Atmospheric oxidative and non-oxidative leaching of Ni-Cu matte by acidified ferric chloride solution

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Synopsis

The atmospheric leaching of copper-bearing matte by acidic ferric chloride solution was studied at the laboratory scale. The aim was to achieve maximum copper and nickel recovery by investigating the mechanisms of leaching, as well as identifying the effect of temperature, and concentration of ferric chloride and oxygen. Djurleite ($Cu1.96S$), hazelwoodite (Ni_3S_2), and Ni alloy were the primary phases detected in the matte. The quantitative composition of the matte was Cu 31%, Ni 50%, S 13%. Fe and Co constituted 2%, with platinum group metals (PGMs) accounting for 0.5%. A maximum nickel extraction of 98% was achieved using two-stage oxidative leaching at 90°C and 11 g/L Fe^{3+} as compared to 65% under non-oxidative conditions. A copper extraction of 99% was achieved in the first 45 minutes using two-stage non-oxidative leaching, and copper was recovered from solution by cementation. Three processes took place simultaneously throughout the leaching process, namely: dissolution, cementation/metathesis, and oxidation. The leaching process was found to be diffusion-controlled.

Keywords
Ni-Cu matte, acid leaching, cementation, ferric chloride, leaching mechanism.

Introduction

Hydrometallurgy has become one of the most economical processes for recovering metals from low-grade matte. Matte is a mixture of metal sulphides and precious metals produced from the smelting of sulphide ores. Acid leaching unselectively separates the base metals from the precious metals, producing a liquor rich in base metals and leaving a solid residue rich in precious metals. Solvent extraction (SX) and electrowinning (EW) can be used to recover marketable base metal products from the liquor. Gaseous reduction can also be employed to produce base metal powders (Agrawal *et al.*, 2006).

There are different types of leaching techniques and each type has requirements in terms of particle size, leaching time, agitation rate, etc. to ensure an efficient process and high percentage metal extraction. Agitation leaching in batch vessels operated under atmospheric or high pressure has been widely used commercially for processing Ni, Cu, and Co sulphide concentrates. Leaching of these

mattes has been conducted using ammonia or acid solutions following the developmental work of Sherritt Gordon in the period 1950–1969 (Forward and Mackiw, 1955; Pearce *et al.*, 1960). The choice between acid and ammonia leaching has been based on local conditions or the composition of the matte. Acid leaching has been used for mattes with substantial cobalt contents (above 3%), while ammonia leaching has been widely used for Ni-Cu mattes with low cobalt contents (Pearce *et al.*, 1960). However, with further developments in acid pressure leaching technology by Sherritt Gordon in the 1960s most Ni-Cu mattes have been treated using acid leaching. Impala Platinum commissioned the first commercial acid pressure leaching process for treating Ni-Cu mattes containing platinum group metals (PGMs) in horizontal autoclaves in 1969, and since then acid leaching has been widely used in the South African platinum industry (Plasket and Romanchuk, 1978).

Acid leaching can be conducted in a sulphate or chloride medium. The sulphate medium has been widely used, especially in South Africa, because the process equipment used is more adaptable to sulphate rather than chloride systems and there is no possibility of platinum dissolution as in chloride systems (Brugman and Kerfoot, 1986). However, chloride systems have the following advantages; most metal chlorides are more soluble than sulphate salts, leaching can be performed at moderate temperatures, and the oxidation process yields elemental sulphur, which is environmentally more acceptable than sulphate from sulphuric acid leaching (Park *et al.*, 2006). Given these advantages and the development of corrosion-resistant material,

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the leaching behaviour of typical South African PGM-containing Ni-Cu mattes in chloride media is worth investigating.

This study investigated the atmospheric leaching of PGM-containing Ni-Cu matte by acidic ferric chloride solution. The aim of this project was to achieve maximum Ni and Cu recovery from the Ni-Cu enriched matte by investigating the mechanisms of leaching, as well as identifying the effect of processing variables; namely, temperature and concentration of lixiviant under oxidative and non-oxidative conditions.

The sulphide chemistry is very complex due to the fact that sulphide concentrates usually consist of highly intergrown sulphide minerals. This is one of the reasons why there is a lack of understanding and knowledge of the mechanism of leaching. These processes are thus often not operated at optimum conditions (Rademan, 1999). Furthermore, the morphology and mineralogy of complex sulphide ores differs in nature, thus there is a need for a separate study for each type of matte. Leaching of Ni-Cu mattes is normally conducted in two stages, with the first stage aimed at removing most of the nickel and cobalt and precipitating the Cu by cementation. The second stage is normally aimed at removal of Cu and the remaining base metals to produce a platinum-rich residue (Lamya and Lorenzen, 2009). Although the entire leaching process can be achieved in a single stage, multiple stage leaching is highly selective, enabling the recovery of the base metals in subsequent processes (Hofirek and Kerfoot, 1992). In addition, higher metal extraction levels are achieved. Two-stage leaching studies were therefore conducted in this work.

Methodology

The parameters investigated were temperature and concentration of lixiviant. Single- and two-stage leaching processes under oxidative and non-oxidative conditions were conducted. The effect of temperature was investigated using single-stage non-oxidative leaching at temperatures of 50, 70, and 90°C ± 5°C for each experimental run, with a constant Fe^{3+} concentration of 5 g/L. Non-oxidative two-stage leaching was used to investigate the effect of ferric chloride concentration (lixiviant), with varying concentrations of 5, 8, and 11 g/L Fe^{3+} and a constant temperature of 90°C for each experimental run. The ferric chloride concentration and temperature were the same for both the first- and second-stage leaching. Based on the results of the temperature investigations, a temperature of 90 ± 5°C was chosen for further investigations.

Apparatus and reagents

The non-oxidative atmospheric leaching experiments were performed in a 5 L glass vessel fitted with four baffles, a variable-speed overhead stirrer with a flat blade turbine-type impeller, and a heating element with a temperature controller. The cover of the vessel had two ports for holding a pH/temperature probe and for taking samples. These ports allowed for minimal air ingression into the reactor during the experiment.

The matte was obtained from Impala Platinum Refinery, and ferric chloride was used as the leaching agent. Hydrochloric acid was used to control the pH below 3.

Characterization

The matte before and after leaching was characterized by X-ray diffractometry (XRD) with a Cu Kα radiation source (Xpert Phillips) to determine the mineralogical phases present in the matte, and X-ray fluorescence (XRF) (PW 2540 VRC Sample changer) to determine the elemental composition of the matte. Scanning electron microscopy (SEM) (JOEL JSM 5600) coupled with energy dispersive spectroscopy (EDS) was used to confirm the mineralogical phases in the matte and capture the particle morphology. A laser diffraction technique (Malvern Mastersizer 2000) coupled to a liquid dispersing unit (Hydro 2000G) was used to determine the particle size distribution (PSD) of the matte before and after leaching. Ni and Cu concentrations in the leach liquor were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES (Spectro Arcos Fsh12) and atomic absorption spectroscopy (AAS) (Thermo Scientific ICE 3000 instrument).

Experimental procedure

Leaching solution (4 L) was heated in the reactor with agitation until the required temperature was reached; 40 g of matte of particle size -105+75 μm was then added into the vessel. The stirrer was set to the required constant speed of 600 r/min and timing of the experiment started. HCl solution (1.5 M) was added stepwise to the mixture to keep the pH below 3. Temperature and pH at t=0 were recorded and thereafter monitored every 15 minutes. Liquor samples of 25 mL were taken after every 15 minutes for the 200-minute duration of leaching; which was considered a sufficient time to yield a high percentage extraction. The liquor samples were filtered and the filtrate was kept in sample bottles for chemical analysis. At the end of each experiment, the pulp was allowed to cool to room temperature and then filtered. The filter cake was washed with demineralized water and dried overnight. The residue samples were also kept for chemical analysis.

For non-oxidative two-stage leaching, the general procedure as outlined above was followed. However, after 200 minutes of first-stage leaching, the leaching solution was decanted from the reactor and then filtered. Thereafter 4 L of fresh leaching solution of the desired concentration was then added to the reactor and the filtered cake returned to the reactor to commence second-stage leaching. The concentrations of Fe^{3+} used in the non-oxidative two-stage leaching tests were 5, 8, and 11 g/L Fe^{3+}. The concentration was kept constant for both first- and second-stage leaching.

For the two-stage oxidative leaching the experimental procedure was similar to that of the non-oxidative two-stage leaching, with the exception of the introduction of oxygen, and a fixed Fe^{3+} concentration of 11 g/L Fe^{3+} and a constant temperature at 90 ± 5°C were used based on the findings of the previous experiments. In the first stage, fresh matte was contacted with fresh lixiviant for 200 minutes, and in the second stage, solid residue from the first stage was contacted with fresh solution and further leached for 200 minutes. Oxygen below 5 kPa was spurged into the solution throughout the 200-minute experimental run. The oxygen pressure was kept constant.

Results and discussion

Matte characterization before leaching reaction

The XRD pattern of the matte before leaching is shown in Figure 1. The major phases detected in the matte were djurleite ($Cu_{1.96}S$) and hazelwoodite (Ni_3S_2). Hazelwoodite had the highest peak intensity of 100% at 31.0532 angle position, and djurleite had the highest relative intensity of 25% at 32.5175 angle position.

The phases identified by SEM-EDX were Ni alloy, hazelwoodite, djurleite, and some PGMs (Figure 2).

The elemental composition of the matte before leaching as determined by XRF is shown in Table I. Copper constituted 31 mass % while nickel (i.e. Ni alloy and Ni_3S_2) was the major element in the matte, representing nearly half of the matte. Since the matte is a sulphide, sulphur also constituted a significant amount (13 mass %). The remaining 2% consisted of Fe and Co, while PGMs like Pt and Pd accounted for only 0.5%.

SEM of the matte showed that the particles were irregularly shaped with a smooth outer surface layer i.e. no cracks and veins on the particles (Figure 3).

The PSD of the matte generated by a laser diffraction technique is shown in (Figure 4). The modal size of the matte was 138 μm before leaching. The volume distribution
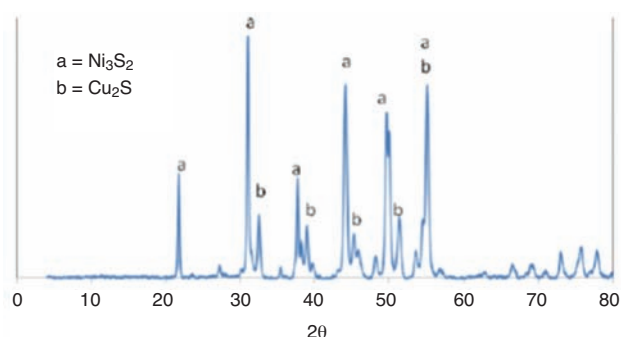
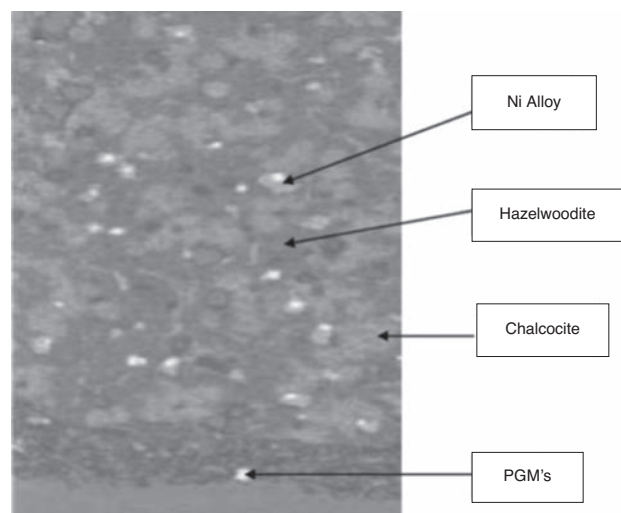(Figure 4a) was transformed into the number distribution (Figure 4b) and shows that the matte consisted of a larger number of smaller sized particles, which however; contributed a small volume percentage.

The $d(0.1)$ showed that 10% of the particles were smaller than 86.27 μm before leaching, whereas the $d(0.9)$ demonstrated that 90% of the particles were smaller than 209.58 μm.

Table I

Elemental composition of the matte before leaching, mass %

Co	Cu	Fe	Ni	Pb	Pd	Pt	S	Se	Si	Other
0.4	31	1.4	50	0.081	0.21	0.27	13	0.09	1.2	2.35

Figure 3—SEM images of the matte particle before leaching (magnification 100×)

Figure 1—XRD spectra of the matte before leaching

Figure 2—SEM-EDX micrographs of the matte before leaching
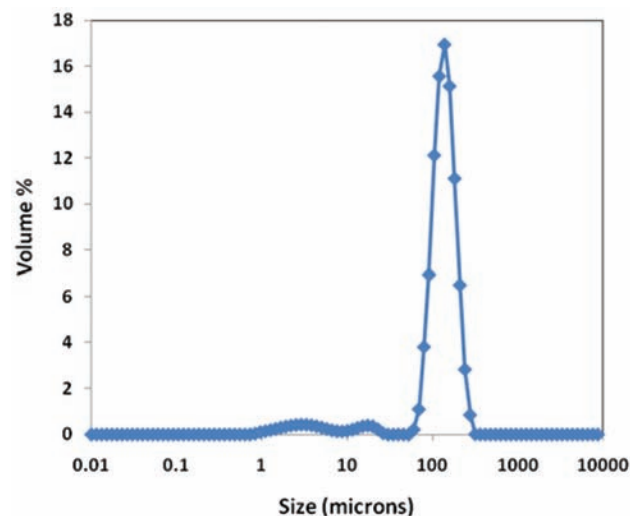
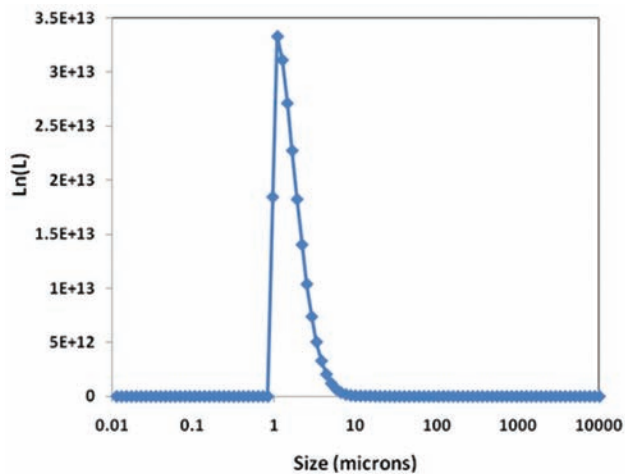Figure 4a—Particle size distribution (by volume) of the matte before leaching

Figure 4b—Particle size distribution (by number) of the matte before leaching

Effect of leaching variables

Temperature

Experiments were conducted at temperatures of 50, 70, and 90°C ± 5°C, at a constant concentration of 5 g/L Fe^{3+}. The recoveries of Ni and Cu as a function of leaching time are shown in Figure 5. Maximum percentage extractions of Ni for temperatures of 50, 70, and 90°C were 18, 27, and 55% respectively. The highest Ni recovery was obtained at 90°C.

A temperature of 90°C was therefore chosen as the optimum temperature in this study, since it is advantageous to leach at a temperature near the boiling point of ferric chloride of approximately 105°C (Dutrizac, 1992). Researchers such as Park *et al.* (2006), Rademan *et al.* (1999) and Dutrizac. (1992) have demonstrated that temperature has a direct influence on leaching. The higher the temperature, the higher the leaching rate, therefore the higher the metal recovery. The results obtained in this study are in agreement with this conclusion. The extraction of copper, however, decreased with increasing temperature (Figure 5b) due to cementation. At 50, 70, and 90°C the maximum percentage extractions of Cu were 14, 4, and 2% respectively. The cementation process was favoured by higher temperatures. Cu extraction was highest at 50°C because the Ni extraction rate was the lowest at this temperature, thus allowing a small amount of copper to be leached. Cu was rejected at this temperature from 14% to approximately 4% in the leach liquor by the end of 200 minutes.

The elemental composition of the matte before and after leaching at 90°C is shown in Table II.

The copper content was 31% before leaching and 42% after leaching. This increase was due to the increased surface exposure of copper sulphide in the residue as a result of leaching. The relative proportion of Ni in the matte decreased by 14% after leaching (Table II). This seemed very low at this stage, but was attributed to the fact that Ni alloy was the phase that leached the most. This finding was substantiated by the SEM-EDS analysis after leaching at 90°C. Figure 6 shows that hazelwoodite and copper sulphide are the remaining minerals in the matte after leaching, thus proving

that almost all the Ni alloy was extracted. This finding agrees with that of Rademan *et al.* (1999), who stated that Ni alloy was the most reactive phase, followed by Ni_3S_2, and lastly Cu_2S.

Micro-cracks on the particles can be seen in Figure 6. Micro-cracking enhances the leaching rate by increasing the surface area available for reaction; thus increasing the rate of diffusion of the lixiviant and products. The metathesis process was also believed to be taking place simultaneously with cementation according to Equation [1].
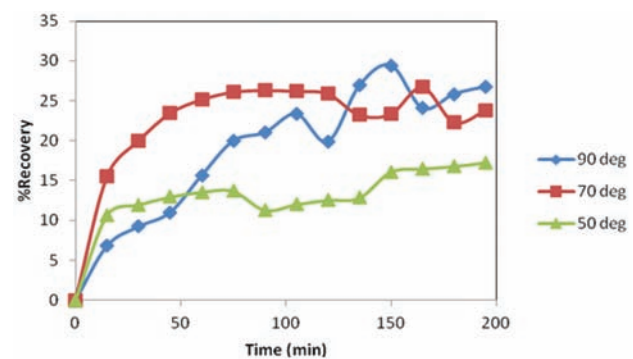
$$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+} \qquad [1]$$

Figure 5a—Percentage extraction of Ni after single-stage non-oxidative leaching with 5 g/L [Fe^{3+}]
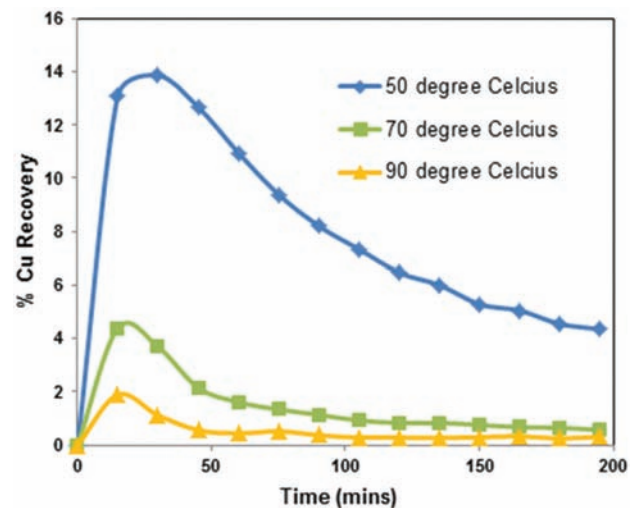

Figure 5b—Percentage extraction of Cu after single-stage non-oxidative leaching with 5 g/L [Fe^{3+}]

Table II

Quantitative elemental composition of the matte before and after single-stage non-oxidative leaching with 5 g/L [Fe^{3+}] at 90° C, mass%

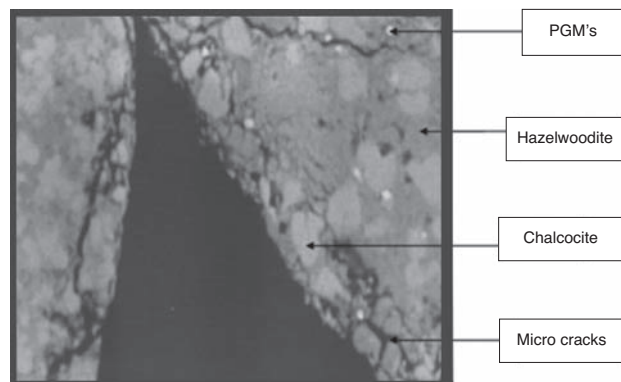|	Co	Cu	Fe	Ni	Pb	Pd	Pt	S	Other
Before	0.4	31	1.4	50	0.081	0.21	0.27	13	2.35
After	0.06	42	0.67	36.0	0.213	0.306	0.405	7.6	12.16

Figure 6—SEM-EDS image of the matte after single-stage non-oxidative leaching with 5 g/L [Fe³⁺] at 90°C

However, the XRD analysis (Figure 7) shows that no mineral transformation took place during the leaching process.

The inability of XRD to detect NiS can be attributed to three reasons: (1) the leaching reaction had not run to completion, (2) the NiS concentration was too low to be detected, or (3) NiS was oxidized by ferric ions according to Equation [2] thus liberating elemental sulphur.
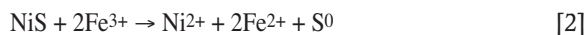
$$NiS + 2Fe^{3+} \rightarrow Ni^{2+} + 2Fe^{2+} + S^0 \qquad [2]$$

Table II also shows that other base metals, such as Co and Fe, are oxidized by Fe^{3+}, depleting the concentration of Fe^{3+}. These elements show a decrease in concentration after leaching (Table II). Little attention was paid to these metals in this study because they are present in small amounts compared to Ni and Cu, and their mineralogical phases were not detectable by either SEM or XRD. Based on the initial findings, it was proposed that to obtain maximum Ni and Cu extraction, it is advantageous to leach in two stages at 90°C. The first stage results in a higher extraction of Ni. Second-stage leaching was carried out using fresh leaching solution on the partially leached solid residue to extract the remaining Ni and Cu. It was also concluded that the ferric ion solution should be prepared at higher concentrations, so that the Ni and Cu dissolution rates and extractions are not compromised by other Fe^{3+}-depleting agents.

Concentration

The concentrations of Fe^{3+} investigated were 5, 8, and 11 g/L, at a constant temperature of 90°C. It was therefore advantageous to leach in two continuous stages because the percentage Ni extraction increased from 18% for single-stage leaching (Figure 5) to 26% (Figure 8) for two-stage leaching at 90°C using 5 g/L Fe^{3+}.

The Ni percentage extractions for 5, 8, and 11 g/L of Fe^{3+} were approximately 26, 29, and 62% respectively. Thus further tests to establish the leaching mechanisms and particulate processes were conducted for samples obtained when leaching with 11 g/L Fe^{3+}.

XRF analysis (Table III) showed a decrease in initial Ni content of the matte from 50% to approximately 17% after leaching.

Sulphur mass percentage also decreased, implying that sulphur was liberated into the solution. XRD identified the

mineralogical phases containing Ni after leaching with Fe^{3+} 11 g/L as NiS, Ni_3S_2, and Ni_3S_4 (Figure 9).

Ni_7S_6 was, however, detected only after leaching with 5 g/L Fe^{3+}. This can be explained by the fact that this Fe^{3+} concentration resulted in the slowest leaching rate, allowing the quasi-intermediate product Ni_7S_6 (a mineral species that is stable for only a short period during the reaction) to be detected. XRD also detected elemental sulphur; this is the sulphur produced from the possible oxidation of NiS (Equation [2]).

According to Rademan *et al.* (1999) base metals are gradually leached out of the sulphide lattice to form species with lower metal-to-sulphur ratios. It is proposed that the transformation proceeded as follows: Ni_3S_2 is rapidly altered to Ni_7S_6, then forms NiS, and finally Ni_3S_4. Sulphide minerals
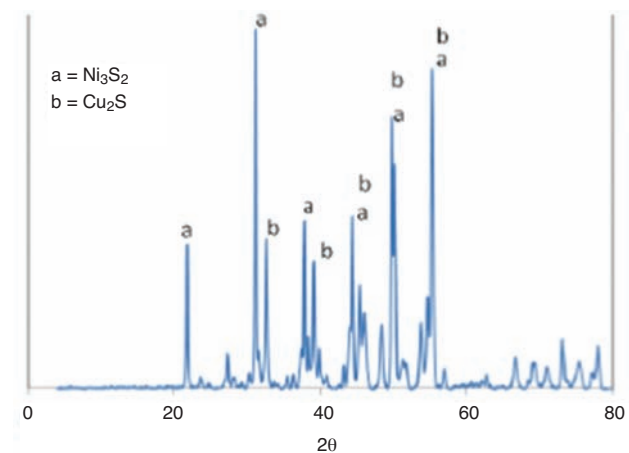

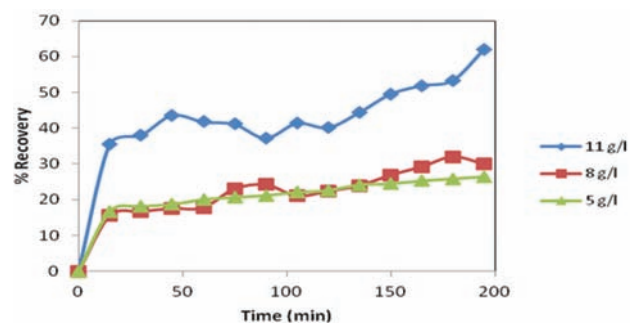Figure 7—XRD pattern after single-stage non-oxidative leaching with 5 g/L [Fe³⁺] at 90°C

Figure 8—Percentage extraction of Ni after two-stage non-oxidative leaching with varying [Fe³⁺] at 90°C
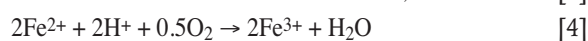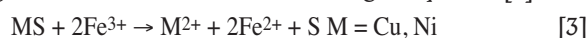
Table III

Quantitative elemental analysis after two-stage non-oxidative leaching with 11 g/L [Fe³⁺] at 90°C, mass%

	Co	Cu	Fe	Ni	Pb	Pd	Pt	S	Other
Before	0.4	31	1.4	50	0.081	0.21	0.27	13	2.35
After	0.074	46.63	7.54	17.38	0.104	0.184	0.231	5.84	22.01

can be solubilized in acid or basic medium but form elemental sulphur only under oxidizing conditions. The leaching of sulphides in acid medium in the presence of ferric chloride takes place readily with the liberation of elemental sulphur (Havlík, and Kammel, 1995). The tests performed in this study were non-oxidative; but elemental sulphur was liberated, as shown in Figure 9. This demonstrates that ferric ions performed two functions – one of oxidizing the sulphide lattice and the other of attacking (acid leaching) the ore. This finding agrees with that of Park *et al.* (2006). The only disadvantage with non-oxidative ferric chloride leaching (Equation [3]) is that the ferrous ions formed cannot be regenerated back to ferric ions according to Equation [4]:

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S \quad M = Cu, Ni \qquad [3]$$

$$2Fe^{2+} + 2H^+ + 0.5O_2 \rightarrow 2Fe^{3+} + H_2O \qquad [4]$$

The leaching of copper sulphides is slightly more complex than that of nickel sulphide, as seen in the single-stage temperature leaching studies. A similar pattern is observed in the two-stage leaching process, where higher extractions are obtained in the first few minutes of the experiment, followed by Cu cementation as early as 40 minutes into the reaction time (Figure 10). At the end of the two-stage leaching
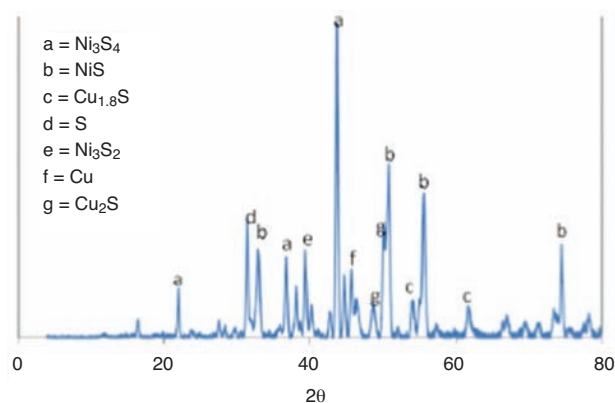

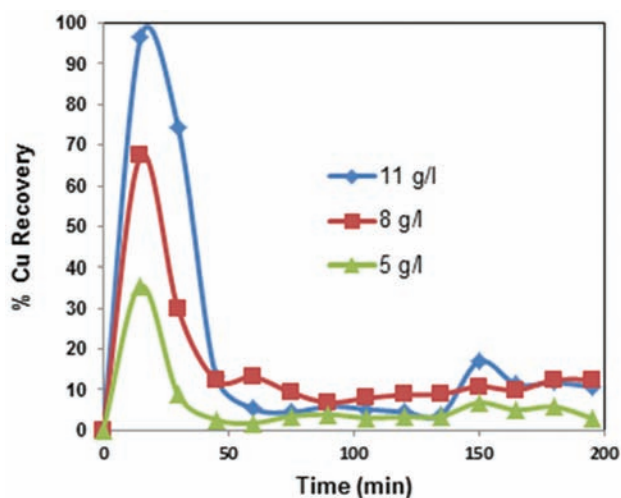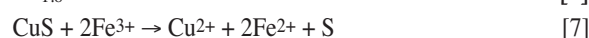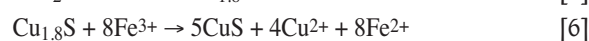Figure 9—XRD pattern after two-stage non-oxidative leaching with 11 g/L [Fe³⁺] at 90°C

Figure 10—Percentage extraction of Cu after two-stage non-oxidative leaching with varying [Fe³⁺] at 90°C

process using 5, 8, and 11 g/L of Fe³⁺, the Cu extractions were 3, 11, and 11% respectively. However, the highest extractions, of 35, 67, and 96% for Fe³⁺ concentrations of 5, 8, and 11 g/L respectively, were obtained in the first 15 minutes, before the cementation process began.

Table III shows an increase in the Cu content; this is because a Cu–rich cake was created as a result of cementation, while more Ni was dissolved into the solution. Rademan *et al.* (1999) stated that Cu_2S is leached to form digenite ($Cu_{1.8}S$), with ($Cu_{31}S_{16}$) forming as a quasi-intermediate product. The digenite leaches further to form covellite (CuS). Figure 9 shows that Cu_2S was transformed to $Cu_{1.8}S$, with $Cu_{31}S_{16}$ detected only with leaching at 5 g/L Fe³⁺. The leaching of copper proceeded as shown in Equations [5–7]:

$$5Cu_2S + 2Fe^{3+} \rightarrow Cu_{1.8}S + Cu^{2+} + 2Fe^{2+} \qquad [5]$$

$$Cu_{1.8}S + 8Fe^{3+} \rightarrow 5CuS + 4Cu^{2+} + 8Fe^{2+} \qquad [6]$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S \qquad [7]$$

However, CuS formed by Equation [6] was not detected by XRD (Figure 9), possibly as a result of copper rejection and the slow leaching rate. An oxidative two-stage leach was therefore conducted at the selected temperature of 90°C and 11 g/L Fe³⁺ concentration to increase the overall leaching rate and base metal extraction. During first-stage leaching i.e. the leaching of nickel alloy, micro-cracking of the particles occurred, exposing the Ni_3S_2 and Cu_2S on the edges of the cracks (barely visible) and on the outside of the particles (Figure 6), thus increasing the surface area available for leaching. In the second stage the size of the micro-cracks increased as the leaching process continued until the particles becomes lightly porous, depositing PGMs on their surface, and finally particle breakage occurred as shown in Figure 11.

Effect of oxygen

According to Qui *et al.* (2007) oxygen diffuses initially into the solution from the gas/liquid interface and then diffuses further into the solid/liquid interface. Oxygen participates in the reaction after it contacts the ore surface. The solubility of oxygen in water is affected by the temperature and partial pressure. Increasing the partial pressure of oxygen increases its solubility. However; Deng *et al.* (2001) stated that
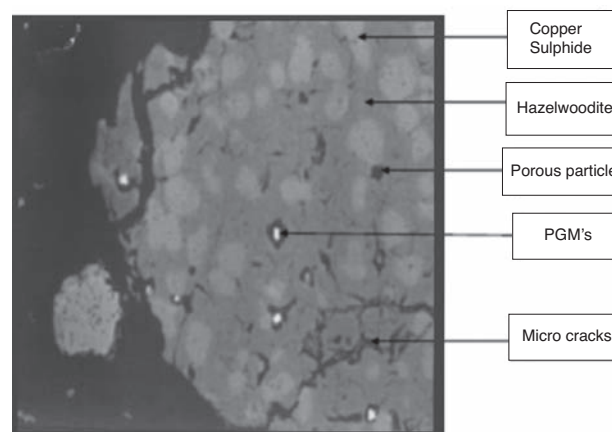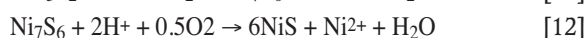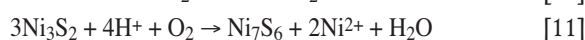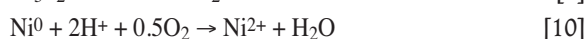

Figure 11—Electron micrograph of the matte after two-stage non-oxidative leaching with 11 g/L [Fe³⁺] at 90°C

leaching at a temperature above 85°C is not desirable, because oxygen solubility in the slurry decreases at higher temperatures, especially near the boiling point of the solution. Since the oxygen partial pressure for this study was low and the leaching temperature was high, oxygen solubility was enhanced by the high impeller speed of 600 r/min, leading to good dispersion and dissolution of oxygen in the leach slurry. Figure 12 illustrates how effective and important oxygen is to the leaching process.

Approximately 98% Ni was extracted under oxidative leaching. Ni alloy was extracted simultaneously with almost all of the Ni_3S_2. Under non-oxidative conditions, only a total of 62% Ni was extracted. Nickel was dissolved via metathesis (Equation [9]) and oxidation (Equations [10–12]).

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H+ \qquad [8]$$

$$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+} \qquad [9]$$

$$Ni^0 + 2H+ + 0.5O_2 \rightarrow Ni^{2+} + H_2O \qquad [10]$$

$$3Ni_3S_2 + 4H+ + O_2 \rightarrow Ni_7S_6 + 2Ni^{2+} + H_2O \qquad [11]$$

$$Ni_7S_6 + 2H+ + 0.5O2 \rightarrow 6NiS + Ni^{2+} + H_2O \qquad [12]$$

Equation [10] shows that oxygen is responsible for Ni alloy dissolution, and copper rejection is a result of Ni metathesis (Equation [9]). The intermediate product Ni_7S_6 formed (Equation [11]) quickly transformed into NiS (Equation [12]). This confirms the findings of Rademan *et al.* (1999). It can thus be concluded that oxygen increases liberation from the intricate sulphide bonds, thus enhancing the dissolution process. Cu extraction from a copper–nickel complex sulphide ore was more complex than Ni extraction. Figure 13 depicts the extraction of Cu.

The leaching chemistry changed and the solubilized Cu was re-deposited on the residue. It was evident that under non-oxidizing conditions Cu is extracted rapidly and suddenly undergoes cementation. The same process occurred under oxidizing conditions. The nickel remaining in the partially leached residue of the first stage was further dissolved by metathesis and oxidation in the second-stage leaching. It was concluded that no copper was leached from matte in the two stages. The majority of the copper originally present in the matte remains intact through the oxidative leaching, because copper is not as easily oxidized as nickel and as a result of copper cementation by nickel. To enhance the extraction of Cu, a third oxidative leaching stage is necessary, as Figure 5 shows that in the absence of cementation most of the Cu is extracted within the first 50 minutes of leaching. Chalcocite will be leached and transformed to covellite (CuS). It is predicted that copper sulphide would be attacked by ferric ions (Equations [13–16]), and oxygen in this instance would serve as an oxidant responsible for the regeneration of ferrous ions to ferric ions, according to Equation [13].

$$2Fe^{2+} + 2H+ +0.5O_2 \rightarrow 2Fe^{3+} + H_2O \qquad [13]$$

$$5Cu_2S + 2Fe^{3+} \rightarrow Cu_{1.8}S + Cu^{2+} + 2Fe^{2+} \qquad [14]$$

$$Cu_{1.8}S + 8Fe^{3+} \rightarrow 5CuS + 4Cu^{2+} + 8Fe^{2+} \qquad [15]$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S \qquad [16]$$

After the first-stage non-oxidative leaching, micro-cracking of the matte was observed (Figure 6), and after the two-stage non-oxidative leaching, extensive micro-cracking occurred with minor pores formed on the particles (Figure 11). Figure 14 shows extensive pores formed on the particle under two-stage oxidative leaching, exposing more PGMs. It is believed that in the third stage, the particles would proceed to complete breakage as a result of increased oxidation and dissolution.

The XRF results agreed with those from SEM, as they showed that after oxidative leaching the relative proportions of Pd and Pt in the matte was increased enabling them to be detected by XRF (Table IV).

Figure 13—Cu extraction at 90°C with 11 g/L [Fe^{3+}]

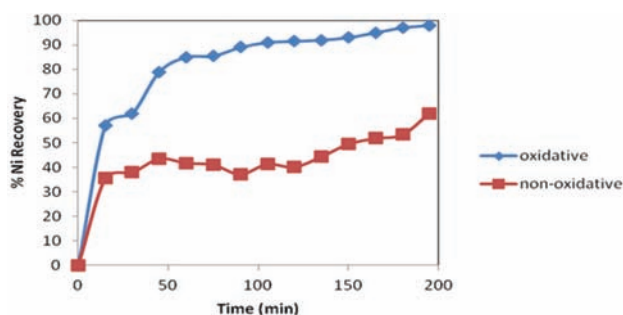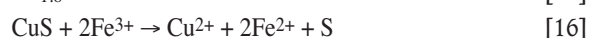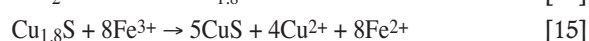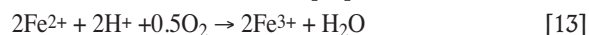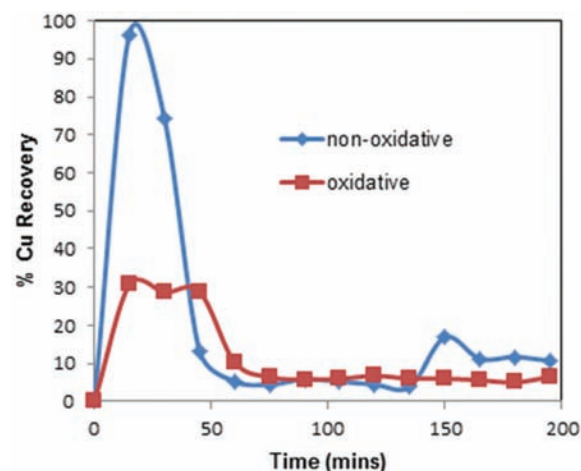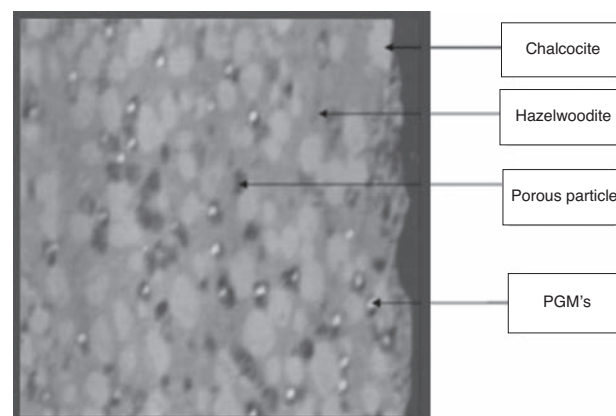Figure 14—Electron micrograph of the matte after two-stage oxidative leaching with 11 g/L [Fe^{3+}] at 90°C

Figure 12—Ni extraction after two-stage oxidative and non-oxidative leaching with 11 g/L [Fe^{3+}] at 90°C

Quantitative elemental analysis after two-stage, oxidative leaching with 11 g/L [Fe³⁺] at 90°C, mass%

	Co	Cu	Fe	Ni	Pb	Pd	Pt	S	Other
Before	0.4	31	1.4	50	0.081	0.21	0.27	13	2.35
After oxidation	0.068	48.0	1.90	26.0	0.090	0.350	0.560	6.90	16.13

Since XRF expresses the elemental compositions as fractions of the total mass of the sample, during leaching some constituents of the matte are removed, changing the relative proportion of the elements in the matte Copper mass% increased as a result of cementation, while Ni content decreased because of dissolution. Sulphur was also liberated into the solution; however, no evidence of sulphur passivation in the leaching process, as observed by Park *et al.* (2006), was found in this study. XRD did not detect any hazelwoodite (Ni_3S_2) or chalcocite (Cu_2S) in the leached residue (Figure 15). The Ni transformed as far as NiS and a part of the Ni was oxidized to NiO. XRD confirmed that copper underwent dissolution in the first 45 minutes, as the copper phase detected was $Cu_{1.8}S$.

Particulate processes

The PSD of the matte obtained by a laser diffraction technique is shown in Figure 16.

The peaks represent the modal size (the particle size with the highest volume percentage). The modal size of Ni-Cu matte before leaching was 138 μm. The modal size after leaching at 90°C using 5 g/L Fe^{3+} (single-stage LX) reduced to 107 μm. This suggests a decrease in particle size either as a result of dissolution or breakage of the particles in the larger size fraction. There was no significant shift in the volume distribution and modal size after two-stage non-oxidative leaching using 11 g/L Fe^{3+}; however, there was a decrease in the volume percentage of the mode. This indicates a decrease in the proportion of larger particles as the number of leaching stages was increased. The modal size after oxidative leaching was the same as that reported after non-oxidative leaching, but shifted slightly to the left and decreased in height, implying a greater number of particles decreased in size.

Kinetics

Various researchers such as Fan *et al.* (2010) and Jin *et al.* (2009) have found that the dissolution kinetics of Ni-Cu matte during the leaching process follow the shrinking core model (SCM). Only nickel dissolution kinetics were investigated in this study, because nickel was the only metal dissolved during the leaching process since copper was precipitated. The shrinking core model gave a satisfactory fit to the experimental data only at 90°C, and the most suitable model was the product layer/ash diffusion model (Equation [17]) which had a correlation coefficient of 0.8 (Figure 17a). The experimental data at 90°C was fitted to the three-dimensional diffusion model by Jander (Equation [18]) and yielded a correlation coefficient of 0.93 (Figure 17b):

$$[1-(1-X)^{1/3}]^2 = k_1t \qquad [17]$$

$$[1-3(1-X)^{2/3} + (1-X) + \alpha \, (1-(1-X)^{1/3})]^2 = k_2t \qquad [18]$$

where X is the fraction reacted, k_1 and k_2 are reaction rate constants, and α is a constant.

These results show that the leaching mechanism is diffusion controlled as result of the formation of a porous sulphur layer on the surface of the particles during leaching.
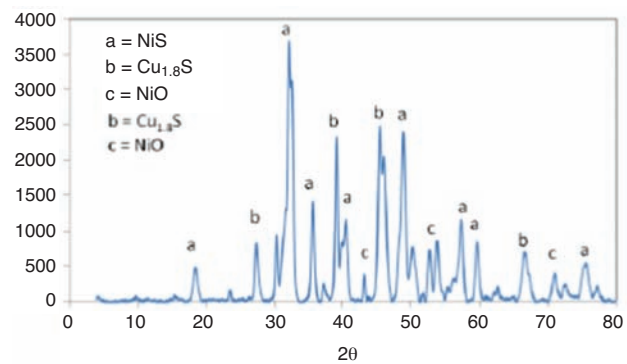

Figure 15—XRD pattern after two-stage oxidative leaching with 11 g/L [Fe³⁺] 90°C
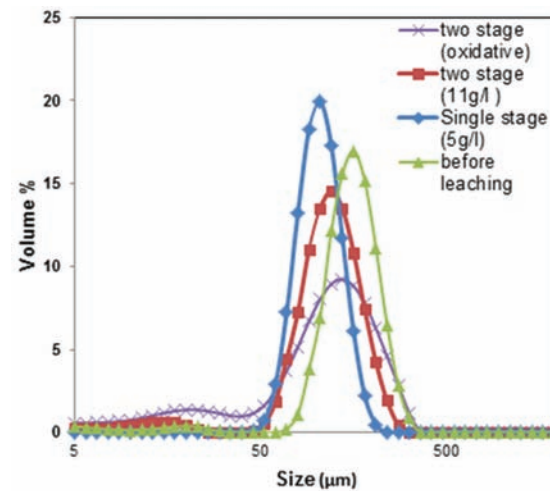

Figure 16—PSD (by volume) curves for the matte before and after leaching
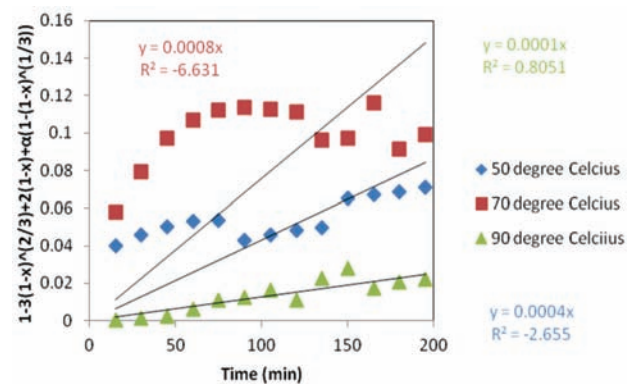

Figure 17a—Plot of the mixed (surface and product layer/ash diffusion) controlled process at various temperatures

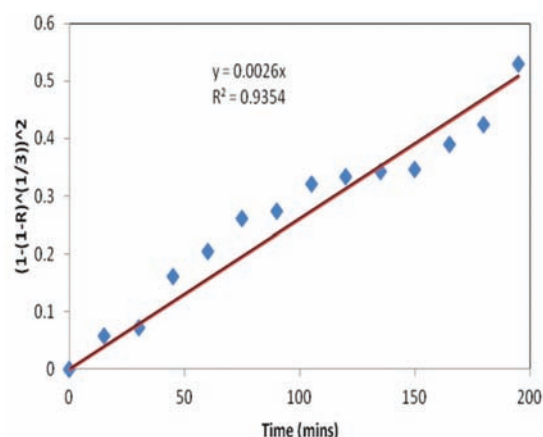# Atmospheric oxidative and non-oxidative leaching of Ni-Cu matte

Figure 17b—Plot of the data at 90°C on the three-dimensional diffusion model by Jander

For a better fit it is recommended that the PSD of the matte be included in the SCM. Due to non-fitting models at lower temperatures, the activation energy could not be determined.

Conclusion

Ni was selective leached from a Ni-Cu matte using a two-stage oxidative leaching process at 90°C and 11 g/L Fe^{3+}. The Ni extraction was 98%. Non-oxidative leaching was found to be less effective than oxidative leaching, as only 62% of the Ni was extracted under the same conditions. Cu was entirely rejected from solution by cementation, which would enable it to be selectively extracted in a third leaching stage. Oxygen was found to enhance the liberation of metals from the intricate sulphide bonds, thus enhancing the dissolution process. The major disadvantage of non-oxidative leaching is that ferrous ions can not be regenerated back to ferric ions, leading to lower metal extractions. The shrinking core model did not give an acceptable fit to the experimental data at temperatures below 90°C, with the three-dimensional diffusion model by Jander giving the best fit at 90°C. Leaching resulted in extensive micro-cracking and pore formation on the particle surfaces, resulting in particle breakage. Although a porous sulphur layer was formed on the surface of the particles during leaching, sulphur passivation was not found to occur.

Acknowledgements

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