Parametric Effects on Leaching Behavior of Nickel-Copper Matte in Ammonia

E. Muzenda [a] , I. M. Ramatsa [a] , F. Ntuli [a] , A. S. Abdulkareem [b] & A. S. Afolabi [b]

[a] Department of Chemical Engineering, Faculty of Engineering and the Built Environment , University of Johannesburg , Johannesburg , South Africa

[b] Department of Civil and Chemical Engineering , College of Science, Engineering and Technology University of South Africa , Johannesburg , South Africa
Accepted author version posted online: 15 Oct 2012.Published online: 24 May 2013.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Parametric Effects on Leaching Behavior of Nickel-Copper Matte in Ammonia

E. MUZENDA,[1] I. M. RAMATSA,[1] F. NTULI,[1] A. S. ABDULKAREEM,[2] and A. S. AFOLABI[2]

[1]*Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Johannesburg, South Africa*
[2]*Department of Civil and Chemical Engineering, College of Science, Engineering and Technology University of South Africa, Johannesburg, South Africa*

Leaching, which is described as the extraction of soluble constituents from a solid by means of a solvent, is an important separation technique in the refining of precious metals from their matte. It is, therefore, important to investigate the extraction behavior of metals from the matte, which is the focus of this study. This study reports the influence of concentration of the solvent (ammonia), leaching temperature, leaching time, and pH on the recovery of nickel and copper from the matte. The elemental composition analysis of the matte indicated that it contains 23% copper, 37% nickel and 1.1% ferrous compound. The analysis also showed that the major mineral phases present in the matte were heazlewoodite (Ni_3S_2), chalcocite (Cu_2S), djurleite ($Cu1.9S$), and nickel alloy. The leaching parameters studied were concentration of ammonia (1.5, 2.0, 2.5, and 3.0 M), leaching time (0–270 min, at 15 min sampling interval), leaching temperatures (50°C, 60°C, and 70°C), and pH (9.3–11.2). The results obtained revealed that the recovery of nickel and copper from the matte was greatly influenced by the concentration of ammonia, leaching time, leaching temperature, and pH. It was established from this study that the highest dissolution of nickel and copper was obtained at 3 M and 2 M ammonia concentration, respectively. The results also revealed that a decrease in the pH of the solution resulted in a decrease in both nickel and copper recovery, with maximum leaching time of 270 min. It was observed that less than 50% of both nickel and copper was leachable due to the presence of metal alloys. The analyses of the results also showed that as the leaching temperature increased from 50°C to 60°C, the amount of nickel and copper that was recovered from the matte significantly increased. However, there was reduction in the amount of nickel and copper recovered from the matte as the temperature was increased from 60°C to 70°C, due to loss of ammonia by evaporation. The shrinking core model was used to explain the behavior of the recovery of these metals at different temperatures, and both metals were found to be favored by diffusion controlled reaction.

Keywords: Ammonia concentration, copper, leaching temperature, leaching time, nickel, pH

1. Introduction

The recovery of base metals from matte (a mixture of metal sulfides and precious metals) has been an important process in the refining of precious metals. Nickel–copper mattes are conventionally produced by smelting nickel and copper sulfide concentrates. Iron and cobalt minerals are usually also present, and, in some cases, nickel mineralization is closely associated with platinum group metals (PGMs), as is the case with nickel minerals in South Africa (Llanos et al. 1974; Lamya and Lorenzen 2006). 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 by hydrometallurgical

process to produce marketable nickel, copper, cobalt, and any available precious metals. The first step in the hydro-metallurgical 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 (Symens et al. 1979; Filmer 1981; Makhubela 2008). For many years, studies were conducted on the leaching of Ni-Cu matte under atmospheric and pressure leaching in acidic copper–nickel sulfate solution, with oxygen as the oxidizing agent (Forward and Peters 1985; Habashi 1999; Muir and Ho 1979). In this process, the matte is first leached under atmospheric conditions followed by a pressure leach, and in both steps O_2/air is charged 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, or in some cases, fed to a smelter (Filmer 1981; Makhubela 2008). The other leaching process route employs a pre-leach step, which is essentially
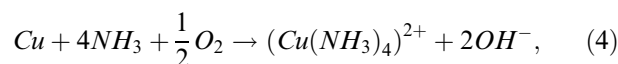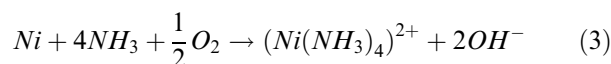
Address correspondence to: A. S. Afolabi, Department of Civil and Chemical Engineering, College of Science, Engineering and Technology University of South Africa, P/Bag X6, Florida 1710, Johannesburg, South Africa. E-mail: afolaas@unisa.ac.za

a matte repulping step, prior to a pressure leach step (Weiss 1985; Moskalyk and Alfantazi 2002). The repulping process may be considered to be basically a nonoxidative atmospheric leach stage since leaching of the matte starts immediately when 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 and iron are precipitated from the solution, and any PGM present remains in the solids. In both of these Ni-Cu 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 sulfate crystals. Copper can be recovered as metal by electrowinning from the sulfate solution or by electrorefining if the precipitated copper was produced by the smelting process (Rademan 1999). Ammonia as an effective lixiviant has been widely used in a number of hydrometallurgical processes for many years due to its inherent advantages over alternative reagents. The main advantage is that the basic leach solution alleviates several corrosion problems encountered in acidic systems. Leaching with ammonia solution removes the major wasteful components like iron as an insoluble oxy/hydroxyl compounds. This allows selective extraction of the valuable metals (e.g., copper, cobalt, nickel) as soluble amine complexes through reactive nitrogen-containing group, leading to higher solubility in most cases (Mackinnon 1971; Forward and Peters 1985; Hofirek and Kerfoot 1992). Ammonia is also advantageous in that ammonia and ammonium ion constitute a pH buffer solution. However, it has the disadvantage of requiring relatively high temperature and pressure for efficient leaching. The chemistry of leaching of minerals and matte of Ni and Cu in ammoniacal leaching systems is presented in Equations (1)–(4). The metal values being solubilized as complex amines and the sulfur being oxidized via number of intermediate ions to sulfate ions and subsequently recovered by crystallization as ammonium sulfate as shown in these equations.

Ammonia leach of metal sulfides

$$NiS + 2O_2 + 6NH_3 \rightarrow Ni(NH_3)_6SO_4 \qquad (1)$$

$$CuS + 2O_2 + 6NH_3 \rightarrow Cu(NH_3)_6SO_4 \qquad (2)$$

Ammonia leach of metals/matte

$$Ni + 4NH_3 + \frac{1}{2}O_2 \rightarrow (Ni(NH_3)_4)^{2+} + 2OH^- \qquad (3)$$

$$Cu + 4NH_3 + \frac{1}{2}O_2 \rightarrow (Cu(NH_3)_4)^{2+} + 2OH^-, \qquad (4)$$

In this present study, the effects of various factors such as concentration of the solvent (ammonia), temperature and time on the extraction of nickel and copper from the matte are investigated, with the purpose of establishing the best conditions for the extraction of nickel and copper from the matte. The matte was obtained from Impala Platinum in South Africa, which is one of world's largest precious metal producers.

2. Materials and Method

2.1 Materials and Equipment

The material used in this study was a Ni-Cu matte from Impala Platinum. The chemical composition of the matte was determined using various analytical techniques such as x-ray diffraction (XRD) (Philips Xpert Diffractometer, Germany), scanning electron microscope (SEM) (JOEL JSM 5600, Germany), atomic absorption spectroscopy (AAS) (ICE 3000 Thermo Scientific, Germany), and Spectro-Arcos inductive coupled plasma-optical emission spectroscopy (ICP-OES). The lixiviant used in this study was analytical grade ammonia (98–99.5%). The leaching tests were performed in a 3-liter stainless steel vessel provided with baffles, a cover, a thermometer, a pH electrode fitted with a variable speed overhead stirrer coupled to a paddle. The setup was submerged in a water bath with temperature control.

2.2 Methodology

The effects of varying the process parameters (i.e., temperature, leaching time, ammonia concentration, and pH) on the leaching behavior of Ni-Cu matte were investigated. The temperature range studied was between 50°C and 70°C, ammonia concentration was varied from 1.5, 2.0, 2.5, to 3.0 M, while the leaching time ranged from 0 to 300 min. The stirring speed was kept constant at 410 rpm, while the particle size fractions was 80% passing $-75\,\mu m$. Prior to the leaching process, the as-received matte sample was analyzed to determine its chemical composition and crushed using a pulverizing machine and screened to obtain a desired particle size of 80% passing $-75\,\mu m$. A predetermined quantity of the ammonia solution was added to the leaching vessel and heated to the desired temperature. Then, 66.7 g of the Ni-Cu matte was added and stirred at the required speed. The pH of the mixture was monitored at regular intervals and samples of this mixture were pipetted and transferred into measuring flask and contents (Ni, Cu) in the solutions were determined by the use of atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP).

3. Results and Discussion

The recovery of base metals from matte (a mixture of sulfides and precious metals) has been an important process in the refining of precious metals. Matte is produced from the smelting of sulfide ores to separate the valuable metals. The matte is further processed by leaching, leaving behind a solid residue rich in precious metals and producing base metals rich liquor. It is, therefore, important to investigate the effects of various parameters such as concentration of solvent, leaching temperature, and leaching time on the rate of leaching of base metals from the matte, which is the focus of this study. Before and after leaching of nickel and copper, the morphology and chemical composition of the matte were analyzed and the results obtained are presented in Figure 1 and Table 1, respectively. It can be seen from the chemical composition of the matte that the major constituents are the copper (23%) and nickel (37%). The results also revealed
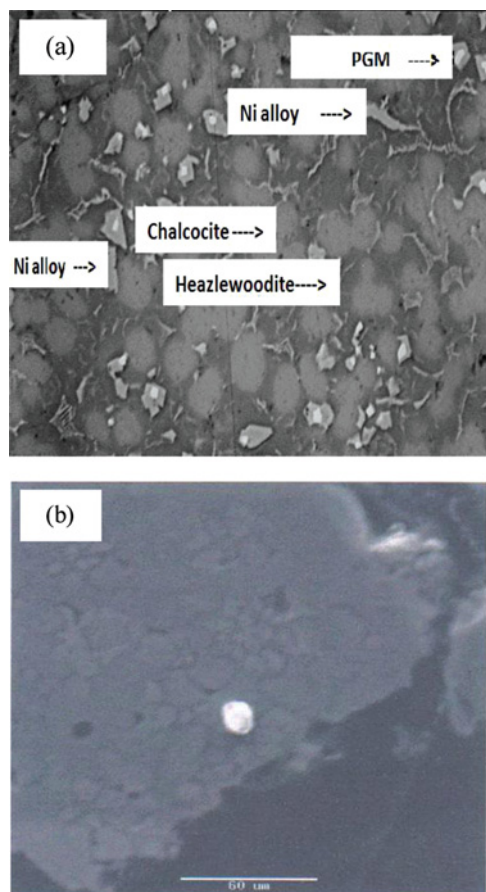
Fig. 1. SEM images of the matte sample a) before and b) after leaching. (Figure is provided in color online.)

the presence of ferrous and aluminum compounds; sulfur was also present in the matte, while palladium, cobalt, and platinum in are present in minute quantities as shown in Table 1. The useful information about the characteristics of the matte can be obtained by combined application of XRD and SEM. The matte sample was subjected to XRD analysis before and after leaching to observe the phase change and/or the product that formed during the leaching process as shown in Figure 2.

3.1 Effect of Ammonia Concentration

Reagent concentration plays a vital role in any leaching operation and since the reagent costs are a major part of the operating costs, optimization of the reagent concentration is important to minimize consumption while maximizing extraction (Hofirek and Kerfoot D.G.E. (1992). The influence of ammonia concentration on the amount of nickel and copper leached from the matte was studied by

varying its concentration from 1.5 to 3 M at constant temperature (70°C) and constant stirring speed (410 rpm). The results obtained are presented in Figures 3 and 4 for nickel and copper, respectively. Figure 3 shows that the percentage of leached nickel depends strongly on the concentration of ammonia as the percentage of nickel recovered from the matte increases with the increase in ammonia concentration from 1.5 to 3 M. After the first 50 min, the nickel extraction obtained was about 23.2% for 3 M, 12.1% for 2.5 M, 9.6% for 2 M, and 1.8% for 1.5 M concentrations, respectively. After a 270-min leaching period, the highest Ni extraction observed were 33% for 3 M, 22% for 2.5 M, 17% for 2 M, and 4% for 1.5 M. It can, thus, be concluded that high Ni extraction is achieved with higher concentrations of ammonia. Figure 4 shows the amount of copper recovered from the matte at various concentrations of ammonia. The results show an increase in the amount of copper that is recovered with increase in the concentration of ammonia. It can be observed that the amount of copper recovered is generally low for all concentrations of ammonia after a leaching period of 130 min, while ammonia concentrations above 2.5 M show little improvement on the recovery of this metal from the matte. It is observed that more copper was leached as the leaching time increased. It is interesting to note that the highest percentage of copper recovery (45.9%) was achieved at the ammonia concentration of 2 M; however, this value was not significantly higher than that obtained at 3 M (45.5%). The highest percentage recovery of nickel (32.9%) was achieved with ammonia concentration of 3 M. This deviation from can be attributed to the cementation of the copper from the solution (Kyung et al. 2007).

3.2 Effect of Temperature

The effect of temperature is also an important parameter on the rate of extraction of metal from its ore (Demirkiran et al. 2005). The effect of temperature on the leaching behavior of the Ni-Cu matte was investigated by varying the temperature between 50°C and 70°C, while keeping other variables constant. Although, increase in leaching temperature was indirectly employed to increase the solubility of the matte and minimize the gangue dissolution, care was taken not to increase the temperature above the boiling point of the solvent. This situation could result in the loss of the solvent by evaporation, thereby reducing the quantity of metal that can be recovered from the matte. The results obtained on the effects of leaching temperature on the recovery of nickel and copper from the matte are presented in Figures 5 and 6, respectively.
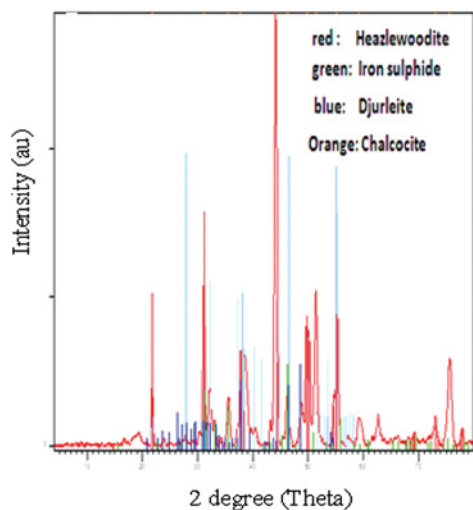
The results in Figure 5 on the effect of temperature on the extraction of nickel from the matte show that increase in

Table 1. Percentage chemical composition of the matte sample

Element/chemical	Al$_2$O$_3$	Co	Cu	Ni	Pd	Pt	S	Fe$_2$O$_3$
Matte (wt%)	0.65	0.29	23	37	0.15	0.20	10	1.10
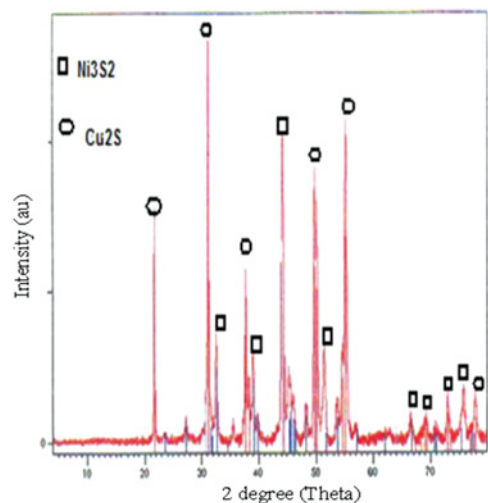
Fig. 2. X-ray diffraction patterns of the matte sample a) before and b) after leaching. (Figure available in color online.).
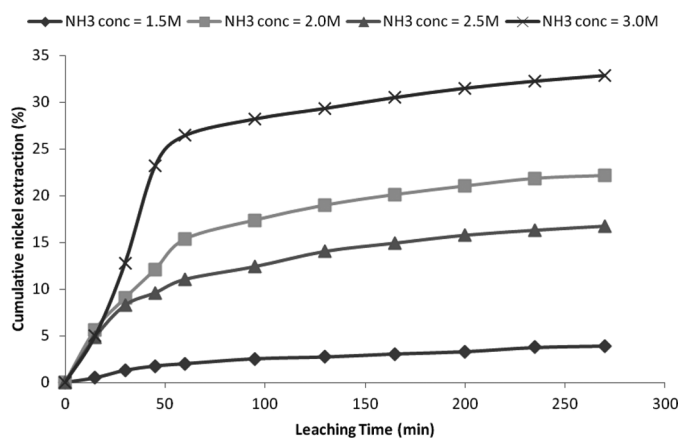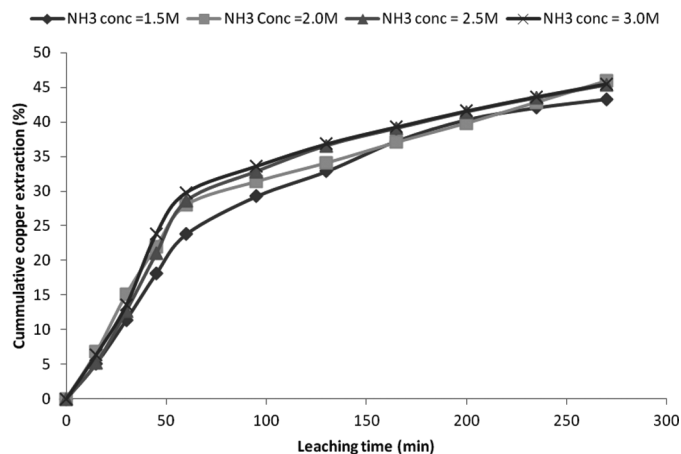

Fig. 4. Variation of copper extraction with ammonia concentration and leaching time.

temperature from 50°C to 60°C increased the extraction of nickel. After 45 min of leaching, the amount of nickel extracted was 9.3%, 16.7%, and 23.2% for 50°C, 60°C, and 70°C, respectively. The reduction in the amount of nickel recovered when the temperature was increased from 60°C to 70°C can be attributed to the evaporation of the ammonia from the system which reduced the concentration of the solvent. Figure 6 also indicates that temperature influences the amount of copper leached from the matte. The results indicate that after a leaching period of 270 min, 10.8%, 99.7%, and 50.7% of copper was recovered at 50°C, 60°C, and 70°C, respectively (Figure 6). Though, the general expectation was that an increase in temperature will increase the solubility of the material to be extracted and the diffusion coefficient, thus increase the amount of nickel and copper extracted. This expectation was observed in this study only when the temperature was increased from 50°C to 60°C as shown in Figures 5 and 6 for the extraction of nickel and copper from the matte.

By observation, one would anticipate the possibility of evaporation of ammonia from the system as the temperature
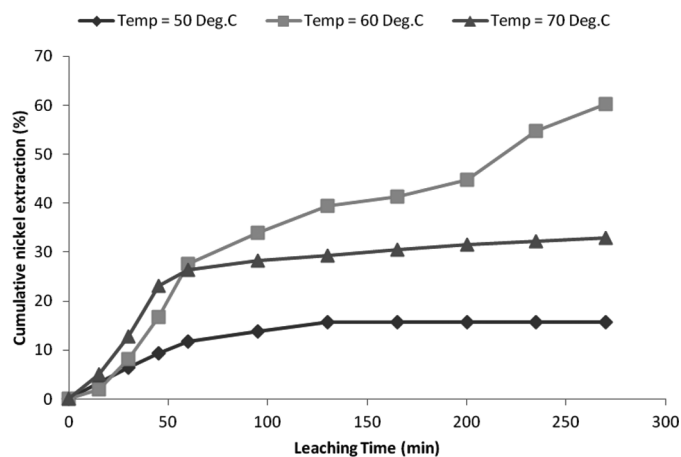

Fig. 3. Variation of nickel extraction with ammonia concentration and leaching time.

Fig. 5. Variation of nickel extraction with leaching temperature and time.
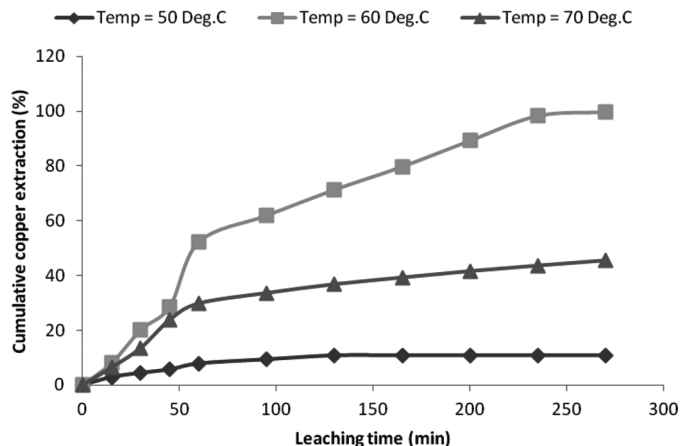
Fig. 6. Variation of copper extraction with leaching temperature and time.

was increased from 60°C to 70°C, In conclusion, the results obtained on the effect of temperature on the extraction of nickel and copper from the matte indicate that the amount of copper recovered was higher than that of nickel at 60°C and 70°C. A different trend was observed at a leaching temperature of 50°C where the amount of nickel recovered was higher than that of copper (Figure 7). This variation can be attributed to the solubility of the extracted metals in the solvent employed and the possibility that nickel might have displaced copper at this temperature.

3.3 Effect of Leaching Time

The time taken to leach a certain amount of base metals from the matte is important, since the production targets of the base metals need to be met per period of time. It is, therefore, worthwhile to investigate the effects of recovery time on the leaching of nickel and copper from the matte. The effect of varying the leaching time from 15 to 270 min on the percentage recovery of copper, and nickel was studied using 3 M concentration of ammonia and at a temperature of 70°C and the results are presented in Figure 8. A concentration
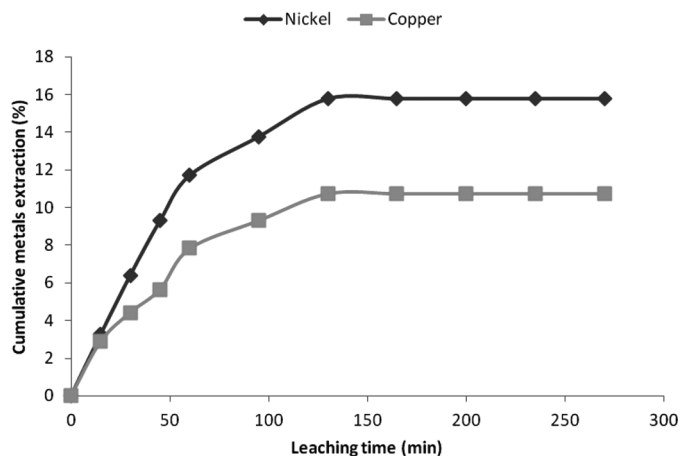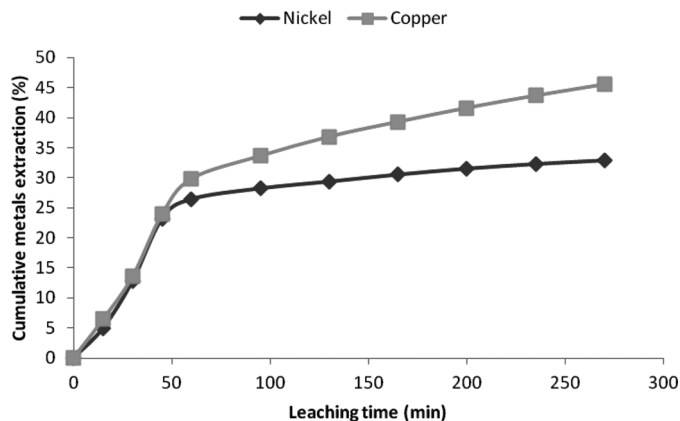

Fig. 8. Effect of leaching time on recovery of nickel and copper.

of 3 M of ammonia was selected since it gave a higher percentage recovery for both metals considering that the amount of copper extracted using 2 M ammonia was not significantly higher than that at 3 M (Figures 3 and 4). It can be seen from Figure 8 that the two metals show similar behavior in terms of their percentage recovery. The two curves show relatively fast initial rate and then slow down as the extraction asymptotically approaches the maximum obtainable extraction rate. For instance, within 60 min, 29.8% Cu, and 26.5% Ni recovery was achieved. This increased to 45.5% and 32.9% for Cu and Ni, respectively, after the 270-min leaching period. It can be observed that the overall extraction of both Ni and Cu are less than 50%. This can be attributed to the fact that the metal alloys were not completely leached after 270 min of leaching.

3.4 Influence of pH

The initial pH of the ammonia was varied from 11.2 to 9.3, at 70°C, and constant concentration (3.0 M) of ammonia for leaching period of 270 min. It can be seen from Figure 9 that the extraction of Ni is higher than that of Cu at initial pH of
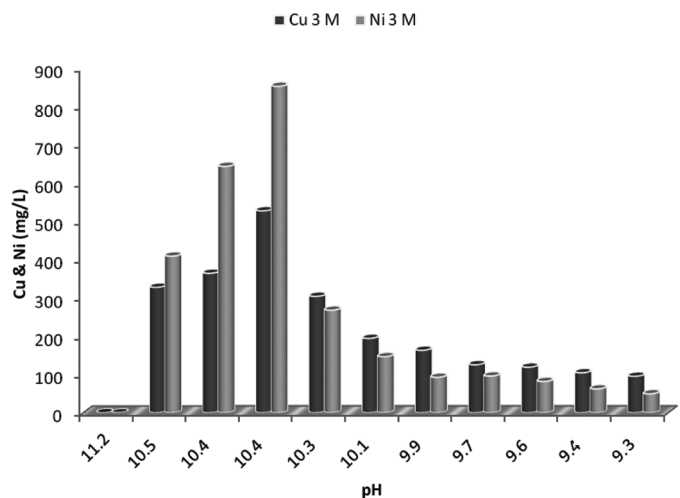

Fig. 7. Variation of nickel and copper extraction at 50°C.

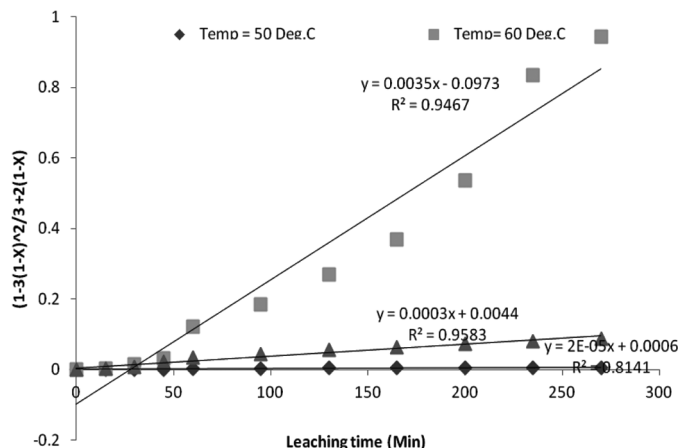**Fig. 9.** The effect of pH on the extraction of nickel and copper.

Fig. 10. Plot of $[1-3(1-X)^{2/3}+2(1-X)]$ against time at different temperatures for copper recovery.

11.2 to 10.4; however from the pH 10.4 to 9.3 the extraction of Cu conversely is higher than that of Ni thereafter. The differences in the levels of extraction of Cu and Ni with pH can be attributed to the differing stability of nickel and copper ammine complexes. At pH values greater than 10.4, nickel ammine complexes tend to be more stable than copper ammine complexes and as the pH drops below 10.4, both metals begin to precipitate as they is not enough ammonia to form stable complexes. However, copper complexes tend to more stable than nickel in this range. The maximum extraction for both Ni and Cu is observed at the pH 10.4; thereafter, it decreases. It can be inferred from these results that the pH has a great influence on the nickel and copper extraction. The stable nickel and copper complexes require a more basic pH, at a range between 8.3 and 10.8, as shown in Figure 9. The pH range is within the range of stable copper complexes. The low recovery of nickel and copper at low pH values can be attributed to the possibility of ammonia forming ammonium (NH_4^+) complexes, which could not bond with nickel and copper in the matte.
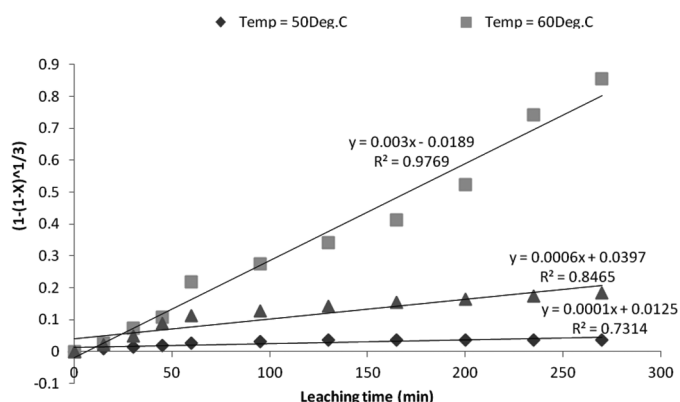

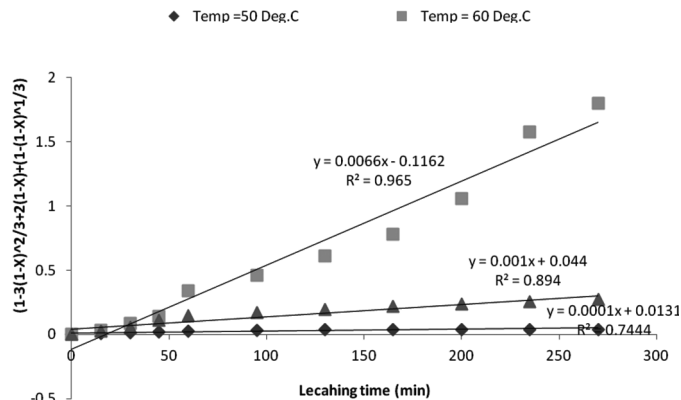**Fig. 11.** Plot of $[1-(1-X)^{1/3}]$ against time at different temperatures for copper recovery.

Fig. 12. Plot of $[1-3(1-X)^{2/3}+2(1-X)+1-(1-X)^{1/3}]$ against time at different temperatures for copper recovery.

4. Kinetic Model

The shrinking core model was used to describe the rate of the recovery of nickel and copper from ammonia solution (Jing and Xue 2011). Equations (5)–(7) are used to describe this system, where x is the fractional metal leached, t is the reaction time, and k is the apparent rate constant. For a surface chemical reaction-controlled process, the equation that applies is

$$1 - (1-x)^{\frac{1}{3}} = kt. \qquad (5)$$

For a diffusion-controlled process, Equation (6) is applicable.

$$1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = kt, \qquad (6)$$

while Equation (7) can be used to describe a mixed controlled process (i.e., surface chemical reaction and product layer diffusion)

$$[1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)] + \alpha[1 - (1-x)^{\frac{1}{3}}] = kt. \qquad (7)$$

In this study, the dissolution kinetic of the metals was characterized with the shrinking core model using the metals dissolution kinetics data obtained from the experiment conducted. The plots shown in Figures 10–12 represent the core kinetic model for the extraction of copper from the matte. Equation (5), which describes the chemical controlled reaction, is shown in Figure 10, while the plots of

Table 2. Values of R^2 at different temperature and kinetics model

	R^2 at different temperatures					
	50°C		60°C		70°C	
	Ni	Cu	Ni	Cu	Ni	Cu
Diffusion control	0.81	0.81	0.95	0.95	0.82	0.96
Surface reaction control	0.72	0.73	0.95	0.98	0.69	0.85
Combination of diffusion and surface reaction	0.74	0.74	0.97	0.96	0.73	0.90

Equations (6) and (7) that describe the diffusion and mixed controlled are shown in Figures 11 and 12. It can be observed from the Figures 10–12 and Table 2 of R^2 that the three kinetic models best fitted the experimental data for the extraction of nickel and copper at a temperature of 60°C. At this temperature the mixed controlled process gave the best fit, however, the diffusion control gave a better fit at the other two temperatures as shown in Table 2.

5. Conclusions

The effects of ammonia concentration, leaching temperature, leaching time, and pH on the recovery of nickel and copper from the Impala matte were investigated in this study. Based on analyses of the results obtained on the various experiments conducted, it can be deduced that the concentration of the leaching solvent increased with the extraction of nickel with maximum extraction obtained at ammonia concentration of 3 M, while the maximum extraction of copper was achieved at ammonia concentration of 2 M. The results also revealed that the maximum amount of nickel and copper were recovered from the matte after a leaching time of 270 min. Increase in temperature from 50 to 60°C increased the recovery of copper from 35% to 90%, and the nickel extraction from 15% to 60%, however, further increases in temperature to 70°C resulted in a drop in metal recovery for both metals due to evaporation of ammonia from the system. Investigations conducted on the influence of pH showed that, the extraction of Ni was higher than that of Cu from pH of 11.2–10.4; however from the pH 10.4–9.3 the extraction of Cu conversely was higher than that of Ni thereafter. The extraction of copper and nickel from the matte obeyed the shrinking core model and the diffusion control best favored the kinetics model at all temperatures when compared to other kinetic models.

References

Demirkiran, N., A. Ekmekyapar, A. KunKul, and A. Baysar. 2007. A kinetic study of copper cementation with zinc in aqueous solutions. *Hydrometallurgy* 82: 80–85.

Filmer, A. O. 1981. The non-oxidative dissolution of nickel mattes in aqueous acidic solution. *Journal of South African Institute of Mining and Metallurgy* 74–84.

Forward, F. A., and A. Peters. 1985. Leaching principles. In *SME Mineral Processing Handbook*, ed. N. L. Weiss, Vol. 2, 13. New York: SME.

Habashi, F. 1999. *Textbook of Hydrometallurgy*, Métallurgie Extractive Québec, 2nd ed., 750. Québec City, Québec: Métallurgie Extractive Québec.

Hofirek, Z., and D. G. E. Kerfoot. 1992. The chemistry of the nickel-copper matte leach and its application to process control and optimisation. *Hydrometallurgy* 29: 357–381.

Jing, H., and K. Xue. 2011. Selective recovery of copper, zinc and nickel from printed circuit boards from ammonia leaching under pressure. *Institute of Process Engineering, Chinese Academy of Sciences* 32: 596–602.

Kyung, H. P., M. B. Debasish, R. Ramachandra, and W. N. Chul. 2007. A study on the oxidative ammonia/ammonium sulphate leaching of a complex (Cu–Ni–Co–Fe) matte. *Hydrometallurgy* 86: 164–171.

Lamya, R. M., and L. Lorenzen. 2006. Atmospheric acid leaching of nickel-copper matte from Impala Platinum refineries. *Journal of the South African Institute of Mining and Metallurgy* 106: 395–394.

Llanos, Z. R., P. B. Queneau, and R. S. Rickard. 1974. Atmospheric leaching of matte at the port nickel refinery. *CIM Bulletin* 64: 74–81.

Mackinnon, D. J., T. R. Ingraham, and R. Kerby. 1971. Copper cementation on nickel discs. *Canadian Metallurgical Quarterly* 10 (3): 165–169.

Makhubela, P. 2008. Copper leaching from matte. B-Tech Report, Department of Chemical Engineering, University of Johannesburg, South Africa.

Moskalyk, R. R., and A. M. Alfantazi. 2002. Nickel laterite processing and electrowinning practice. *Mineral Engineering* 15: 593–605.

Muir, D. M., and E. Ho. 1979. Process review and electrochemistry of nickel sulphides and nickel mattes in acidic sulphate and chloride media. *Mineral Processing and Extractive Metallurgy (Transaction of Institute of Mineral and Metallurgy)* 115 (2): 57–64.

Rademan, J. A. M., L. Lorenzen, and J. S. J. Van Deventer. 1999. The leaching characteristics of Ni-Cu matte in the acid-oxygen pressure leach process at Impala platinum. *Hydrometallurgy* 52: 231–252.

Symens, R. D., P. B. Queneau, E. C. Chou, and F. F. Clack. 1979. Leaching of iron containing copper-nickel matte at atmospheric pressure. *Canadian Metallurgical Quarterly* 18: 145–153.

Weiss, N. L. 1985. *SME Mineral Processing Handbook*, Vol. 2. Littleton, CO: Society for Mining, Metallurgy, and Exploration.