Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries

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Synopsis

The leaching behaviour of nickel–copper matte in an acidic–copper sulphate solution during the repulping stage at Impala Platinum Refineries has been studied. The base metal recovery process consists of a matte repulping stage prior to a series of pressure leach stages. Therefore, the repulping stage is basically an atmospheric leach stage in which the matte containing mostly Ni and Cu is leached in copper-spent electrolyte from the tank house, resulting in dissolution of nickel and precipitation of almost all the copper. To understand the nature of the leaching process during this stage of the operation, the effects of temperature stirring rate and matte particle size on the rate and extent of base metal dissolution and copper rejection from the solution have been investigated. The leaching mechanism of the matte in the investigated system is also proposed.

Introduction

Nickel–copper mattes are conventionally produced by smelting nickel and copper sulphide concentrates. Iron and cobalt minerals are usually also present, and in some cases nickel mineralization is closely associated with platinum group metals (PGM), as is the case with nickel minerals in South Africa. Matte refers to the intermediate product that is produced from a furnace (converter furnace) during the smelting process of ores. It is the product that contains metal values, which is further processed to recover the contained metals. The Ni-Cu matte is further treated hydrometallurgically to produce marketable nickel, copper, cobalt and any available precious metals. The first step in the hydrometallurgical processing of the Ni-Cu matte is the leaching stage in which the metal values are first dissolved and later recovered as final products in the subsequent stages.

For many years numerous studies have been conducted on the leaching of Ni-Cu matte under atmospheric pressure (Llanos *et al.*, 1974; Symens *et al.*, 1979 and Filmer, 1981) as well as high pressure conditions (Dutrizac and Chen, 1987; Rademan *et al.*, 1999). Other workers (Hofirek and Kerfoot, 1992; Plasket and Romanchuk, 1978; Filmer, 1981; Hofirek

and Nofal , 1995; Steenekamp and Dunn, 1999; Fugleberg *et al.*, 1995) have studied the operations and improvements made to the existing Ni–Cu matte refining processes.

Conventionally, two process routes are employed for leaching Ni-Cu matte. The first one involves both atmospheric and pressure leaching in acidic copper–nickel sulphate solution, with oxygen being the oxidizing agent. In this process the matte is first leached under atmospheric conditions followed by a pressure leach step, and in both steps O_2/air is sparged into the leaching vessels. During atmospheric leaching substantial quantities of nickel and cobalt are dissolved while copper and iron are precipitated from the solution, and any PGM present remains in the solids. The precipitated copper and any unleached nickel and cobalt are dissolved in the subsequent pressure leach step or, in some cases, fed to a smelter. The other leaching process route employs a pre-leach step, which is essentially a matte repulping step, prior to a pressure leach step. The repulping process may be considered to be basically a non–oxidative atmospheric leach stage since leaching of the matte starts immediately it comes into contact with the $CuSO_4$–H_2SO_4 repulping solution. During the pre-leach stage nickel, iron and cobalt are partially dissolved, while the copper is precipitated. In both of these Ni-Cu matte process route alternatives, nickel and cobalt can be recovered from the solution as metal by electrowinning or hydrogen reduction, or they may be recovered as sulphate crystals. Copper can be recovered as metal by electrowinning from the sulphate solution or by electrorefining if the precipitated copper was produced by the smelting process.

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The pre-leach stage in the second process route alternative, described above, is the subject of this study. The study investigates the leaching behaviour of Ni–Cu matte in H_2SO_4-$CuSO_4$ solution during the repulping stage at Impala Platinum Refinery. Effects of variations in the process parameters, namely temperature, stirring speed and particle size have been studied.

Experimental

Materials

The material used in this study was a Ni-Cu matte from Impala Platinum Refinery. The chemical composition of the matte is shown in Table I. The principal phases present in the matte were heazlewoodite (Ni_3S_2), chalcocite (Cu_2S), djurleite ($Cu_{1.9}S$) and nickel alloy. The leaching solution was acidic copper sulphate solution (spent electrolyte) from the copper tank house of the same refinery; its chemical composition is also presented in Table I. The as-received matte was wet ground using a rubber lined ball mill and screened to obtain the desired particle size distribution, which is shown in Table II. Part of the matte was screened in three different size fractions which were used to investigate the effect of particle size on the leaching characteristics of the matte. The size fractions investigated are shown in Table III together with their chemical analyses.

Experimental procedure

The leaching tests were performed in a 3-litre stainless steel vessel provided with baffles, a cover, a thermometer, a pH electrode and fitted with a variable speed overhead stirrer. The stirrer had a blade type impeller and the rate of stirring was set by a tachometer. The set-up was then placed in a water bath with temperature control. Effects of three process variables on the rate and degree of Ni, Co and Fe dissolution

and copper cementation from the solution were investigated. These variables were temperature, rotational speed of the stirrer and particle size of the matte. Thus, temperature values ranged between 50–80°C and the stirring speed was varied from 145 to 400 rpm, while the particle size fractions investigated were below 300 μm (Table IV). The pulp density was kept constant at 1.7kg/l.

The typical experimental procedure was as follows: a predetermined quantity of the acidic copper sulphate solution was added to the leaching vessel and heated to the desired temperature. Then an appropriate quantity of the matte was added and the stirrer was set to the required speed. At predetermined time intervals, pH of the reaction mixture was monitored and samples taken using a pipette and immediately filtered. At the end of each experiment, the pulp was filtered and the solids washed with distilled water before drying in an oven at 100°C for at least 24 hours. The dried solid samples were kept for chemical analysis.

Chemical analysis and mineralogical studies

The solution samples were analysed for Ni, Cu, Co and Fe using inductively coupled plasma (ICP). Solid samples were analysed either by XRF or by dissolving them in a suitable solution and analysed for the same elements using the ICP, while total sulphur was determined using a Leco sulphur analyser. Characterization of the solid samples was done by means of a TOPCON ABT60 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyser; and also by X-ray diffraction analysis using a Philips X-ray Diffractometer

Results and discussion

Leaching mechanism of matte based on mineralogical investigations

Leaching kinetics of base metals from the Ni-Cu matte are dependent on the phases in which the metals are present. Therefore changes in the mineral phase characteristics have

Table I

Chemical composition of the matte and the leaching solution

Element/chemical	Matte (wt%)	Spent electrolyte conc.(g/l)
Nickel	47.9	24.6
Copper	31.0	25.0
Iron	0.60	0.7
Cobalt	0.34	0.2
Sulphur	20.1	–
H_2SO	–	90

Table II

Particle size distribution of the matte

Particle Size (μm)	Particle size distribution (%)
+300	9.8
- 300 + 212	12.6
- 212 + 150	9.9
- 150 + 75	12.3
75 + 45	5.0
- 45	50.4

Table III

Chemical analysis of size fractions used to investigate the effects of particle size on leaching characteristics of the matte

Size Fraction (μm)	Component (wt %)			
	Ni	Co	Cu	Fe
-300+150	49.1	0.3	30.4	0.7
-106+45	47.9	0.3	31.6	0.6
-45	48.8	0.4	30.5	0.6

Table IV

Experimental leaching conditions

Variable	Values investigated
Temperature (°C)	50, 60, 70, 80
Stirring rate (rpm)	145, 205, 400
Particle Size (μm)	-300+150, -106+45, -45

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an influence on the leaching mechanism of the matte. In this study only changes in the minerals of nickel and copper were considered. This was because these minerals were the major components of the matte, estimated at 50% Ni_3S_2, 34% Cu_2S and 15% Ni alloy. Cobalt and iron minerals constituted less than 1% of the matte.

Results of mineralogical investigations indicated the presence of heazlewoodite (Ni_3S_2), djurleite ($Cu_{1.96}S$) and chalcocite (Cu_2S). Cobalt and iron phases could not be detected by XRD analysis due to the small amounts of these elements in the matte (0.34% Co and 0.6 % Fe). However, other studies (Spandiel, 1999) have indicated that cobalt in the Impala converter matte is present as Co_3S_2 and iron as Fe in the nickel alloy phase, FeS in the Ni_3S_2 matrix and as FeAsS. Berezowsky (2003) suggested that some cobalt may exist in the metallic form. SEM-EDS analysis showed the presence of Ni-Fe alloy and Ni-Cu alloy but was not able to detect any cobalt phase. Figure 1 shows SEM images of matte particles before leaching. A particle of nickel alloy in the Ni-Cu sulphide matrix can clearly be seen. It was observed that the nickel and copper mineral phases were intergrown, with copper minerals always present in nickel minerals and vice versa. Figure 2 shows images of a matte particle taken after 5 hours of leaching. It can be seen that the nickel alloy was leached out of the matte particle, leaving holes in the particle. This is evident from Figure 3, which shows holes created by the dissolution of the Ni-Cu alloy (spots 2, 3 and 4) and Ni-Fe alloy (spot 1). Figure 3 revealed also that the metal alloys

were not completely dissolved after 5 hours of leaching. The presence of Ni-Cu and Ni-Fe-Cu alloys in converter matte has been reported by other researchers, including Rademan *et al.* (1999), Llanos *et al.* (1974), and Hofirek and Kerfoot (1992). Mackinnon *et al.* (1971) stated that the preparation of mattes involves a slow cooling process during which a Ni-Cu alloy is formed. Rademan *et al.* (1999) carried out an extensive study of the pressure leaching process at Impala base metals refinery and noted the same mineral phases in the converter matte as those observed in the present study. They reported that mineral structure of the nickel and copper sulphides can be visualized as layers of sulphides anions with nickel and copper cations filling some of the spaces in this layer, where the filling of the nickel and copper cations in the sulphides lattice will determine the crystal structure of the mineral and hence its properties. Nickel and copper are gradually leached out of the sulphides lattice to form minerals with lower nickel and copper to sulphur ratio. The metals in the alloy phase were leached out of the matte particles and no mineral matrix disintegration was observed.

Leaching mechanism based on process chemistry

Under the leaching conditions employed in this study, where no oxidant was added, the metals were not expected to be leached to any significant degree, especially from the sulphides minerals.

The leaching mechanism of the matte under the investigated conditions can be divided into two parts:
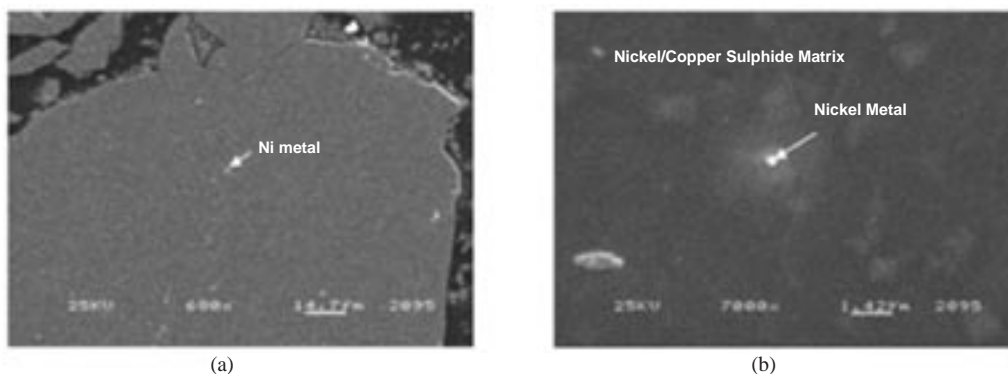

(a)   (b)

Figure 1—SEM images of matte particle before leaching: (a) Nickel metal in the Ni/Cu sulphide matrix at low magnification of 680x; (b) Nickel metal in the Ni/Cu sulphide matrix at high magnification of 7000x

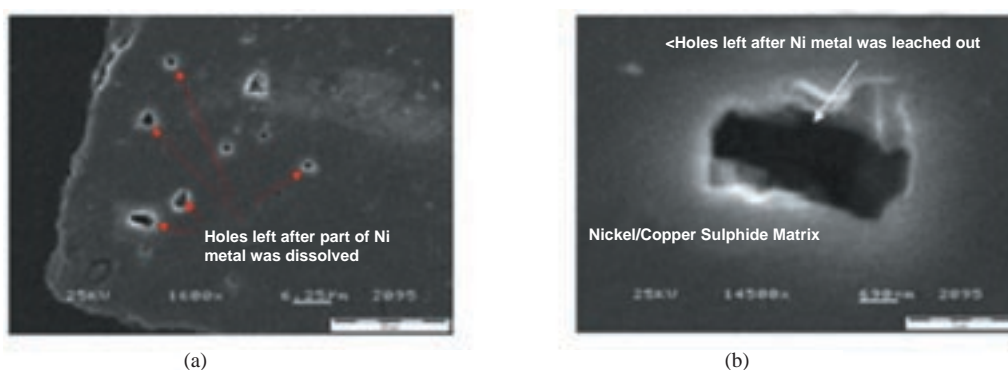(a)   (b)

Figure 2—SEM images of matte particle after 5 hours of leaching. It shows that holes are formed in the particle after metal alloy is leached out: (a) 1600x magnification; (b) 14500x magnification

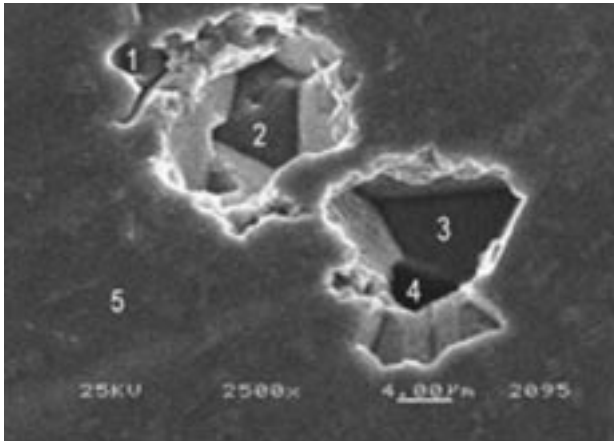# Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries

Figure 3—SEM image of matte particle after 5 hours of leaching. It shows that the Ni metal and Ni-Fe alloy are not completely dissolved: spot 1: Ni-Fe alloy; spots 2, 3 and 4: Ni-Cu alloy; spot 5: Ni/Cu sulphides
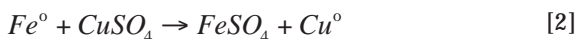
➤ Leaching of metals with simultaneous precipitation of aqueous copper via the cementation process.

➤ Leaching of metals by direct acid attack in the absence of the copper cementation process.

Leaching of metals with simultaneous precipitation of aqueous copper via the cementation process

The major mineral phases in the matte were Ni_3S_2, Cu_2S (Cu_2S plus $Cu_{1.96}S$) and Ni alloy. The nickel in the alloy was leached by the process of cementation according to reaction [1]:

$$Ni^\circ + CuSO_4 \rightarrow Cu^\circ + NiSO_4 \qquad [1]$$

This reaction is substantiated by the fact that metallic copper was clearly visible on the sides of the leaching vessel and in the leach solids. The Ni alloy continued to be leached throughout the five-hour leaching period and was not dissolved completely, as is evident from Figure 3. The dissolution of metallic iron from the Ni-Fe alloy was believed to proceed according to the well-known reaction of cementation of copper by metallic iron:

$$Fe^\circ + CuSO_4 \rightarrow FeSO_4 + Cu^\circ \qquad [2]$$

The ability of Ni-Cu matte to precipitate Cu^{2+} from solution with simultaneous leaching of Ni, is a well-known fact (Llanos *et al.*, 1974; Rademan *et al.*, 1999; Hofirek and Kerfoot, 1992; Plasket and Romanchuk, 1978). Therefore some of the aqueous copper may be precipitated by the heazlewoodite according to the following reactions:

$$Ni_3S_2 + CuSO_4 \rightarrow Cu^\circ + 2NiS + NiSO_4 \qquad [3]$$

$$Ni_3S_2 + CuSO_4 \rightarrow Cu_2S + NiS + 2NiSO_4 \qquad [4]$$

$$Ni_3S_2 + Ni + 4CuSO_4 \rightarrow 2Cu_2S + 4NiSO_4 \qquad [5]$$
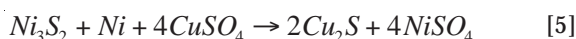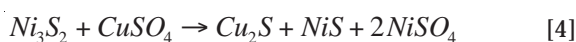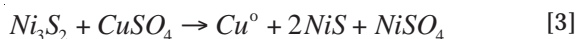
The formation of Cu_2S and NiS was supported by the presence of these phases in the leach solids examined by XRD. No copper precipitation by hydrolysis (Reaction [6]) was expected to occur, since under normal operating conditions copper hydrolysis takes place above pH 4 (Hofirek and Kerfoot, 1992; and Symens *et al.*, 1979). In all the experiments it was observed that copper was completely rejected by the cementation Reactions [1]–[5] before pH 4 was attained. This was why basic cupric sulphate $Cu_3(OH)_4SO_4$ (antlerite) was not detected in the leach solids.
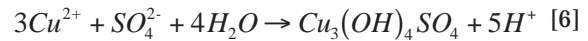
$$3Cu^{2+} + SO_4^{2-} + 4H_2O \rightarrow Cu_3(OH)_4SO_4 + 5H^+ \quad [6]$$

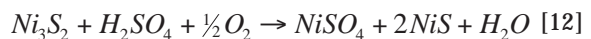*Leaching of metals by direct acid attack in the absence of the copper cementation process*

In the absence of an oxidant, such as air or oxygen, some of the nickel and iron from the alloy can be leached by the sulphuric acid according to Reactions [7] and [8]:

$$Ni\text{-}Fe + 2H_2SO_4 \rightarrow NiSO_4 + FeSO_4 + 2H_2 \qquad [7]$$

The other possible reactions are the leaching of NiS and FeS by the sulphuric acid (Reactions [8] and [9]). FeS is reported to be in the Ni_3S_2 matrix (Spandiel, 1999), while NiS is formed during the leaching process by Reactions [3] and [4].

$$NiS + H_2SO_4 \rightarrow NiSO_4 + H_2S \qquad [8]$$
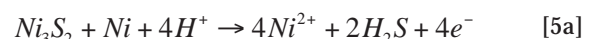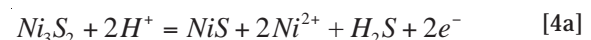
$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \qquad [9]$$
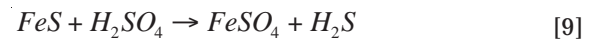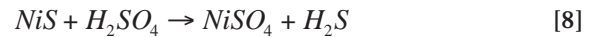
Although the leaching vessel was covered during the experiments, some air may have entered the leaching system. Thus in the presence of air some of the nickel, iron and a small potion of the heazlewoodite may have been leached by oxidative dissolution in the sulphuric acid according to the following reactions:

$$Ni^\circ + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow NiSO_4 + H_2O \qquad [10]$$

$$Fe^\circ + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow FeSO_4 + H_2O \qquad [11]$$

$$Ni_3S_2 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow NiSO_4 + 2NiS + H_2O \quad [12]$$

It was not possible to determine the form of cobalt in the matte, due to the small amount of this element present in the matte (0.34%). If it is assumed that some of it existed in metallic form, as reported by Berezowsk (2003), then it was leached according to Reaction [13]:

$$Co^\circ + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow CoSO_4 + H_2O \qquad [13]$$

Reactions [4] and [5] show that some of the copper precipitated as Cu_2S; this can be attributed to the presence of H_2S that is generated by Reactions [4a] and [5a]. Rademan *et al.* (1999) indicated that the formation of H_2S occurs through the oxidative (anodic half-cell) reaction of the cementation of copper with Ni_3S_2 and Ni alloy as shown below:

$$Ni_3S_2 + 2H^+ = NiS + 2Ni^{2+} + H_2S + 2e^- \qquad [4a]$$

$$2Cu^{2+} + H_2S + 2e^- = Cu_2S + 2H^+ \qquad [4b]$$

$$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+} \qquad [4c]$$

$$Ni_3S_2 + Ni + 4H^+ \rightarrow 4Ni^{2+} + 2H_2S + 4e^- \qquad [5a]$$

$$4Cu^{2+} + 2H_2S + 4e^- \rightarrow 2Cu_2S + 4H^+ \qquad [5b]$$

$$Ni_3S_2 + Ni + 4Cu^{2+} \rightarrow 4Ni^{2+} + 2Cu_2S \qquad [5c]$$

where Equations [4] and [5] represent the overall reactions.

The H_2S subsequently reduces the Cu^{2+} ion to Cu_2S. It was found that about 30 per cent of the aqueous copper precipitated as Cu_2S. The precipitation of some aqueous copper as Cu_2S explained the increase in the sulphur content of the leached matte (Figure 4). Sulphur increased from 20.1% in the original matte to about 22% in the leached matte.

However, no smell of H_2S was detected during the leaching experiments, probably due to the fact that Reactions [4b] and [5b] were faster than Reactions [4a] and [5a]. Hence, H_2S was probably consumed faster than it was produced.

One interesting observation was that the pH of the solution increased sharply immediately after Cu^{2+} ions were completely precipitated out of solution, as can be seen in Figures 5,6 and 7, which also show metal concentrations of the leach solution as a function of leaching time at temperatures of 60, 70 and 80°C respectively. The reason for this behaviour was attributed to the fact that prior to complete copper cementation part of the matte leaching process occurred via the cementation process (Reactions [1]–[5]), and by direct attack with H_2SO_4 (reactions [7]–[13]. After complete copper rejection, the leaching process was, mainly by direct reaction of the matte with H_2SO_4, which consumed most of the acid and hence raised the solution pH. The leaching of metals from sulphide minerals can also be attributed to the galvanic interaction that exists between the nickel alloys and the nickel /copper sulphides. This is possible because the Ni alloy and the mineral phases are highly intergrown. It is a well-known fact that when conducting or semi-conducting minerals in contact with each other are subjected to a leaching solution, galvanic interaction may occur, which can lead to dissolution of the mineral with lower open circuit potential (Reddy *et al.*, 1987; Holmes and Crundwell, 1995; Lorenzen and van Deventer, 1992).
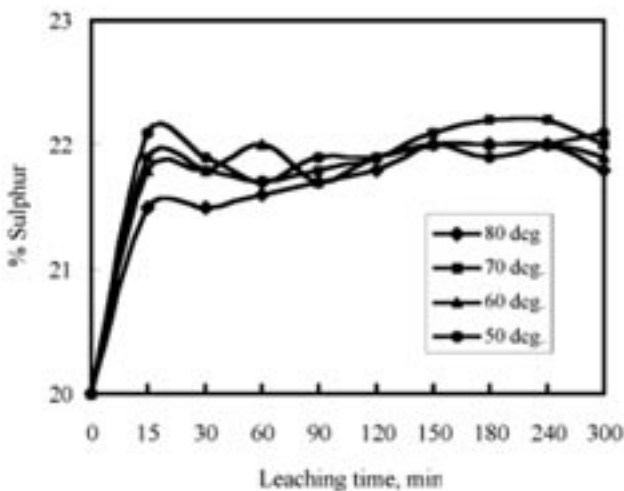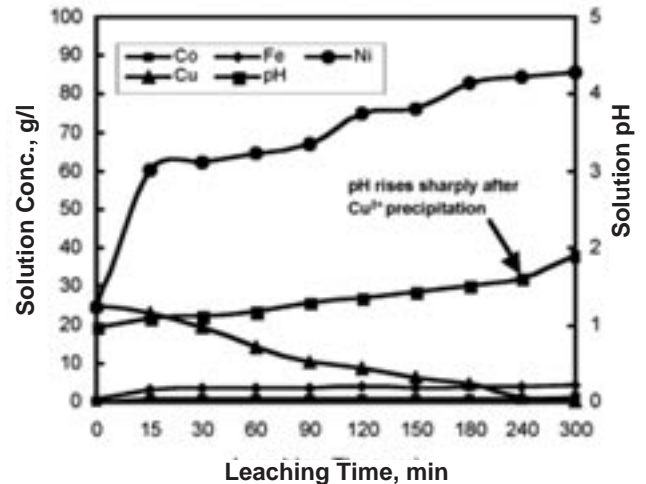

Figure 5—Variation of metal concentrations in leach solution as a function of leaching time at 60°C (stirring rate: 205 rpm; pulp density: 1.7 kg/l)
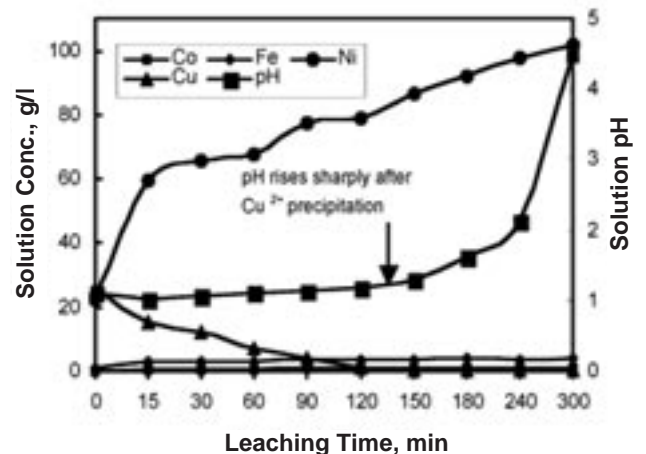

Figure 6—Variation of metal concentrations in leach solution as a function of leaching time at 70°C (stirring rate: 205 rpm; pulp density: 1.7 kg/l)
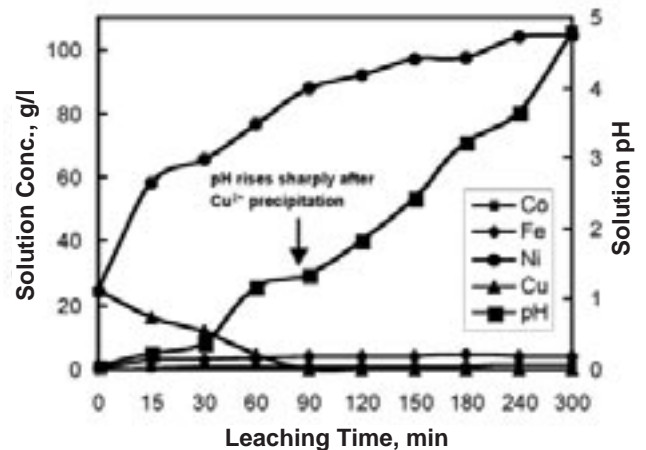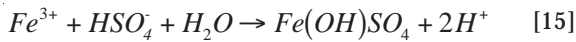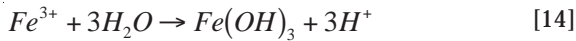

Figure 4—Sulphur content of leached matte as a function of leaching time (Stirring rate: 205 rpm; pulp density: 1.7 kg/l

Figure 7—Variation of metal concentrations in leach solution as a function of leaching time at 80°C (stirring rate: 205 rpm; pulp density: 1.7 kg/l)

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The rise in the pH resulted in the precipitation of iron at pH values above 3. It should be noted that the rise in pH to above 3 was only observed in the experiments where the Cu^{2+} ions were completely precipitated.

The iron hydrolyses to form ferric hydroxide or basic ferric sulphate (parabutlerile) as shown in Reactions [14] and [15].

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad [14]$$

$$Fe^{3+} + HSO_4^- + H_2O \rightarrow Fe(OH)SO_4 + 2H^+ \qquad [15]$$

Under the leaching conditions applied in this study, where the leaching vessel was covered and no air/oxygen was added, most of the iron was expected to be in the ferrous form. However, due to the fact that the leaching vessel was not air-tight some air from the atmosphere may have entered the system and oxidized some of the ferrous iron to ferric according to Reaction [16]:

$$2Fe^{2+} + 2H^+ + \tfrac{1}{2}O_2 \rightarrow 2Fe^{3+} + H_2O \qquad [16]$$
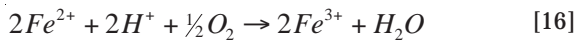
It is also known that copper is an effective catalyst for oxidation of ferrous iron (Symens *et al*, 1979; and Hofirek and Kerfoot. 1992). The rate of iron oxidation and hydrolysis increases significantly in the presence of copper ions. If cupric ions are rejected from the leach solution, as was the case in this study, iron hydrolysis and precipitation requires longer reaction time for complete precipitation. Yuhua and Xianxuan (1990) stated that the rate of iron oxidation increases because the Cu^{2+} ions can oxidize Fe^{2+} ions in solution as shown in Reaction [17]:

$$Fe^{2+} + Cu^{2+} \rightarrow Cu^+ + Fe^{3+} \qquad [17]$$
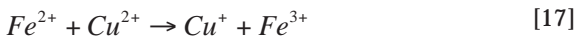
The Cu^+ is then re-oxidized to Cu^{2+} by air.

Some of the iron in the leaching solution (copper spent electrolyte) was expected to be in the ferric form, which, however, can easily be reduced to the ferrous state. Hofirek and Kerfoot (1992) indicated that the dissolved iron acts as an electron carrier and enhances the leaching rates according to the following reaction:

$$Ni_3S_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2NiS + Ni^{2+} \qquad [18]$$
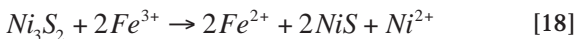
To determine how much of the iron was in the ferrous form, the leaching solution (copper spent electrolyte) and the leach solutions from some of the experiments were titrated with potassium permanganate. It was found that about 40% of the iron in the leaching solution was in the ferrous state. However, in the leach solutions about 70% of the iron was found to be in the ferrous state; this was probably the reason most of the iron was not hydrolyzed even in the cases where the solution pH was as high as 4.8. Only about 25% of the dissolved iron was found to precipitate.

To determine the nature of the iron precipitate, the precipitate was examined by XRD and SEM-EDX. The SEM-EDX analysis showed presence of Fe; however, the XRD did not show any iron compound probably because not enough was formed. It was therefore concluded that the iron may have precipitated as ferric hydroxide, as the SEM–EDX indicated the presence of Fe in the precipitate.

Effect of leaching temperature

Results of tests conducted to investigate the effect of leaching temperature on the leaching rate of the Ni-Cu matte are presented in Table V and graphically illustrated in Figures 8–10. The experiments were conducted for the temperature range 50–80°C at a pulp density of 1.7 kg/ℓ and stirring rate of 205 rpm. Table V shows overall extractions of nickel, cobalt and iron as well as final concentrations of these metals and copper in the leach solutions after 5 hours of leaching. Figures 8, 9 and 10 show the rate of extractions as a function of leaching time for nickel, cobalt and iron respectively. Table V shows that increasing the temperature from 50°C to 80°C generally increased the overall extraction of nickel and cobalt. However, iron extractions could not be determined with certainty due to its hydrolysis and subsequent precipitation above pH 3. Figure 8 shows that both the rate and overall nickel extraction increased with increasing temperature from 50°C to 80°C. The overall nickel extractions were 13.2%, 14.9%, 18.6.9% and 19.5% at 50°C, 60°C, 70°C and 80°C, respectively. Figure 9 shows that the rate of Co extraction also increased with increasing temperature in the investigated range of 50–80°C. The overall cobalt extractions also increased gradually with the final values being 26.5%, 28.7%, 30.4% and 35.3% at 50, 60, 70

Table V

Ni, Co, and Fe overall extractions and final metal concentrations of the solution during atmospheric leaching of the matte at different temperatures (stirring rate: 205 rpm, pulp density: 1.7 kg/ℓ)

Temperature (°C)	Overall extraction (%)			Final solution concentration (g/L)			
	Ni	Co	Fe *	Ni	Co	Fe	Cu
50	13.2	26.5	45.8	76.56	0.94	4.24	7.9
60	14.9	28.7	70.4	85.84	1.01	4.34	0.0
70	18.6	30.4	70.8	101.60	1.06	3.62	0.0
80	19.5	35.3	73.4	104.59	1.21	3.96	0.0

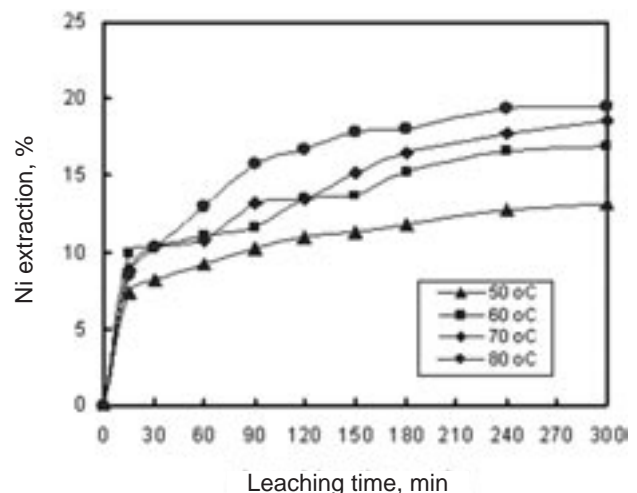*Maximum Fe extraction attained prior to precipitation is shown in this table

Figure 8—Nickel extraction as a function of leaching time at different temperatures (stirring rate: 205 rpm, pulp density: 1.7 kg/ℓ)

Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries
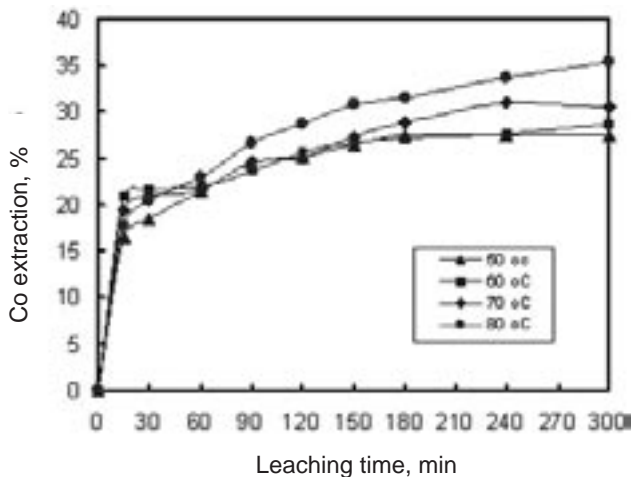

Figure 9—Cobalt extraction as a function of leaching time at different temperatures (stirring rate: 205 rpm, pulp density: 1.7 kg/l)
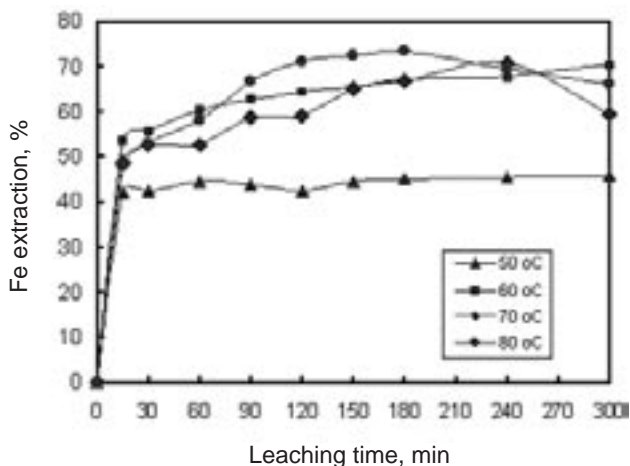

Figure 10—Iron extraction as a function of leaching time at different temperatures (stirring speed: 205 rpm, pulp density: 1.7 kg/l)

and 80°C, respectively. Temperature dependence of iron dissolution, as illustrated in Figure 10 and Table V, also indicated that the rate and degree of iron extraction was sensitive to changes in temperature. The overall extractions increased substantially from 45.8% to 73.4% when the temperature was increased from 50 to 80°C respectively. It was also noted that the aqueous iron began to precipitate from solution when the pH value rose above 3 (Figure 10).

The initial dissolution rates of all the three metals were relatively high during the first 15 minutes of leaching (Figures 8–10). The high rates of metal dissolution were probably due to the fast chemical reaction kinetics of the matte in the initial stages of leaching (0–15 min.) when fine particles were still present. About 45% of the 'leacheable nickel' was extracted within the first 15 minutes, while more than 50% of leacheable cobalt and iron were solubilized. The term leacheable nickel (or leacheable metal) in this case refers to the maximum nickel extraction obtainable under the leaching conditions employed in this study. The leacheable nickel is believed to leach from the Ni alloy through

Reactions [1], [7] and probably [10]. The remainder originated from Ni_3S_2 through Reactions [3], [4], [5] and probably [12]; as well as through galvanic interaction between the Ni alloy and copper/nickel minerals.

The results show different degrees of extraction for the three metals: iron extraction was the highest followed by that of cobalt; and nickel extraction was the lowest. This indicates that at least 50% of the iron in the matte occurs in an alloy form, probably as Ni-Fe alloy, which was leachable under the conditions employed in this study (Figure 3). Cobalt extraction was the second highest and it is believed that part of it exists as an alloy and the rest as sulphide. However, it was difficult to detect it with the SEM-EDX and XRD analyses because the matte had very low cobalt content (0.3%). It is possible that the metallic cobalt was responsible for the high cobalt dissolution observed in this study. As expected, the degree of nickel extraction was the lowest since most of the Ni in the Ni-Cu matte exists as Ni_3S_2 (~ 50 %) and about 15% occurs as an alloy, which is more likely to leach under the conditions employed where no oxygen was added.

Effect of temperature on the cementation rate of copper during the atmospheric leaching of the matte in the temperature range 50–80°C is illustrated in Figure 11, which shows copper concentration as a function of leaching time. It can be seen that the rate of copper cementation was very sensitive to changes in the leaching temperature, and increased with increasing temperature. At 80°C all the aqueous copper was precipitated, whereas at 50°C about 8 g/l Cu remained in the leach solution (Table V). The observed behaviour of copper suggested that if copper needs to be removed from the solution as fast as possible during the repulping stage (pre-leach stage), the temperature should be increased. It was noted that the faster the rate of copper cementation, the faster the rate of nickel dissolution (Figures 5–7). This was probably due to the fact that a substantial amount of the nickel was leached by the cementation process before the copper ions were completely depleted.
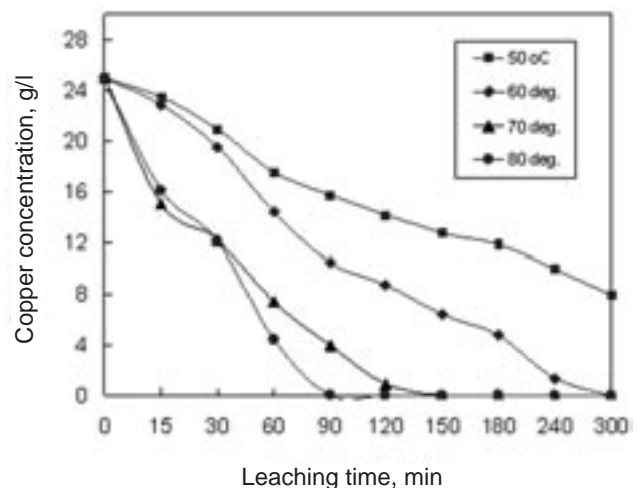

Figure 11—Copper concentration of leach solution during atmospheric leaching of the matte at different temperatures (stirring rate: 205 rpm, pulp density: 1.7 kg/l)

Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries

Effect of stirring rate

To investigate the effect of stirring rate on metal dissolution and precipitation, leaching experiments were conducted at three different stirring rates, namely 145, 205 and 400 rpm; while keeping the temperature at 60°C, pulp density at 1.7 kg/l and residence time of 5 hours. The results indicated that the rate of stirring affects the rate of dissolution of nickel, cobalt and iron. Overall metal extractions are presented in Table VI. Figures 12, 13 and 14 show the effect of stirring rates on the rate of nickel, cobalt and iron extractions as a function of leaching time, respectively. Figure 12 shows that nickel extraction rate did not increase significantly when the stirring rate increased from 145 to 205 rpm; however, increasing the stirring rate from 205 rpm to 400 rpm resulted in high increase in nickel extraction rate. The overall nickel extractions were 12.3%, 14.9% and 19.2% for 145, 205 and 400 rpm, respectively (Table VI). Figure 13 shows the effect of stirring rate on the rate of cobalt extraction. It can be seen

in this case also that cobalt extraction rate did not increase with increasing stirring rate from 145 to 205 rpm, but increased significantly when the stirring rate was increased from 205 rpm to 400 rpm. The overall cobalt extraction increased from 30.1% at 205 rpm to 36.6% at 400 rpm. The influence of stirring rate on iron dissolution rate was similar to that observed for cobalt, i.e. at the stirring rates of 145–205 rpm iron extraction rate was similar but increased drastically when the stirring rate was increased from 205 rpm to 400 rpm (Figure 14). The overall iron extractions could not be determined accurately due to its precipitation towards the end of the experiments. The fact that nickel, cobalt and iron dissolution rates were affected by stirring rates indicates that the leaching of these metals is probably influenced by transport processes, which is in agreement with the calculated activation energy of 31 kJ/mol (Lamya *et al.*, 2004).

The effect of stirring rate on copper cementation is illustrated in Figure 15, which shows aqueous copper concentration of the leach solution as a function of time. It can be seen that the rate of cementation of the aqueous copper was not significantly affected by variations in the stirring rates. At the stirring rates employed (145, 205 and
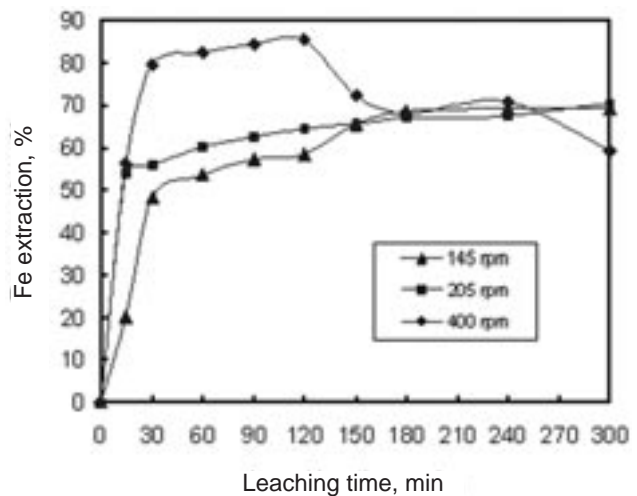

Figure 12—Nickel extraction as a function of leaching time at different stirring rate (temperature: 60°C, pulp density: 1.7 kg/l)

Figure 14—Iron extraction as a function of leaching time at different stirring rates (temperature: 60°C, pulp density: 1.7 kg/l)

Figure 13—Cobalt extraction as a function of leaching time at different stirring rate (temperature: 60°C, pulp density: 1.7 kg/l)

Table VI

Ni, Co, and Fe overall extractions and final metal concentrations of the solution after atmospheric leaching of the matte at different stirring rates

Stirirng rate (rpm)	Overall extraction (%)			Final solution concentration (g/l)			
	Ni	Co	Fe *	Ni	Co	Fe	Cu
145	12.3	30.1	69.4	74.4	1.05	4.22	1.04
205	14.9	28.7	70.4	85.8	1.01	4.24	0.0
400	19.2	36.6	85.5	102.1	1.23	3.49	0.0

*Maximum Fe extraction attained prior to precipitation is shown in this table

Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries

400 rpm) the rate of copper cementation was similar, with complete copper precipitation achieved after 5 hours of leaching at 205 and 400 rpm. The fact that the rate of copper cementation did not vary with varying stirring rates suggests that the copper cementation process is probably chemically controlled. The results suggest that the leaching of the metals from the matte does not entirely depend on the cementation process, but other mechanisms of leaching such as galvanic interaction and direct leaching with H_2SO_4 also play an important role, as indicated earlier. Otherwise the rate of metal dissolution would not have increased significantly when the stirring rate was increased from 145 rpm to 400 rpm, since the rate of the cementation process appeared to be independent of the stirring rate (Figure 15).

Lamya and Lorenzen (2005) found that the cementation reaction proceeds under two rate controlling mechanisms with two distinct activation energies, namely 18.2 kJ/mol at high temperatures (70–80°C) and 74.6 kJ/mol for lower temperatures (50–70°C). These values of the activation energy indicated that the rate of copper cementation was probably controlled by a boundary layer diffusion mechanism at higher temperatures. At low temperatures, the activation energy was quite high, indicating that the rate was probably controlled by a surface reaction. MacKinnon *et al.* (1971) obtained similar results in their studies of cementation of copper on nickel discs. Annamalai and Hiskey (1978) also observed the two rate controlling mechanisms in their study of copper cementation on pure aluminum. The fact that the copper cementation process was independent of stirring rate, and that the calculated activation energy was as high as 74.6 kJ/mol indicate that the rate of cementation is probably chemical reaction controlled under the employed leaching conditions. Nadkarni *et al.* (1967) reported similar results from a kinetic study of copper precipitation on iron.

The results imply that two different process controlling mechanisms are operative during the Ni-Cu matte pre-leaching process; i.e. the metal leaching process is diffusion controlled while the copper cementation process is chemically controlled.

Effect of matte particle size

Results of leaching experiments conducted to ascertain the influence of particle size on the leaching characteristics of the matte are shown in Table VII and Figures 16–18. Three particle size fractions were investigated, namely –300+ 150 μm, -106+45μm, and -45 μm, at the temperature of 60°C, stirring rate of 205 rpm and pulp density of 1.7 kg/l. Table VII shows the overall metal extractions and final leach solution concentrations. It can be seen that the highest metal extractions were achieved with the fine size fraction (-45μm). The overall extractions and final solution concentrations of iron could not be determined accurately because of iron precipitation once the solution pH increased to above 3. It should be noted that, because of iron precipitation, the iron extraction values presented in Table VII were the highest attained during leaching but were not the final values. Figures 16 and 17 show nickel and cobalt extractions as a function of time, respectively. It can be seen that the rate of extraction, as well as overall extractions, of both metals increased with decreasing particle size of the matte. The overall nickel extractions were 16.4%, 17% and 18.7% for the particle size fractions -300+150μm, -106+45μm and -45μm respectively. The overall cobalt extractions were 31.8%, 39.3% and 41.0% for the size fractions -300+150μm, -106+45μm and -45μm, respectively. The leaching behaviour

Table VII

Ni, Co, and Fe overall extractions and final metal concentrations of the solution after atmospheric leaching of the matte at different particle size

Particle size (μm)	Total extraction (%)			Final solution concentration (g/l)			
	Ni	Co	Fe *	Ni	Co	Fe	Cu
-300+150	16.4	31.8	87.1	91.6	1.09	5.05	10.38
-106	17.0	39.3	76.7	94.7	1.31	4.49	0.0
-45	18.7	41.0	75.8	101.8	1.35	4.46	0.0

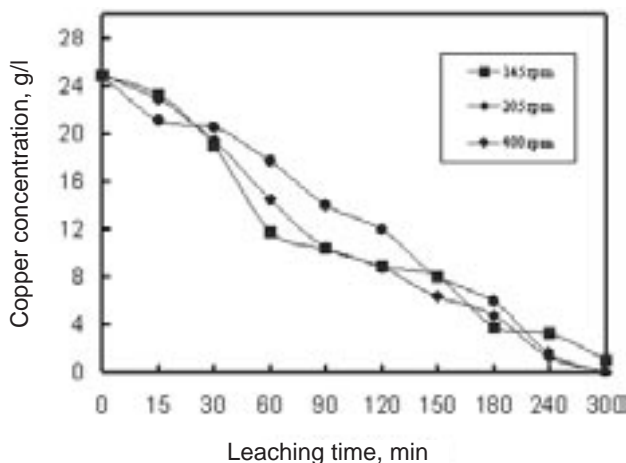*Maximum Fe extraction attained prior to precipitation is shown in this table

Figure 15—Copper concentration of leach solution during atmospheric leaching of the matte at different stirring rates (temperature: 60°C, pulp density: 1.7kg/l)
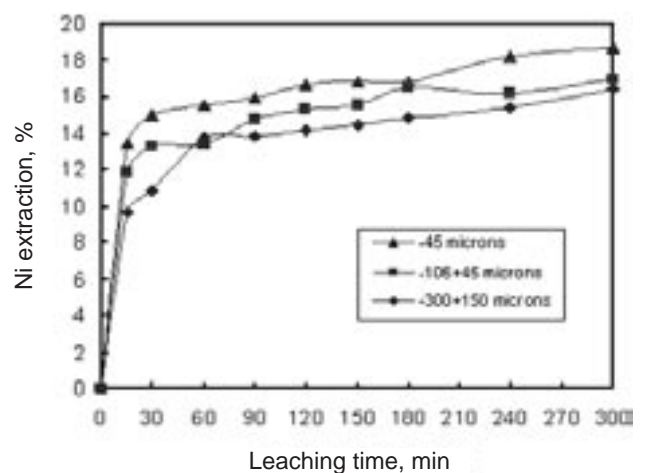

Figure 16—Nickel extraction as a function of leaching time at different particle sizes (temperature: 60°C, stirring rate: 205 rpm, pulp density: 1.7 kg/l)
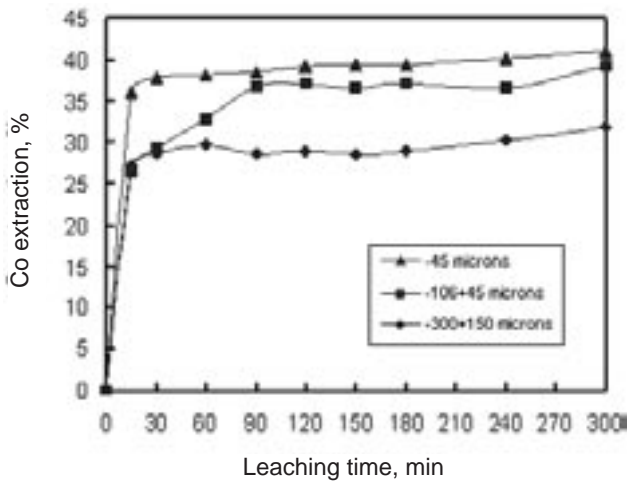
Figure 17—Cobalt extraction as a function of leaching time at different particle sizes (temperature: 60°C, stirring rate: 205 rpm, pulp density: 1.7 kg/l)
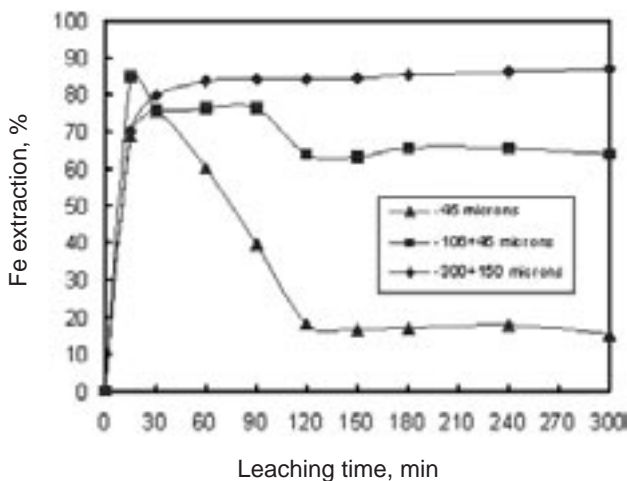

Figure 18—Iron extraction as a function of leaching time at different particle sizes (temperature: 60°C, stirring rate: 205 rpm, pulp density: 1.7 kg/l)

of iron is illustrated in Figure 18 and it can be seen that the initial leaching behaviour was similar to that of nickel and cobalt. However, with the finer size fractions (-106+45μm and -45μm) iron started to precipitate from the leach solution after 15 minutes. This was probably due to depletion of acid caused by the fast reaction kinetics of the small particles. Because of the precipitation of iron during the leaching of fine size fractions, overall iron extractions could not be determined accurately.

The fast reaction kinetics observed with the smaller size fractions was attributed to the larger surface area of small particles, which were exposed to the leaching solution. This suggested that nickel phases, especially the nickel alloy from which most of the dissolved nickel originated, were evenly distributed in the matte. This was evident from the chemical analyses of the three size fractions in Table III.

The effect of matte particle size on copper cementation is illustrated in Figures 19, which shows concentration of the leach solution versus leaching time. It can be seen that the rate of copper cementation increased with decreasing particle size. At particle sizes of -45μm and -106+45 μm, all the
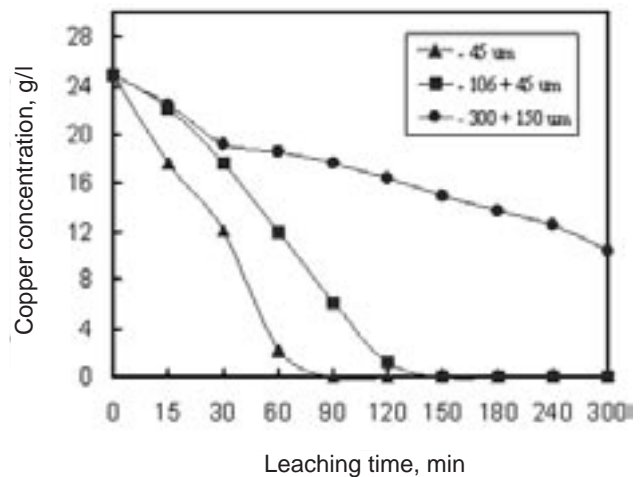
Figure 19—Copper concentration of leach solution during atmospheric leaching of the matte at different initial copper concentrations (stirring rate: 205 rpm, temperature: 60°C, pulp density: 1.7 kg/l)

aqueous copper was precipitated, whereas with the –300+150 μm particle size about 10 g/l copper remained in the leach solution after 5 hours of leaching.

The faster rate of copper cementation observed with the finer size fraction may be attributed to the larger cathodic surface area presented by the finer particles. Lamya and Lorenzen (2005) observed that the rate of cementation was more sensitive to particle size in the last period of the cementation reaction for the finer size fractions (-45 μm and –106+45 μm), This was attributed to the changes in the matte particle morphology and lattice structure, which opened up and exposed more Ni particles to the solution. The morphology and structure of the cemented particles may also have an effect on the rate of cementation.

Conclusions

➤ As much as 20% Ni, 40% Co and 80% Fe can be extracted from the Ni-Cu matte during the repulping stage of the leaching process studied.

➤ Rate of Ni, Co and Fe dissolution generally increased with increasing temperature and stirring speed, and with decreasing particle size.

➤ Metals are believed to leach from the matte by the processes of cementation, direct leaching with H_2SO_4 and galvanic interaction between the Ni alloys and the sulphide minerals.

➤ Aqueous copper can be rejected from the leach solution within 90 minutes of preleaching if the temperature is raised to 80°C. However, under the present preleach temperature of ± 60°C complete copper cementation can only be achieved after about 5 hours of pre-leaching. Copper cementation rate was found to be independent of the stirring speed, but the rate increases with decreasing particle size. The aqueous copper precipitated as metallic copper and as Cu_2S.

➤ Two different process controlling mechanisms were found to be operative during the pre-leaching of the Ni-Cu matte under the investigated conditions: The metal dissolution process was found to be diffusion controlled while the copper cementation process was chemically controlled.

Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries

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SA can benefit from redefinition of mining risk, says Wits Gold*

South Africa should grab the chance to emphasize its low political risk and the presence of proven resources now that the 'Super Cycle' is prompting new definitions of mining risk.

The call comes from Dr Marc Watchorn, CEO of Witwatersrand Consolidated Gold Resources (Wits Gold), the Johannesburg-based gold exploration company that will be seeking a JSE listing at the end of April.

He points out: 'Our planned listing is an opportunity to focus international investor attention on the low-risk advantages of gold exploration in South Africa.

'The so-called Super Cycle or prolonged commodity boom has created renewed interest in exploration worldwide. Higher potential gains have encouraged some investors to redefine risk and target remote, exotic locations where political risk is a factor.

'In South Africa, mining risk has nothing to do with remoteness or political uncertainty. It applies solely to the depth of known deposits in areas like the Wits Basin, the world's biggest source of gold. Now's a good time to remind the world about South Africa's 'democracy dividend' and the fact that our resources are not an unknown quantity, they're part of the proven geological record.'

Wits Gold holds gold prospecting rights to 798 km² in 'brownfields' areas close to existing mines in the area the company refers to as the Potchefstroom goldfield, the southern Free State goldfield and the Klerksdorp goldfield. The ground could potentially hold 142 million ounces of gold and 134 lb of uranium oxide.

Wits Gold has acquired detailed historic information from 203 boreholes including the core (representing 526 km of drilling and containing 2 882 reef cuts).

Resources have been identified at depths ranging from 500 m to 5 000 m.

The company's original resource estimates have been confirmed in a Competent Person's Report by the international technical expert, Snowden Mining Industry Consultants.

Says Dr Watchorn: 'Deep mining risk should be put in perspective. In South Africa, gold is already being mined on an economically viable basis at depths approaching 4 000 m.

'Additional investment in refrigeration and ventilation is obviously required, but experience to date indicates that these costs need not be prohibitive. We believe these risks can be managed; especially as the requisite deep mining expertise is close at hand—just next door, in fact.'

Wits Gold has contractual ties to three of South Africa's major gold mining groups. They conferred on Wits Gold selected 'old order' mineral rights to areas outside their existing mining leases. Wits Gold's strong BEE credentials helped it to convert the rights to 'new order' prospecting rights in line with the new Mineral and Petroleum Resources Development Act (MPRDA).

Energetic exploration by Wits Gold will ensure the MPRDA's use-it-or-lose-it provisions will not be invoked in relation to these rights. Should Wits Gold prove that exploitation of gold resources in these areas is economically viable, a claw-back option enables the majors to participate in any new mining venture. These companies have decades of deep mining experience.

Negotiations with the mining majors were concluded when the gold price was between $350 and $400.

A gold price significantly above $500 has further strengthened the Wits Gold business case and the prospect of successful risk management, says Dr Watchorn.

Wits Gold is the brainchild of former Harmony Gold chairman Adam Fleming. Its principal empowerment partners are Continental African Gold Resources (represented by Prof. Taole Mokoena) and Tranter Kismet Investments (represented by Dr Humphrey Mathe).

Wits Gold is being positioned to the investment community as long-term option on gold.

Witwatersrand Consolidated Gold Resources Limited (Wits Gold) is a Johannesburg-based mineral exploration company with 'New Order' prospecting rights over substantial gold resources in the Witwatersrand Basin. The company plans to give investors a long-term option on gold by seeking a JSE listing in April. Wits Gold, led by Adam Fleming, has a 40% broad-based empowerment shareholding, the largest of which is represented by deputy chairman Prof. Taole Mokoena. The Wits Gold mission is to revitalize SA gold exploration and mining by proving the economic viability of resources within 'brownfields' prospecting areas of the Witwatersrand Basin. ◆