings as analysed by XRD with relative phase amounts in absolute weight per cent

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight %</th>
<th>Classification</th>
<th>Mineral group</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diopside</td>
<td>7.05</td>
<td>silicate</td>
<td>Monoclinic pyroxene</td>
<td>MgCaSi₂O₆</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.33</td>
<td>Iron oxide</td>
<td>Oxide</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Lizardite</td>
<td>3.26</td>
<td>Phyllo silicate</td>
<td>Serpentine</td>
<td>Mg₃(Si₂O₅)(OH)₄</td>
</tr>
<tr>
<td>Malachite</td>
<td>1.71</td>
<td>Carbonate</td>
<td>Hydroxide</td>
<td>Cu₃CO₃(OH)₂</td>
</tr>
<tr>
<td>Microcline</td>
<td>16.55</td>
<td>Phyllo silicate</td>
<td>Feldspar</td>
<td>KAl₂Si₅O₈</td>
</tr>
<tr>
<td>Muscovite</td>
<td>12.83</td>
<td>Phyllo silicate</td>
<td>Mica</td>
<td>Al₂(AlSi₃O₁₀)(F,OH)₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>53.27</td>
<td>Framework silicate</td>
<td>Silica</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

Table II. Mineral composition of the upgraded copper tailings as analysed by XRD with relative phase amounts in absolute weight per cent

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight %</th>
<th>Classification</th>
<th>Mineral group</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goetite</td>
<td>1.87</td>
<td>Iron oxide</td>
<td>Oxide</td>
<td>FeO(OH)</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.14</td>
<td>Iron oxide</td>
<td>Oxide</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>8.4</td>
<td>Phyllo silicate</td>
<td>Serpentine</td>
<td>Al₂Si₅O₇(OH)₄</td>
</tr>
<tr>
<td>Malachite</td>
<td>3.53</td>
<td>Carbonate</td>
<td>Hydroxide</td>
<td>Cu₃CO₃(OH)₂</td>
</tr>
<tr>
<td>Microcline</td>
<td>18.15</td>
<td>Phyllo silicate</td>
<td>Feldspar</td>
<td>KAl₂Si₅O₈</td>
</tr>
<tr>
<td>Muscovite</td>
<td>23.99</td>
<td>Phyllo silicate</td>
<td>Mica</td>
<td>Al₂(AlSi₃O₁₀)(F,OH)₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>43.93</td>
<td>Framework silicate</td>
<td>Silica</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

Low-grade nickel ore

Mineralogical analysis showed that the low-grade nickel ore contained lizardite 1T, which is a serpentine nickel-bearing mineral at a grade of 0.1% Ni (Table II). The dominant mineral in the ore was found to be iron-bearing enstatite and other gangue minerals: biotite, diopside, forsterite, anorthite, and quartz.
Table III. Mineral composition of the lateritic ore as analysed by XRD with relative phase amounts in absolute weight per cent

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight%</th>
<th>Classification</th>
<th>Mineral group</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotite</td>
<td>5.94</td>
<td>Layer silicate</td>
<td>Mica</td>
<td>K(FeMg₂(AlSiO₃O₁₀)(OH)₂</td>
</tr>
<tr>
<td>Diopside</td>
<td>14.02</td>
<td>Chain silicate</td>
<td>Pyroxene</td>
<td>CaMgSi₂O₆</td>
</tr>
<tr>
<td>Enstatite</td>
<td>46.45</td>
<td>Chain silicate</td>
<td>Pyroxene</td>
<td>(Mg,Fe) Si₂O₆</td>
</tr>
<tr>
<td>Forsterite</td>
<td>9.28</td>
<td>Island silicate</td>
<td>Olivine</td>
<td>(Mg,SiO₃)</td>
</tr>
<tr>
<td>Lizardite 1T</td>
<td>4.33</td>
<td>Layer silicate</td>
<td>Serpentine</td>
<td>Mg₃(Si₂O₅)(OH)₄</td>
</tr>
<tr>
<td>Plagioclase Anorthite</td>
<td>19.47</td>
<td>Framework silicate</td>
<td>Plagioclase</td>
<td>CaNaAlSiO</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.51</td>
<td>Framework silicate</td>
<td>Silica</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

Experimental aspects

Separate batch atmospheric pressure leaching tests were performed at bench scale using sulphuric acid as the lixiviant. The tests were conducted in a 600 m³ glass beaker that was placed on a magnetic stirrer/hot plate with a stirring rod to maintain homogeneity of the solid/liquid mixture and to prevent agglomeration and settling of the solids. A watch glass was placed on the beaker to prevent loss of the leach solution. Leach solution samples were drawn at predetermined intervals, filtered, and the filtrates analysed for element concentration using inductively coupled plasma–optical emission spectroscopy (ICP-OES) and atomic absorption spectrometry (AAS).

Results and discussion

Leaching of copper tailings

The tailings were upgraded using the Knelson concentrator at 120 G rotational bowl speed and 4.5 ℓ/min fluidization water. Both the upgraded and the raw tailings samples were leached. The leaching tests were conducted at 25°C with a leaching period of 240 min. Solution pH, percentage solids, and stirring speed were kept constant at pH=2, 25%, and 500 r/min respectively.

![Figure 1. Extraction of Cu, Fe, Al, and Mg from untreated tailings](image-url)
Figures 1 and 2 show copper extraction during leaching at pH 2 from raw and upgraded tailings. Co-extraction of iron, magnesium, and aluminium were observed. Maximum copper extraction values obtained were 51% and 59% from the raw and upgraded tailings respectively. Iron co-extraction decreased from 18% from raw tailings to 4% from the upgraded tailings. Iron forms part of the silicate limonite deposit, therefore without upgrading the iron in the feed material will leach out along with copper. Ferrous ions in the leach solution lower the Eh (Dreier, 1999; Jansen and Taylor, 2004), terminating copper dissolution and instigating precipitation of chalcocite (Jackson, 1986). The presence of ferrous ions also causes problems in the solvent extraction and electrowinning stages in copper processing (Cupertino et al., 1999; Sole and Feather, 2003). Magnesium and aluminium are indicative of the presence of hornblende, pyroxene, and Ca-plagioclase, which are highly reactive gangue minerals that lead to high acid consumption (Dreier, 1999). The magnesium content was reduced during the upgrading process, hence the reduction in magnesium extraction from 34% to 0.9% as shown in Figures 1 and 2.

**Leaching of low-grade nickel ore with reducing agents**

The effect of reducing agents was studied by adding sodium chloride (NaCl) and sodium fluoride (NaF) at concentrations between 1.0–5.0% dry ore. NaCl and NaF were added to 4.0M sulphuric acid solution prior to adding the ore sample. The tests were conducted at 25°C and with a leaching period of 240 min. Sulphuric acid concentration, particle size, percentage solids, and stirring speed were kept constant at 4.0M, 45 µm, 10%, and 700 r/min respectively. Leach solution samples were drawn at predetermined intervals, filtered, and the filtrates analysed for elemental concentration using atomic absorption spectrometry (AAS).
Addition of NaCl as a reducing agent improved nickel extraction (Figure 3). A maximum extraction of 87.28% Ni was achieved when leaching with 3.5% NaCl, but this decreased to 76.19% Ni at 5% NaCl. With addition of NaF, nickel extraction decreased with increasing concentration (Figure 4), and only 30% Ni could be extracted.
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Figure 5. Extraction of Ni, Co, Mg, and Fe from the -45 µm fraction at 3.5% NaCl concentration

Figure 6. Extraction of Ni, Co, Mg, and Fe from the -45 µm fraction at 3.5% NaF concentration

It has been noted that the amount of nickel dissolved during leaching is associated with the amount of iron dissolved, leading to contaminated leach solutions and high acid consumption (Büyükakinci, 2008). At 3.5% NaCl, extraction of nickel and cobalt was much higher than that of iron and magnesium (Figure 5). Maximum iron dissolution was 4.31%, and magnesium 6.05%. However, with the addition of NaF magnesium extraction values increased to about 9% after 240 min and iron extraction remained as low as 2% (Figure 6).

**Kinetics and rate constants**

The leaching rates of nickel, copper, cobalt, magnesium, and iron were analysed with the shrinking core model equations. Rate constants ($k$) were used to describe leaching kinetics of the low-grade nickel laterite and the copper tailings.
In order to have better control of the leaching reactions, it is imperative to establish a quantitative measurement of leaching kinetics and the leaching mechanism. This was achieved by determining the rate controlling step of a leaching reaction using two shrinking core models as noted by Habashi (1979) and Sohn and Wadsworth (1979):

\[
1 - (1 - x)^{\frac{1}{3}} = k_1 t \\
1 - \frac{2}{3} x - (1 - x)^{\frac{2}{3}} = k_2 t
\]  

where \(x\) is the fraction of metal dissolved at time \(t\), and \(k_1\) and \(k_2\) are the overall rate constants. Equation [1] is applicable to chemically controlled reactions, while Equation [2] applies to reactions controlled by diffusion through a porous product layer.

- The assumptions considered when using the models are that (Safari et al., 2009):
  - The particles are spherical
  - The particle shrinks uniformly during the process
  - The thickness of the silica layer around the core remains constant
  - Temperature remains constant during the process.

Leaching data was fitted into the shrinking core model equations to determine the rate controlling step. Based on the suitable equation, rate constants for nickel, copper, cobalt, iron, and magnesium were determined.

The effect of upgrading on the leaching rates of copper and impurities is shown in Figures 7 and 8. The copper leaching rate increased 9% from the upgraded tailings, while magnesium and iron leaching rates decreased by 33% and 14% respectively (Figure 8) as compared to the raw tailings (Figure 7). Kinetic data for copper leaching also fitted Equation [2], and the reaction was therefore diffusion controlled.

The effect of NaCl on nickel leaching rates is illustrated in Figure 9. Nickel leaching rates increased with increasing concentration of NaCl, reaching a maximum at 3.5% NaCl and then decreasing with further addition. Kinetic data for nickel leaching with NaCl fitted Equation [2], which indicated that the leaching reaction at the various NaCl concentrations was diffusion controlled. A similar observation was made on the leaching mechanism of cobalt, iron, and magnesium, indicating that as the reaction progressed, the particle core remained unreacted while a diffusion layer formed around the particle (Figure 10).
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Figure 8. Linear fit of copper upgraded tailings leaching data

Figure 9. Linear fit of Ni leaching data at different NaCl concentrations
Conclusions

Leaching at atmospheric-pressure was successfully applied to copper tailings and a low-grade nickel ore, in conjunction with physical and chemical modification techniques to increase metal extraction and limit impurity co-extraction. A Knelson concentrator was successfully used to upgrade tailings and reduce gangue mineral phases (lizardite and diopside) in the tailings prior to leaching. Copper extraction was increased from 51% to 59% after upgrading. Magnesium and iron extraction decreased from 34% to 0.9% and 18% to 4% respectively. The addition of NaCl as a reducing agent improved nickel extraction from the low-grade ore by 55%. Kinetic data for copper and nickel extraction fitted the equation, $1 - \frac{2}{3}x - \frac{(1-x)^{\frac{2}{3}}}{1-x} = k_2t$, which describes a diffusion controlled leaching reaction.

References


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Name is a sincere, motivated and committed individual with a bachelor’s degree in chemical engineering from University of Lubumbashi (DR Congo), a master’s degree in chemical engineer and a doctorate in the same field from Tshwane University of Technology (RSA).

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- Separation technologies
- Mine water and waste treatment

His exceptional, expertise in these fields, strategic management, staff management and technical skills were tested and strengthened while working as process engineer for four years in a big mining company, Sodimiza in DR Congo; six years as business development manager at an international business engineering consultants, dealing also with the import and export of mineral processing equipment; eleven years as lecturer at postgraduate and undergraduate level, supervising PhD, M Tech, and B Tech student projects at Tshwane University of Technology, Pretoria, South Africa in the Department of Chemical and Metallurgical Engineering. He was chairman of one session of Nickel Processing ’12, Mineral Engineering International (MEI) (13 to 15 November 2012, Cape Town). He represented South Africa in a research collaboration between Tshwane University of Technology and the University of Boras (Sweden) on the project ‘Application of scientific computational tools in the design and development of selective adsorbents for water treatment and metal separation’. The project was funded by the National Research Foundation (NRF) and the Swedish Development Cooperation Agency (SIDA).
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Mercy completed her studies for MTech Engineering: Metallurgy from the Tshwane University of Technology (TUT) in 2013. She has worked as a diplomate metallurgist at Skorpion Zinc (Anglo Base Metals) in Namibia. She decided to follow her passion and study for an MTech degree focusing on physical separation and extraction of base metals. During the course of her studies at TUT she worked as a lecturer and laboratory coordinator assisting in metallurgical test work and projects for both researchers and undergraduate students.

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Kentse completed her studies for MTech: Engineering: Metallurgy from the Tshwane University of Technology (TUT) in 2013. She has worked at Exxaro Resources – R&D Facility in the physical beneficiation section. Her passion for research led her to pursue her studies for the MTech degree where she focused on Extractive Metallurgy – base metals hydrometallurgy. While studying at TUT, she also worked as a metallurgical laboratory coordinator overseeing daily laboratory activities and facilitating practical classes for undergraduate students.