

Leaching Behaviour of a Low-grade South African Nickel Laterite

Catherine K. Thubakgale, Richard K.K. Mbaya, Kaby Kabongo

Abstract—The morphology, mineralogical and chemical composition of a low-grade nickel ore from Mpumalanga, South Africa, were studied by scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. The ore was subjected to atmospheric agitation leaching using sulphuric acid to investigate the effects of acid concentration, leaching temperature, leaching time and particle size on extraction of nickel and cobalt. Analyses results indicated the ore to be a saprolitic nickel laterite belonging to the serpentine group of minerals. Sulphuric acid was found to be able to extract nickel from the ore. Increased acid concentration and temperature only produced low amounts of nickel but improved cobalt extraction. As high as 77.44% Ni was achieved when leaching a -106+75 μ m fraction with 4.0M acid concentration at 25°C. The kinetics of nickel leaching from the saprolitic ore were studied and the activation energy was determined to be 18.16kJ/mol. This indicated that nickel leaching reaction was diffusion controlled.

Keywords—Laterite, sulphuric acid, atmospheric leaching, nickel.

I. INTRODUCTION

NICKEL is contained in sulphide and laterite ores hosted by principal economic minerals pentlandite and garnierite, respectively. With the rising depletion of rich-sulphide ores, the focus has recently shifted to low-grade laterite ores [1] which have historically been stockpiled due to difficulties in their processing. Although nickel production from laterites has been in practice for over 100 years, major production has been from rich sulphide ores. Researchers have predicted that future nickel supply will be from laterites [2].

Lizardite, a garnierite mineral $(\text{Ni,Mg})_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, has become a widely researched layered silicate mineral of the serpentine group [3] following the growing interest by researchers as a result of increasing demand for nickel. It has been found that in some laterite ores, nickel is distributed in lizardite and along with magnesium it is mostly amenable to leaching with sulphuric acid than with nitric and hydrochloric acid [4, 5 & 6]. Traditionally, nickel and associated metals have been extracted from ores by mineral processing, smelting and refining processes [7].

Pyrometallurgy and hydrometallurgy routes are both commercially used for processing nickel laterites to recover nickel and cobalt. While limonite minerals, $(\text{Fe,Ni})\text{O}(\text{OH})\cdot n(\text{H}_2\text{O})$, are amenable to hydrometallurgical processing, garnierite ores rich in silica and magnesium are mostly processed by pyrometallurgical methods to produce ferro-nickel and matte. However, this route is disadvantageous as the processes involved require high grade ores and energy inputs resulting in poor cobalt recoveries [8]. Nickel bound within goethite, clay and saprolite ores allows for hydrometallurgical processing by leaching at moderate conditions without high acid consumptions [9] caused by dissolution of iron [10].

Studies on extraction of nickel and cobalt by atmospheric pressure leaching (AL) with sulphuric acid and high pressure leaching (HPAL) processes have indicated that although AL could simply be controlled and maintained at low costs, the resultant high concentrations of iron and aluminium negatively influenced downstream processing of the leach liquors [11, 12]. HPAL was found to give high nickel and cobalt recoveries with negligible iron concentration in the leach liquors, however it is attached to expensive autoclaves with high maintenance costs [13, 14].

Following studies on acid leaching of saprolites, it has been noted that nickel, in saprolites, can be easily extracted than that in limonites because in saprolites, nickel is weakly held in the silicate structure and is easily displaced by acid or other cations through ion exchange, where the octahedral and tetrahedral sheets contain silicon and magnesium, respectively [15]. It has also been noted that although high extractions of nickel from laterites could be achieved by acid leaching, co-dissolution of magnesium and iron may lead to high acid consumptions [16].

The aim of this work was firstly to investigate the leaching behaviour of the ore by evaluating the effects of sulphuric acid concentration, leaching temperature, leaching time and particle size on extraction of nickel from the nickel laterite material. Leaching behaviour of cobalt, as a by-product [17] was also studied. Secondly, leaching kinetics of nickel from the ore were studied.

II. MATERIALS

A. Materials characterisation

A nickel laterite ore collected from a satellite area of the Bushveld Complex in Mpumalanga, South Africa, was used in the experiments. Chemical and mineralogical compositions of the sample were studied by X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses, respectively (TABLE I).

C. K. Thubakgale is with the Department of Chemical and Metallurgical Engineering at Tshwane University of Technology, Private Bag X680, Pretoria, South Africa.

R.K.K. Mbaya is with the Department of Chemical and Metallurgical Engineering at Tshwane University of Technology, Private Bag X680, Pretoria, South Africa. (phone: +27123823597; fax: +27123824392; email: MbayaR@tut.ac.za)

K. Kabongo is with Bohlaba Mines Pty Ltd, Colbyn, Pretoria, South Africa.

The lower amount of Fe₂O₃ (13.32%) and a higher MgO (18.72%) amount (TABLE I) indicated that the ore under investigation was a saprolitic nickel laterite.

III. EXPERIMENTAL PROCEDURE

A. Ore preparation

The ore sample was received as lumps. Using laboratory primary crushers and a rod mill, the particle size was reduced to -250µm.

B. Leaching experiments

Atmospheric leaching experiments were conducted for 480minutes (min) in a 600ml glass beaker placed on a hot plate that was temperature controlled and magnetically stirred at 200rpm. A watch glass was placed on the beaker to prevent evaporation thus promoting condensation of the leach solution. Parameters under investigation included sulphuric acid (H₂SO₄) concentration, leaching temperature and ore particle size in order to determine optimum leaching conditions.

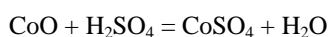
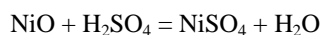
Acid solutions of known concentrations were prepared and placed in the glass beaker. When the solution reached the desired temperature, the ore sample was added into the beaker and magnetically stirred for the duration of the leaching period. The amount of ore sample added was weighed to make up a pulp of 10% solids. Samples were drawn throughout the leaching period at pre-determined intervals and diluted according to atomic absorptions spectrometer (AAS) analysis requirements.

TABLE I

CHEMICAL COMPOSITION OF THE ORE AT -250µm

Component	wt%
Co	0.02
Ni	0.08
CuO	0.01
Fe ₂ O ₃	13.32
MgO	18.72
Others	21.34
SiO ₂	46.48

Leaching of nickel and cobalt in sulphuric acid occurred according to the following reactions:



IV. RESULTS AND DISCUSSION

A. Materials characterisation

The ore was mainly composed of silica (46.48 wt%) along with significant amounts of pyroxene (diopside and enstatite) and plagioclase (anorthite) group minerals. Low amounts of olivine (forsterite), serpentine (lizardite 1T) and mica (biotite) minerals were observed (Fig.1). The density of the ore was determined by pycnometry and found to be 2.65 g/cm³.

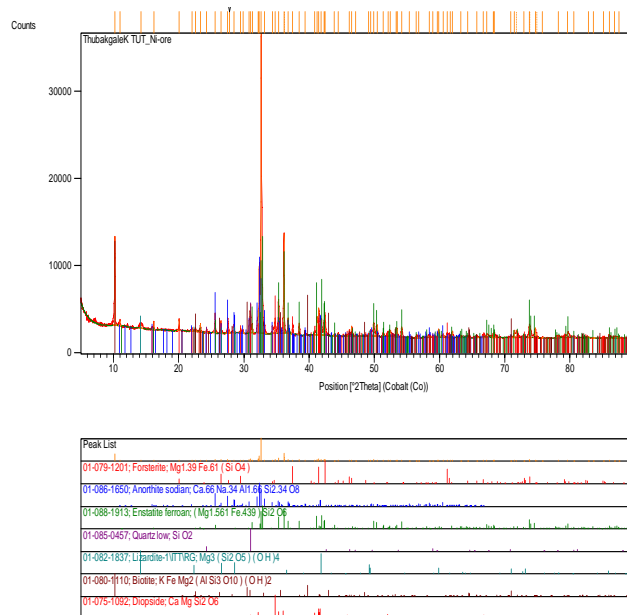


Fig. 1 X-ray diffraction pattern of the -250µm sample.

The morphology of the sample was studied by scanning electron microscope (SEM) on a -1mm fraction sample (Fig.2). It was observed that at the ore particles had irregular shapes throughout the wide size range.

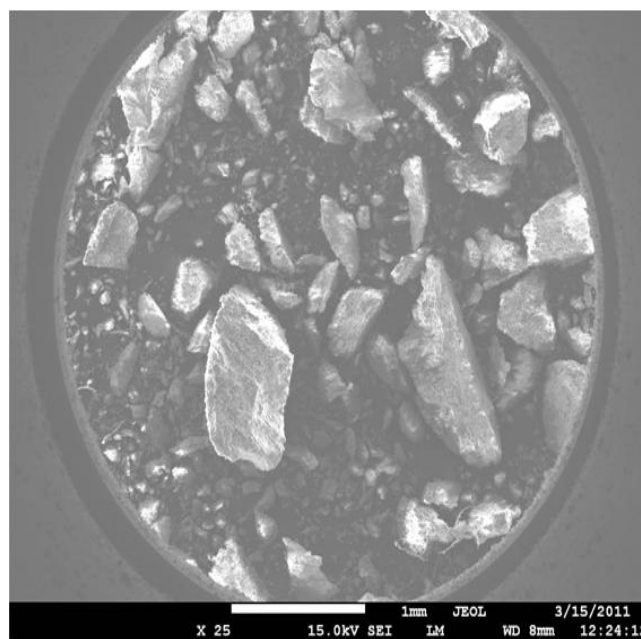


Fig. 2 SEM image of the saprolitic laterite sample (-1mm) showing the irregular shape of the particles

B. Effect of acid concentration and temperature

These tests were conducted at different sulphuric acid concentrations and temperatures. During the tests, the sample particle size, percent solids and stirring speed were held constant at -250µm, 10% and 200rpm, respectively. Temperature tests were conducted at 25°C, 40°C and 90°C with acid concentration of 1.0Molar (M) and acid

concentration tests were conducted at 25°C with acid concentrations 1.0M, 2.0M and 4.0M.

1.0M acid concentration at different temperatures over a time range of 0 – 480min.

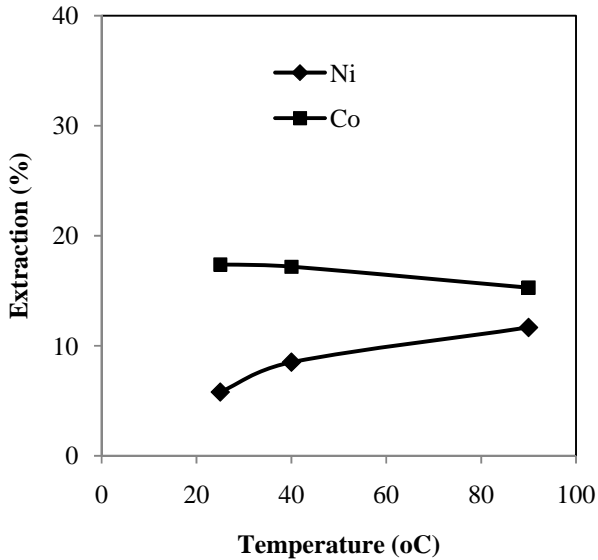


Fig. 3 Effect of leaching temperature of extraction of Ni and Co with 1.0Molar

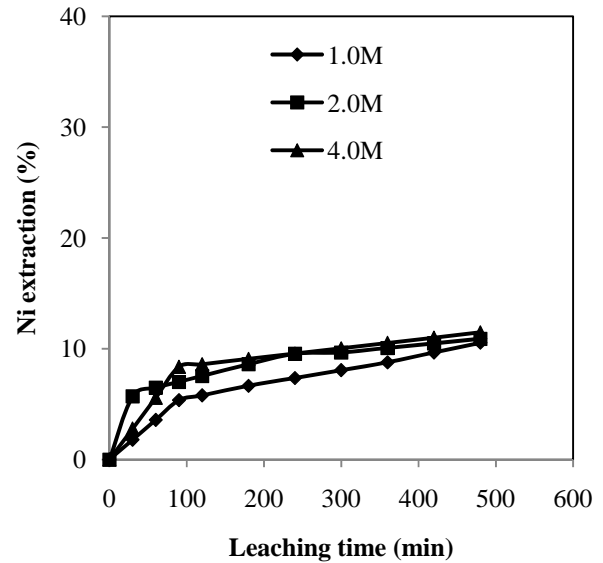


Fig. 5 Effect of leaching time on extraction of Ni with different acid concentrations at 25°C

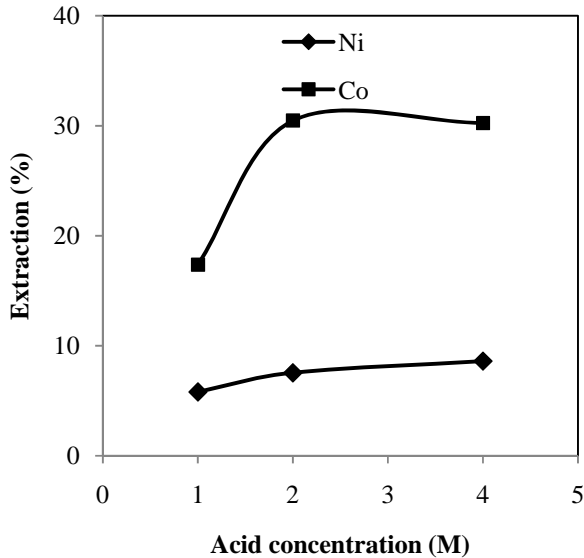


Fig. 4 Effect of acid concentration on extraction of Ni and Co at 25°C

Results for nickel and cobalt extraction after 120min are shown in Fig.3 and Fig.4. Nickel extraction increased with rising temperatures but cobalt's extraction decreased, only 11.66% Ni and 17.37% Co were the highest amounts leached at 90°C and 25°C, respectively. Both nickel and cobalt extraction values increased with increasing acid concentration, 8.61% Ni and 30.25% Co were the maximum values obtained after leaching with 4.0M. Cobalt extraction occurred at a faster rate than nickel

C. Effect of leaching time

The effect of leaching time was investigated by leaching at 25°C with different acid concentrations and leaching with

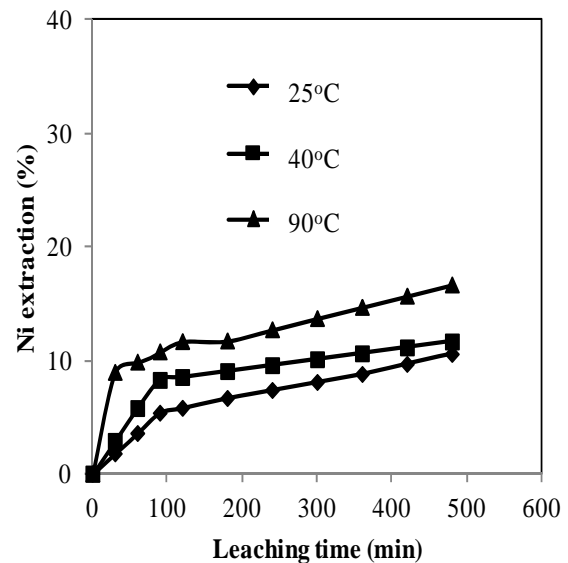


Fig. 6 Effect of leaching time on extraction of Ni with 1.0Molar acid concentrations at different temperatures

Evaluating the effect of time on nickel extraction using different acid concentrations (Fig.5) showed that at 25°C, increasing acid concentration does not have an influence on extraction of nickel even for a period of 480min, only 11.94% Ni could be leached with 4.0M.

When evaluating the effect of time at different temperatures (Fig.6), nickel extraction values only increased by very little amounts where only 16.66% Ni was extracted after 480min at 90°C. Cobalt extraction increased significantly with time when leaching at the different acid concentrations as well as at different temperatures (Fig.7 and Fig.8).

Leaching with 4.0M for 480min resulted in 59.32% Co in solution and about 39% at 40°C and 90°C.

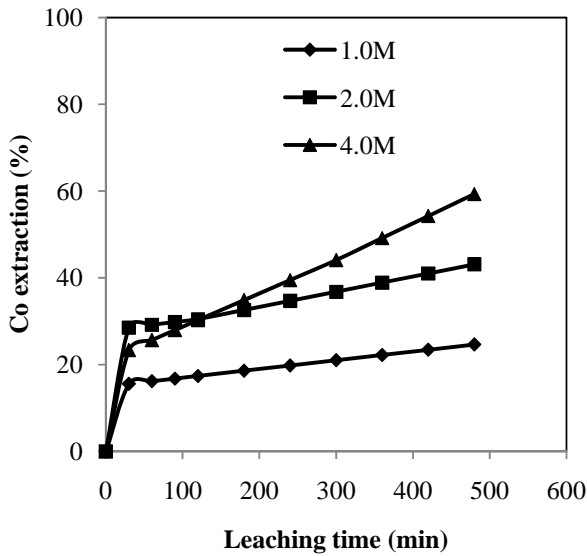


Fig. 7 Effect of leaching time on extraction of Co with different acid concentrations at 25°C

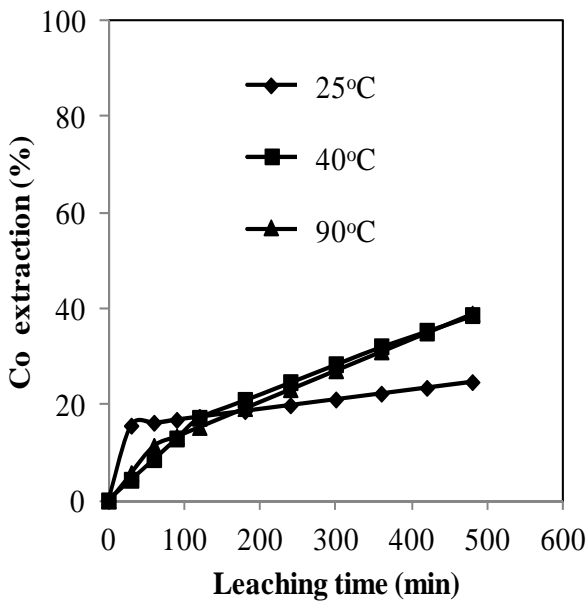


Fig. 8 Effect of leaching time on extraction of Co with 1.0Molar acid concentrations at different temperatures

D. Effect of particle size

The milled sample was classified into particle size fraction: -106+75, -75+45 and 45µm in the attempt to upgrade nickel concentration by screening. The chemical composition of the three particle size fractions was analysed by XRF and the results are given in TABLE II. Nickel concentration increased with decreasing particle size, -45µm contained three times as much nickel than the -106+75µm fraction. The tests were conducted at 25°C with constant acid concentration of 4.0M and stirring speed of 200rpm.

TABLE II
 CHEMICAL COMPOSITION OF THE DIFFERENT PARTICLE SIZE FRACTIONS

Particle size (µm)	Component (wt%)						
	SiO ₂	Others	MgO	Fe ₂ O ₃	CuO	Ni	Co
-106+75	49.53	35.22	5.93	9.23	0.01	0.02	0.01
-75+45	49.05	34.09	6.74	10.03	0.01	0.03	0.01
-45	49.06	33.93	6.27	10.58	0.02	0.06	0.01

Fig. 9 shows that nickel concentration for this material can be upgraded by sieving to various particle sizes and leaching the particle size fractions under suitable conditions. Extraction of nickel can be influenced by particle size, nickel leaching from coarse particle size resulted in extraction a maximum extraction value of 77.44% while the finest particle size, -45µm yielded 25.91% Ni. The low extraction values in the -45µm fraction could indicate that at in finer particle sizes are more interlocked and less liberated than those in coarse particle sizes.

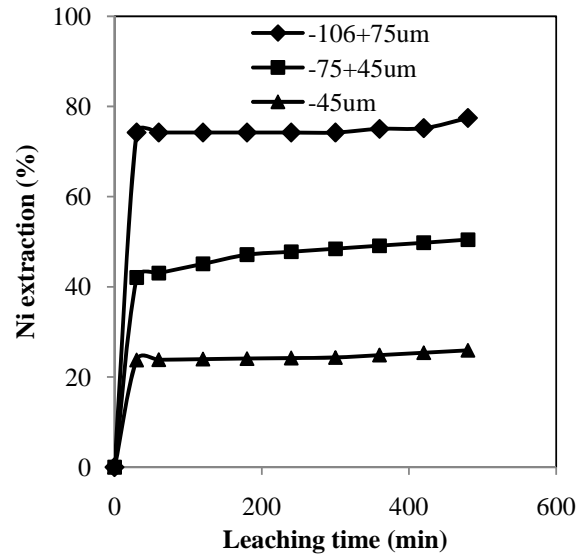


Fig. 9 Effect of particle size on extraction of nickel from the different sample particle sizes.

E. Kinetics of reactions

Data collected from leaching with 1.0M acid concentration at various temperatures was used to evaluate the leaching kinetics and to determine the activation energy for nickel. The kinetic models for describing the shrinking core models [18, 19] were considered:

$$1 - (1 - x)^{\frac{1}{3}} = k_c t \quad (1)$$

$$1 - 2/3 x - (1 - x)^{\frac{2}{3}} = k_d t \quad (2)$$

Where x is the fraction reacted, k is the reaction rate constant and t is the leaching time. Equation (1) assumes that the leaching rate controlling step is the chemical reaction occurring of the mineral particle surface while Equation (2) assumes the rate controlling step as the diffusion through the product layer on the particle surface.

The best linear fit for nickel extraction at various temperatures was found to be with Equation (2) (Fig. 10).

The Arrhenius plot was constructed using k values determined from leaching experiments as a function of the reciprocal of the different leaching temperatures, $1/T$ [20]. The activation energy for nickel leaching was calculated to be 18.16kJ/mol indicating that the leaching reaction was diffusion controlled.

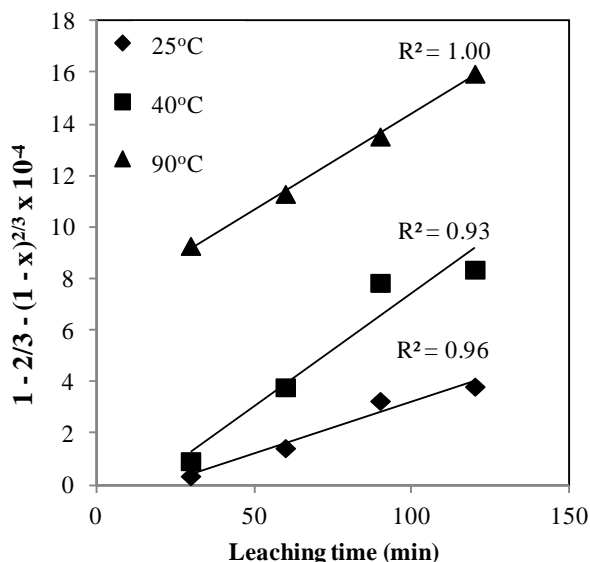


Fig. 10 Linear fit of nickel leaching kinetics at different temperatures

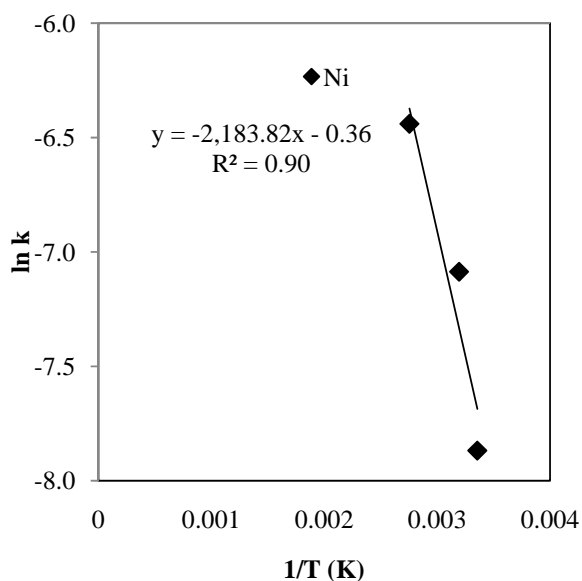


Fig. 11 Arrhenius plot for nickel leaching.

V. CONCLUSION

- Sulphuric acid leaching of the laterite ore has shown that nickel and cobalt can be extracted at atmospheric pressure.
- Nickel concentration in the ore can be upgraded by classification into different particle size fractions thus discarding size fractions that do not contain nickel.
- The best linear fit for $1 - 2/3 x - (1 - x)^{2/3}$ vs. time indicated that nickel leaching was diffusion controlled.

ACKNOWLEDGMENT

Authors would like to extend my gratitude towards my supervisor Dr R.K.K Mbaya and co-supervisor Dr K Kabongo, for their guidance and support throughout the work. Authors would also like to thank Ms. MM Ramakokovhu for her assistance in the experimental set up. Authors acknowledge the Tshwane University of Technology and South Africa's National Research Foundation (NRF) for the financial assistance offered to make this work a success.

REFERENCES

- [1] W. Luo, Q. Feng, G. Zhang and Y. Chen. Kinetics of saprolitic laterite leaching by sulphuric acid at atmospheric pressure. *Minerals Engineering* vol. 23, pp 458 – 462. 2010.
- [2] A. D. Dalvi, W. G. Bacon and R. C. Osborne. "The past and future of nickel laterites," *PDAC 2004 International Convention, Trade Show & Investors Exchange*, pp 1 -27. 2004
- [3] K. Liu, Q. Chen, H. Hu, and Z. Yin. Characterization and leaching behaviour of lizardite in Yuanjiang laterite ore," *Applied Clay Science*, vol. 47, pp 311 – 316. 2010.
- [4] J. P. Golightly and O. N. Arancibia. "The chemical composition and infrared spectrum of nickel- and iron-substituted serpentine from a nickeliferous laterite profile," *Can. Mineral*, vol. 17, no. 4, pp719–728. 1979
- [5] R. A. Oderinde, and E. O. Olanipekun. "Kinetics of hydrochloric acid leaching of laterite," *Pak. J. Sci. Ind. Res*, vol. 35, pp 77 – 80. 1992.
- [6] S. Teir, H. Revitzer, S. Eloneva, C. J. Fogelholm, and R. Zevenhoven, Dissolution of natural serpentinite in mineral and organic acids. *International Journal of Mineral Processing*, vol 83, 36–46. 2007.
- [7] A. E. Yüce, G. Bulut, F. Boylu and G. Önal. "Process flowsheet development for beneficiation of nickel ore," *Mineral Processing & Extractive Metallurgy Review*, vol. 29, pp 57–67. 2008.
- [8] D. Georgiou and V. G. Papangelakis. "Sulphuric acid pressure leaching of a limonitic laterite: chemistry and kinetics," *Hydrometallurgy*, vol. 49, pp 23–46. 1998.
- [9] W. Luo, Q. Feng, L. Ou, G. Zhang, and Y. Lu. "Fast dissolution of nickel from a lizardite-rich saprolitic laterite by sulphuric acid at atmospheric pressure," *Hydrometallurgy*, vol. 96, pp 171 – 175. 2009.
- [10] N. Panagiotopoulos and A. Kontopoulos. "Atmospheric Pressure Sulfuric Acid Leaching of Low-Grade Hematitic Laterites," *The Metallurgical Society*, pp 447- 459. 1988.
- [11] S. Chander. "Atmosphere pressure leaching of nickeliferous laterites in acidic media," *Transactions of the Indian Institute of Metals*, vol. 35, pp 366–371. 1982.
- [12] D. Neudorf. "Atmospheric Leaching Forum, ALTA 2007 Nickel/Cobalt 12," *ALTA Metallurgical Services*. 2007.
- [13] M. T. Anthony and D. S. Flett. "Nickel processing technology: a review," *Minerals Industry International*, pp 26–42. 1997.
- [14] J. H. Canterford. The sulphation of oxidized nickel ores. *International Laterite Symposium, Society of Mining Engineers. American Institute of Mining, Metallurgical, and Petroleum Engineers Incorporated*, pp 636–677. 1979.
- [15] A. L. Auzende, I. Daniel, B. Reynard, C. Lemaire and F. Guyot. "High-pressure behaviour of serpentine minerals: a Raman spectroscopic study," *Physics and Chemistry of Minerals* vol. 31, pp 269–277. 2004.
- [16] R. Hirasawa, and H. Horita. "Dissolution of nickel magnesium from garnierite ore in an acid solution," *International Journal of Mineral Processing*, vol. 19, pp 273 – 284. 1987.
- [17] G. Li, M. Rao, T. Jiang, Q. Huang and Z. Peng. "Leaching of limonitic laterite ore by acidic thiosulfate solution," *Minerals Engineering*. 2011.
- [18] F. Habashi. In: Principles of Extractive Metallurgy Vol. 1 Gordon & Breach vol. 1, pp 11–64. 1979.
- [19] H. Sohn and M. E. Wadsworth. "In: Rate Process of Extractive Metallurgy," *Plenum*, New York, pp 141–143. 1979.
- [20] I. Girgin, A. Obut and A. Üçyıldız. "Dissolution behaviour of a Turkish lateritic nickel ore," *Minerals Engineering* vol. 24, pp 603 -609. 2011.