International Journal of Multidisciplinary Education and Research
www.multidisciplinaryjournals.in
ISSN: 2455-4588
Received: 29-04-2023, Accepted: 15-05-2023, Published: 30-05-2023
Volume 8, Issue 2, 2023, Page No. 46-52

Leaching of oxide and silicate Ni laterites in dilute hydrochloric acid and aqua regia

Ifeoma Mary Ugwu
Department of Geology and Mining, Enugu State University of Science and Technology, Agbani, Nigeria

Abstract
Here we investigate the optimum leaching conditions to effectively extract nickel and cobalt as well as other metals in oxic and silicate Ni laterites. Metals were extracted using 2.75 M HCl and 2.75 M Aqua Regia in 0.01M $NaNO_3$ at 100 °C, with a 1.004 acid to ore ratio and a liquid to ore ratio of 10:1. Leaching of Ni laterites obtained from Cerro Matoso and Kalgoorlie, resulted to 100% Ni, 66.9 to 100% Co, 75.6 to 100% Al, 34.3 to 89.7% Fe, 87.6 to 100% Mg, 77.4 to 100% Mn extraction in 2.75 M HCl for 0.8 to 4 hours. In contrast, leaching of these Ni laterites in 2.75 M qua Regia for 0.3 to 6.7 hours. yielded 90.4 to100% Ni, 94.2 to 100% Co, 68.9 to 100% Al, 33.6 to 100% Fe, 93.5 to 100% Mg and 69.7 to 100% Mn. Aqua Regia with concentration of 2.75M is more effective for extraction of metals from high- and low-grade oxide and silicate Ni laterites compared to 2.75M HCl.

Keywords: Ni laterite, cobalt, nickel, leaching, aqua regia, hydrochloric acid

Introduction

Ni laterite deposits which are located at the tropical regions contribute 59.5% of the world Ni resources (Mudd and Jowitti 2014) [13], and have different mineralogy, grades, geologic ages and dissolution rates (Landers *et al*. 2009; Berger *et al*. 2011) [7, 1]. These variations influence the type of techniques used for extraction of the valuable metals found in Ni laterites. The amount of metal extracted, however, depends on the leaching conditions (Ndlovu *et al*. 2009; Wang *et al*. 2012; MacCarthy *et al*. 2014; Zhang *et al*. 2015) [14, 8, 10, 20]. Consequently, maximum leaching of Ni laterite at optimum conditions are crucial for the economics of Ni laterite.

Hydrometallurgical methods for Ni extraction have numerous advantages when compared to Pyro-metallurgical techniques including being more cost effective and having improved leaching conditions (Whittington and Muir 2008). The methods for hydrometallurgical extraction are High Pressure Acid leaching (Kaya and Topkaya 2011; Zhang *et al*. 2015) [20], Atmospheric Leaching (Wang *et al*. 2012; Li *et al*. 2012; Gao *et al*. 2014; Meng *et al*. 2014; MacCarthy *et al*. 2014; Guo *et al*. 2015) [8, 8, 4, 10, 6] Alkali roasting acid leaching (Guo *et al*. 2014) [4], heap leaching (Watling *et al*. 2011) [19], microbial leaching (Ndlovu *et al*. 2009) [14]. There are Geo-engineering problems associated with Heap leaching of Ni laterite in addition to a low recovery and high acid consumption, particularly for goethite rich ores (Watling *et al*. 2011; Quaicoe *et al*. 2014; Nosrati *et al*. 2014) [19, 15]. Among the hydrometallurgical techniques, Atmospheric leaching (AL) is considered to the best because of high extraction; reduced risk, cost and hazards; application to laboratories and use on an industrial scale; mild extraction conditions and effectiveness for oxide laterite. (McDonald and Whittington 2007; 2008). Inorganic acid (H_2SO_4, HNO_3 and HCl) atmospheric leaching of oxide laterites has been effective (Gao *et al*. 2014; Meng *et al*. 2015) [4] however, depending on cost and target metal of interest, these acids have their have their own particular advantages (McDonald and Whittington 2007; Zhang *et al*. 2015) [20].

In oxide laterite, goethite contains 0.003 to 3.923 wt.% Ni (Foose 1992; Trolard *et al* 1995; Glesson *et al* 2004; Landers *et al* 2009; Dublet *et al* 2012) [7, 3]. Goethite with a high Ni concentration is found in the saprolite zone whereas medium to low grades of Ni occur at the limonite zone (Glesson *et al*. 2004; Dublet *et al*. 2012) [3]. However, authors used different leaching method to extract nickel and cobalt from low- and high-grade Ni laterites. For example, leaching a mixture of equal amounts of oxide (1.02 wt.% Ni and 0.14 wt.% Co) and saprolite (1.99 wt.% Ni and 0.05 wt.% Co) laterites result in 96.6% Ni and 86.0% Co recovery using 2.75 M HCl at 10:1 ml/g acid to ore ratio for 60 minutes (Gao *et al*. 2014) [4]. In contrast, the leaching of Ni laterite from Yunnan province China with 0.47 wt.% Ni and 0.033 wt.% Ni in 8M HCl at a 4:1 acid to ore ratio, 0.15mm particle size and 80ºC for 2 hours results in 92.3% and 61.5% recovery of Ni and Co respectively (Li *et al*. 2012) [8]. Therefore, optimum leaching mechanism that can extract both low grade and high-grade Ni laterites is required.

To this end, we investigate and propose the leaching condition of extracting Ni and Co with 2.75M HCl and 2.75 M Aqua Regia in the presence of 0.01 M sodium nitrate.

Experimental material and method

A total of ten Ni laterites with different concentrations were used in this study. Five of these samples originated from Cerro Matoso (Cordilleran Ranges), Cordoba department, Colombia, and were provided by the British Natural History Museum. The remaining five are from Kalgoorlie, Western Australia provided by Heron Resources Ltd. These samples were dried at 105° C and sieved to fractions passing 106μm.

1. Atmospheric leaching of oxide Ni laterite with 2.75M HCl and 2.75 M aqua regia

These samples were dried at 105° C before weighing and were conducted with 2.75M HCl and 2.75 M Aqua Regia.

Leaching with Hydrochloric acid was carried out in 50ml polypropylene centrifuge tubes with 2.75 M HCl in 0.01M $NaNO_3$ in the ratio of 10 ml: 1.0 g ore. At different time intervals, 5ml was withdrawn from the homogenous suspension with a plastic syringe filtered through 0.22µm cellulose. One millilitre of mixture of 2.75 M HCl and 2.75 M HNO_3 in 0.01M $NaNO_3$ prepared in the ratio of 3:1 was added to 0.1g of ore in 50ml polypropylene centrifuge tubes. The experiments were conducted at 100°C in a shaking water bath and stirred at time interval. Nickel, cobalt and iron in the samples were analysed by Induced Coupled Plasma Atomic Emission Spectroscopy (ICP AES). All the acid used are Fisher Scientific PrimaPlus- Trace Analysis grade.

1. Experimental calculation

The metal recovery (%) of each ion during leaching is calculated using the equation below:

$$X_{metal}\% = \frac{V_{Leach}C_x}{M_{ore}W_x} \times 100$$

Where

C_x = metal concentration after leaching (gm/L)

M_{ore} = initial mass of the ore

V_{leach}= Volume of leaching solution (mL).

W_x = mass concentration of metal (wt.%)

3. X-ray powder diffraction

X – Ray diffraction measurements were obtained using a Cu Kα radiation on a Powder D8 diffractometer operated at 40 KV and 40 mA. The patterns were acquired at scan speed of 1 min^{-1} with slit size of 0.02°in the range of 10 to 70°.Mineral phases present were identified by matching with the database incorporated in EVA software (Bruker, 2006) [2].

Results and discussion

1. Mineralogy and chemistry of oxide Ni laterite

The XRD spectra of the limonitic Ni laterite from Kalgoorlie (Figure 1) reveals the mineralogical differences between the samples. In general, goethite is the dominant mineral with minor quantities of quartz, birnessite, maghematite, halite, cryptomelane and greenalite, lizardite and clinochrystolite.

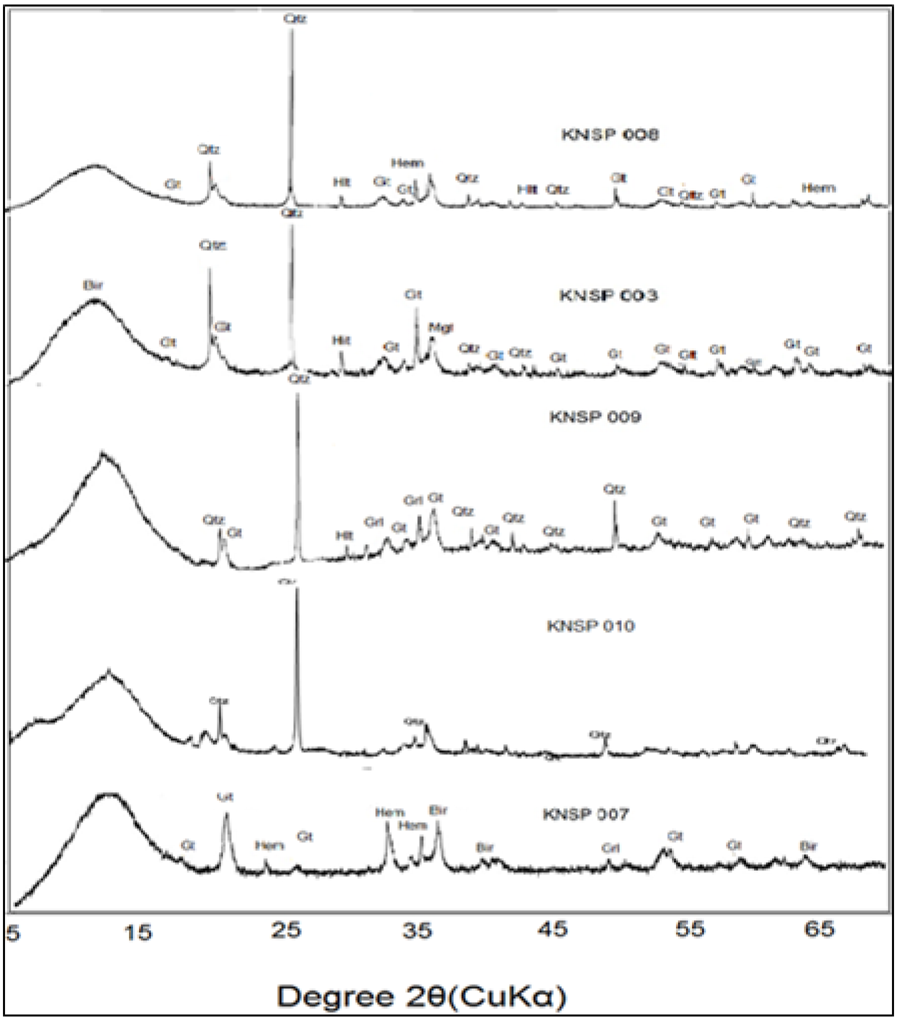

Fig 1: XRD patterns of Kalgoorlie oxide laterites with dominant minerals. Gt =goethite, Qtz = quartz, Hlt= Halite, Mgt = maghemite, Cyp =Crytomelane, Bir = birnessite, Grl = greenalite.

The XRD spectra of the silicate Ni laterite from Cerra Matoso (Figure 2) indicates that the dominant minerals areQtz = quartz, lizardite and clinochrystolite. The chemical composition based on Aqua Regia digest (Table 1) indicates that the samples are oxide Ni laterite with two main zones; limonite and saprolite, distinguishable by their silica, iron and magnesium contents.

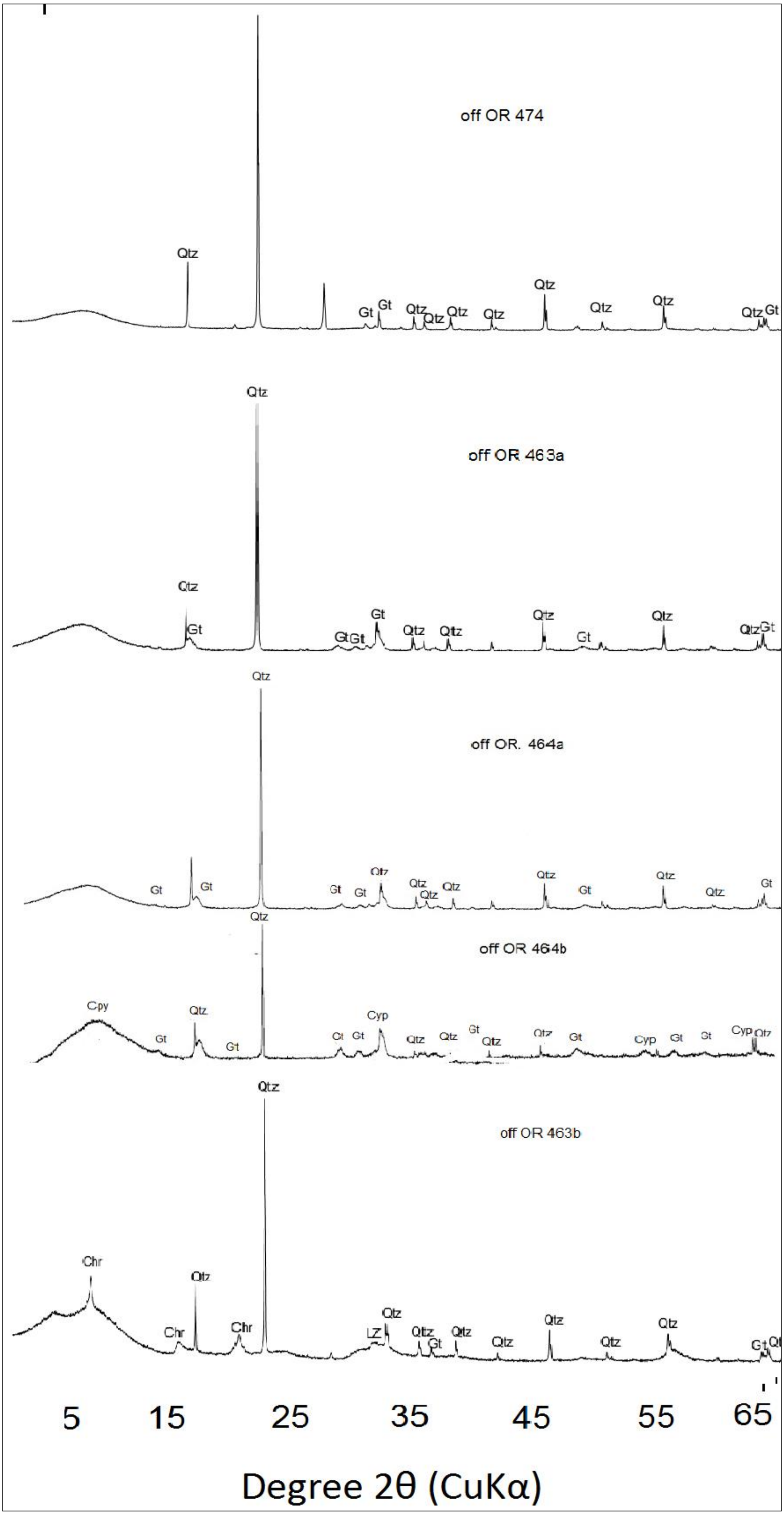

Fig 2: XRD patterns of Cerro Matoso silicate laterites with dominant minerals. Gt =goethite, Qtz = quartz, Lz = lizardite and Chr = clinochrystolite.

Table 1: Chemical composition of Oxide Ni laterite in weight percent based on Aqua Regia digest.

Location	Samples	Al	Ca	Co	Fe	K	Mg	Mn	Ni	Cr
Cerro Matoso	off OR. 474	0.478	0.061	0.050	14.81	0.002	0.680	0.465	0.77	0.092
	off OR. 464a	1.21	0.007	0.039	20.65	Bd	0.044	0.136	0.57	0.382
	off OR. 464b	0.111	0.004	0.015	46.20	Bd	0.017	0.067	0.84	0.213
	off OR. 463a	0.723	0.131	0.037	10.87	0.000	8.56	0.047	4.69	Nd
	off OR. 463b	0.266	0.072	0.041	8.41	0.011	9.33	0.105	4.54	0.058
Kalgoorlie	KNPS003	0.74	0.56	0.075	37.98	0.0119	0.81	0.55	1.32	0.51
	KNPS007	2.8	0.029	0.017	44.40	0.008	0.298	0.104	0.91	0.975
	KNPS008	0.609	0.028	0.034	33.84	0.005	0.201	0.263	0.98	0.639
	KNPS009	0.962	0.031	0.069	28.85	0.018	0.739	0.137	1.31	0.279
	KNPS010	0.769	0.047	0.321	16.07	0.044	2.12	1.08	1.75	0.142
	Big Four	1.800	0.008	0.028	40.83	0.012	0.528	0.049	0.69	0.362

Bd =below detection limit, Nd = not detected

Atmospheric leaching of oxide Ni laterite with 2.75 M HCl and 2.75 M aqua regia

The results of leaching oxide Ni laterite with 2.75 M HCl and Aqua Regia in 0.01M $NaNO_3$ at 100 °C, 1.004 acid to ore ratio and liquid to ore ratio of 10:1 indicate disparities in the rate of dissolution and amount of metal extraction between silicate Ni laterites from Cerro Matoso and oxide Ni laterites from Kalgoorlie. For example, sample Off OR. 474 with 0.77 wt.% Ni dissolved at a faster rate (Figure 3a) when compared to sample off OR. 464a (Figure 3c). For a given Ni laterite sample, leaching results using the same acids are different. Maximum extraction (100%) of Mn, Ni and Co were achieved in 45 minutes with 2.75M Aqua Regia (Figure 3a) whereas Al (99.8%), Mg (94.6%) and Fe (72.5%) were recovered at the same duration with 2.75M HCl from off OR. 474 (Figure 3b). In contrast, 100% recovery of Mn, Co, Ni and Mg (84%), Al (92.2%), Fe (60.72%) were achieved in 2.6 hours in sample off OR. 464a in dilute aqua regia (Figure 3c). However, more than 60% of all the metals were extracted in one hour in aqua regia compared to 40% metal extraction of these metals in one and half hours using 2.75M HCl (Figure 3d).

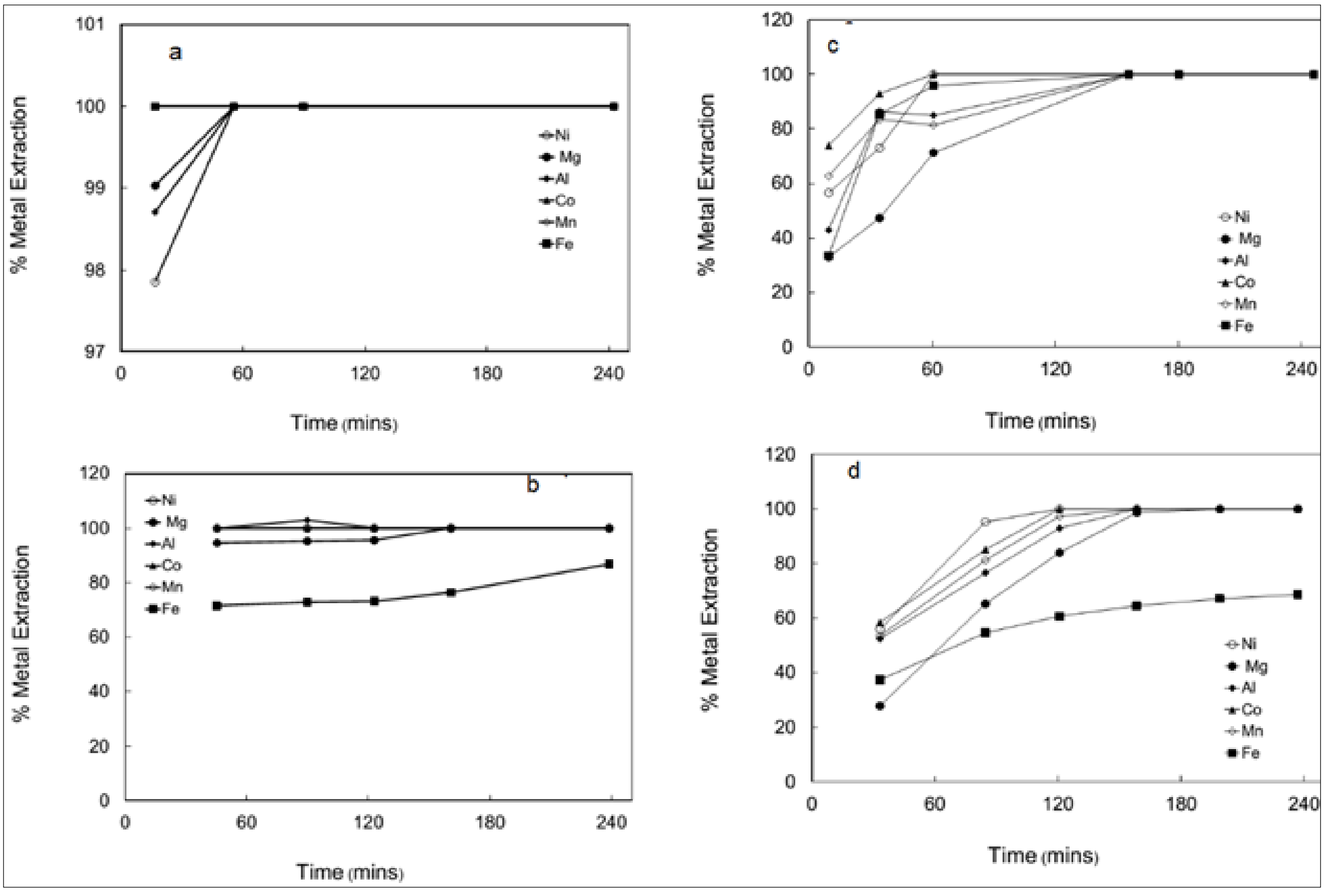

Fig 3: The plot of metal extraction (%) against leaching duration (time, mins) of off OR. 474 in a). Dilute Aqua Regia (2.75 M) b). HCl (2.75 M) and off OR. 464a. in c). Dilute Aqua Regia (2.75 M) c). HCl (2.75 M) in 0.01M NaNO3 with 10:1 liquid to ore ratio at 25°C.

Similarly. leaching of off OR. 463a resulted to more than 75% of nickel and cobalt extracted in one hour in 2.75 M aqua regia (Figure 4a) whereas only 60% of these metals were extracted in 2.75 M HCl (Figure 4b). About 95% of Co and 75% of Ni were extracted from sample Off 463b using 2.75 M aqua regia (Figure 4c) in 1 hr whereas 80% of nickel and cobalt can only be extracted in 90 minutes of extraction using 2.7M HCl (Figure 4d).

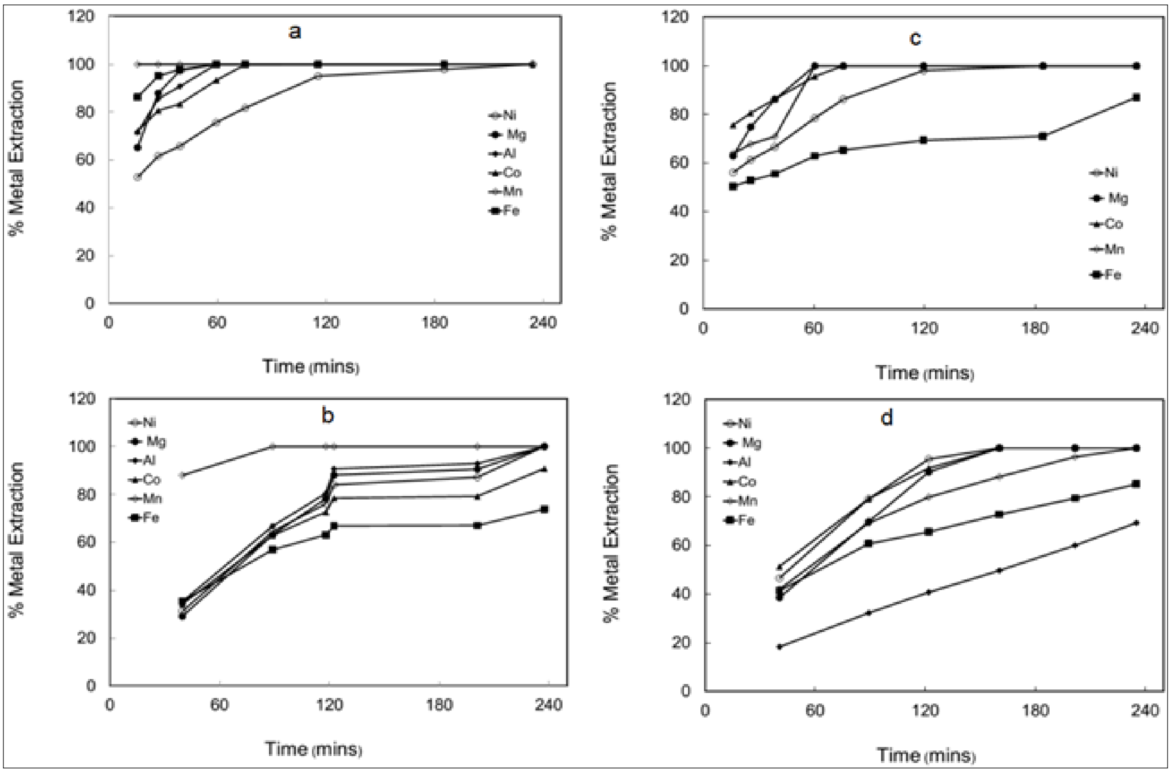

Fig 4: The plot of metal extraction (%) against leaching duration (time, mins) of off OR. 463a in a). Dilute Aqua Regia (2.75 M) b). HCl (2.75 M) and off OR. 463b in c). Dilute Aqua Regia (2.75 M) d). HCl (2.75 M) in 0.01M $NaNO_3$ with 10:1 liquid to ore ratio at 25°C.

In addition, 75% of nickel and cobalt in 1 hour using 2.75M aqua regia (Figure 5a) whereas 35% of cobalt and 38% of nickel in 100 minutes in 2.75M HCl for Big Four sample from Kalgoorlie (Figure 5b). About 50% of nickel and 55% of cobalt were extracted in 1 hour using 2.75M aqua regia (Figure 5c) and approximately 30% of nickel and cobalt in 90 minutes with 2.75M HCl for KNSP009 (Figure 5d). Similarly, 100% cobalt and 45% nickel in 1 hr using 2.75 M aqua regia (Figure 6a) and 38% nickel and 55% cobalt in 1 hr with 2.75 M HCl for sample KNSP 007 (Figure 6b). About 60% nickel and 72% Co were obtained in 1 hr in 2.75 M aqua regia (Figure 6c) and 50% nickel and 52% cobalt in 100 minutes in 2.75 M HCL from sample KNSP 003(Figure 6d). Also, 85% nickel and cobalt were extracted from KNSP 008 in 100 minutes using 2.75 M aqua regia whereas 30% cobalt and 40% nickel in 100 minutes using 2.75 M HCl.

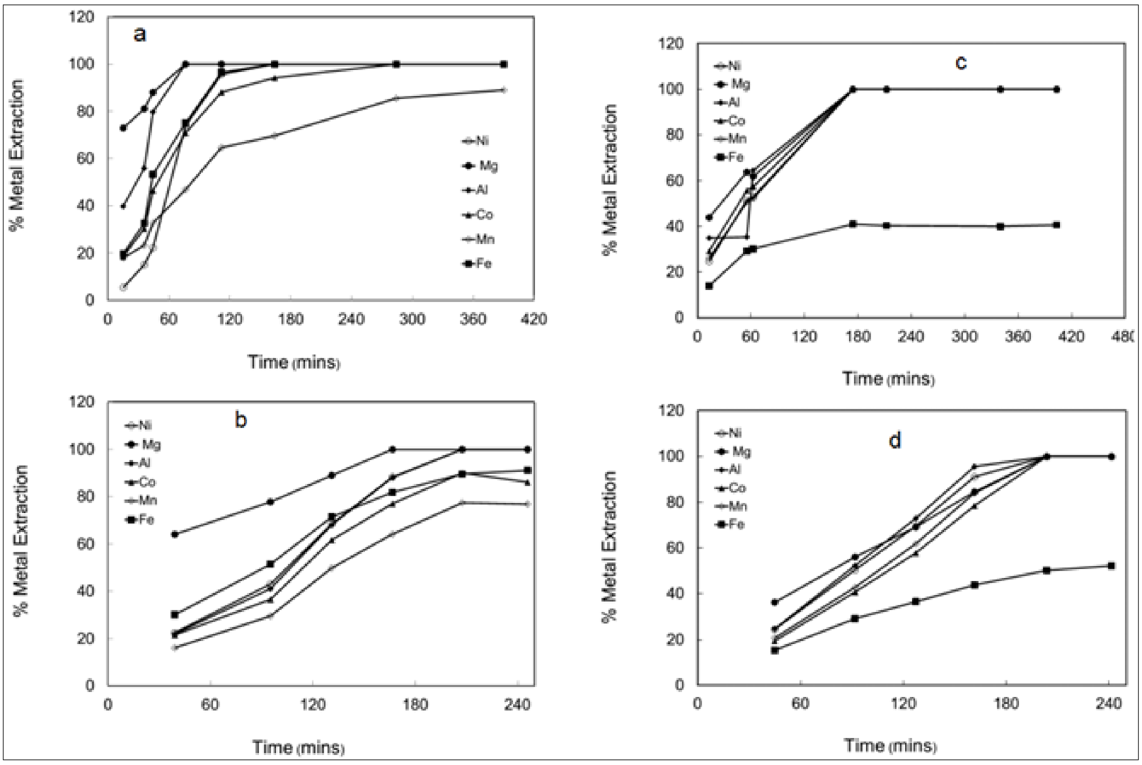

Fig 5: The plot of metal extraction (%) against leaching duration (time, mins) of Big Four in a). Dilute Aqua Regia (2.75 M) b). HCl (2.75 M) and KNSP009 in c). Dilute Aqua Regia (2.75 M) d). HCl (2.75 M) in 0.01M $NaNO_3$ with 10:1 liquid to ore ratio at 25°C.

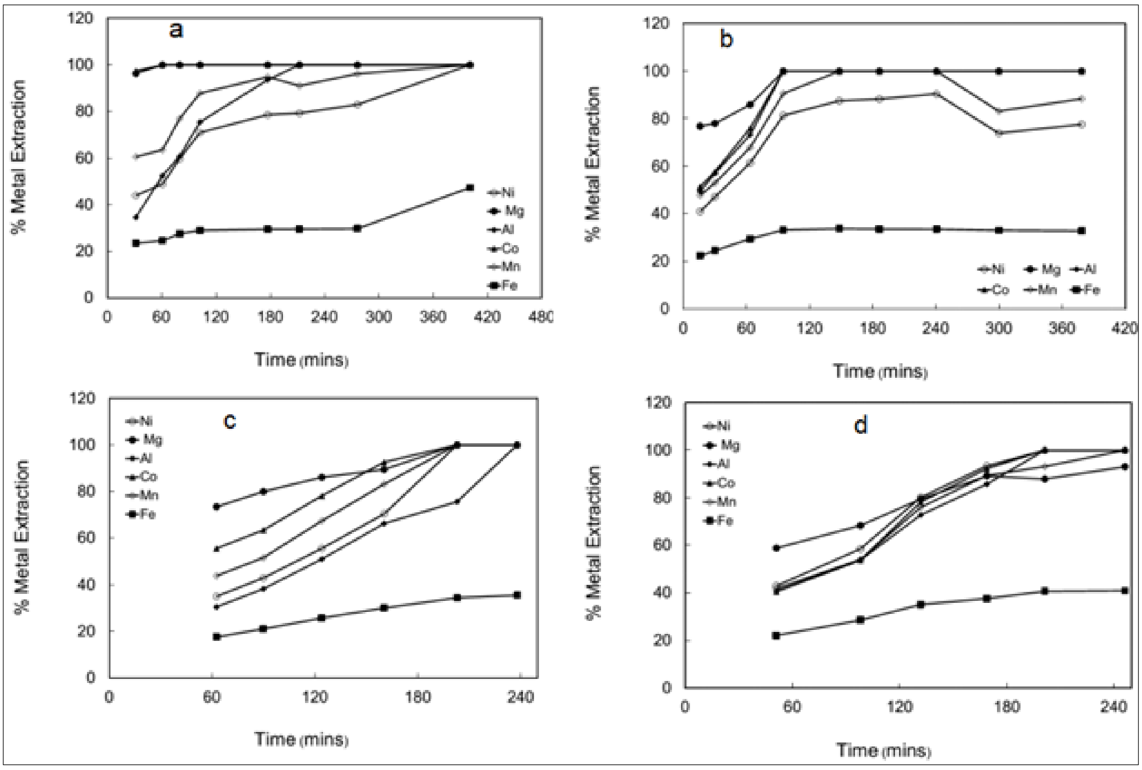

Fig 6: The plot of metal extraction (%) against leaching duration (time, mins) of KNSP 007 in a). Dilute Aqua Regia (2.75 M) b). HCl (2.75 M) and KNSP 003 in c). Dilute Aqua Regia (2.75 M) d). HCl (2.75 M) in 0.01M $NaNO_3$ with 10:1 liquid to ore ratio at 25°C.

In general, the optimum leaching time for oxide Ni laterite from Kalgoorlie (Figures 11 - 15) is approximately 3.4 hours at 100°C, acid to ore ratio of 1 whereas it is 2.6 hours for silicate Ni laterite in 2.75M aqua regia. However, the percentage recovery for the valuable metals differs significantly. For example, Big Four sample from Kalgoorlie leaching in 2.75M aqua regia achieved 100% Ni, 90.0% Co, 100% Al, 89.7% Fe, 100% Mg and 77. 4% Mn recovery in 3.5 hours. Leaching of Ni laterites obtained from Cerro Matoso and Kalgoorlie, resulted to 100% Ni, 66.9 to 100% Co, 75.6 to 100% Al, 34.3 to 89.7% Fe, 87.6 to 100% Mg, 77.4 to 100% Mn extraction in 2.75 M HCl for 0.8 to 4 hours. In contrast, leaching of these Ni laterites in 2.75 M Aqua Regia for 0.3 to 6.7hours. yielded 90.4 to100% Ni, 94.2 to 100% Co, 68.9 to 100% Al, 33.6 to 100% Fe, 93.5 to 100% Mg and 69.7 to 100% Mn.

Atmospheric leaching with 2.75 M Aqua Regia in 0.01 M $NaNO_3$ at 100 °C, 1.004 acid to ore ratio, 10:1 liquid to ore ration indicates that the extraction of these metals is faster and more effective compared to the results obtained from other acid leaching. For example, Mn, Co, Ni and Mg, Fe, Al was completely extracted from off OR. 464a in less than 2.6 hours whist a better recovery was achieved in 16 mins from off OR. 474. In contrast, the leaching of Ni laterite from Yunnan province, China with 0.47 wt.% Ni and 0.033 wt.% Ni in 8M HCl at 4:1 acid to ore ratio, 0.15mm particle size and 80ºC for 2 hours results to 92.3% and 61.5% recovery of Ni and Co, respectively (Li *et al*, 2012) [8]. In general, aqua regia leaching of Ni laterite is effective and maximizes recovery for the valuable metal at short durations. This indicates the syngeric effect of the two acids in extraction of oxide Ni laterite. Aqua Regia leaching is effective for oxide Ni laterite with both high- and low-grade Ni laterite. Depending on the metal of interest, 2.75M HCl or 2.75M aqua regia can be used (Table 2).

Table 2: Metal extraction from Atmospheric leaching with 2.75 M Aqua Regia in presence of 0.01 M $NaNO_3$ at 100 °C and 1.0 acid to ore ratio.

Oxide Ni laterite	Ni	Co	Al	Fe	Mg	Mn	Leaching Time (hrs)
Off OR. 464a	100	100	100	100	100	100	2.6
Big Four	100	94.2	100	100	100	69.7	2.7
Off OR. 474	97.9	100	98.7	100	99.0	100	0.3
KNSP 010	100	100	68.9	66.5	100	100	1.8
KNSP 009	100	100	100	41.0	100	100	2.9
KNSP 008	97.0	100	100	38.7	100	100	3.1
KNSP003	90.4	100	100	33.6	100	100	4.0
KNSP007	100	100	100	47.3	100	100	6.7
Off OR. 464b	95.5	100	100	100	93.5	100	4.0

Conclusion

This paper has investigated the optimum leaching conditions for extracting valuable metals from oxide and silicate Ni laterite. Leaching with 2.75 M HCl and 2.75 M Aqua Regia in 0.01M $NaNO_3$ at 100 °C, 1.004 acid to ore ratio and liquid to ore ratio of 10:1 reveals that metals in these laterites are extracted at a faster rate. In 2.75M HCl, 100% of Mn, Ni and Co, Al (99.8%), Mg (94.6%) and Fe (72.5%)

were leached from Cerro Matoso Ni laterite (off OR. 474) containing 0.77 wt.% Ni were achieved in 45 minutes. In contrast, 100% recovery of Mn, Co, Ni and Mg (84%), Al (92.2%), Fe (60.72%) was achieved in 2.6 and 4 hours from OR 464a (silicate Ni laterite from Cerra Matoso) and Big Four laterites (oxide Ni laterite from Kalgoorlie), respectively. In general, leaching with dilute 2.75 M Aqua Regia is best and effective for both high grade and low-grade Ni laterite. This indicates the synergic effect of the two acids in extraction of nickel and cobalt from Ni laterites.

Acknowledgements

Thanks to Natural History Museum, London and Heron Resources Ltd, Perth for providing the Ni laterites. We thank Dr. P.C. Choi for help with the ICP-OES analysis. This paper is a part of PhD thesis of Ifeoma M. Ugwu and was sponsored by the Tertiary Education Trust Fund (TETFund) of Nigeria.

Disclosure statement

The authors report there are no competing interests to declare.

References

1. Berger VI, DA Singer, JD Bliss, BC Moring. Ni-Co laterite deposits of the world; database and grade and tonnage models, 2011, 30.
2. Bruker. Diffraction Solutions D8 Advance, Germany, 2006. http://ksanalytical.com/wp-content/uploads/2012/02/D8_ADVANCE_e_72dpi_05.pdf. Assessed February, 2016.
3. Dublet G, F Juillot, G Morin, E Fritsch, D Fandeur, G Ona Nguema, *et al*. Ni speciation in a New Caledonian lateritic regolith: A quantitative X-ray absorption spectroscopy investigation. Geochimica et Cosmochimica Acta,2012:95:119-133.
4. Gao JM, ZK Yan, J Liu, M Zhang, M Guo. A novel hydrometallurgical approach to recover valuable metals from laterite ore. Hydrometallurgy,2014:150:161-166.
5. Gleeson SA, RJ Herrington, J Durango, CA Velasquez, G Koll. The mineralogy and geochemistry of the Cerro Matoso SA Ni laterite deposit, Montelibano, Colombia. Economic Geology,2004:99:1197-1213.
6. Guo Q, J Qu, B Han, P Zhang, Y Song, T Qi. Innovative technology for processing saprolitic laterite ores by hydrochloric acid atmospheric pressure leaching. Minerals Engineering,2015:71:1-6.
7. Landers M, RJ Gilkes, M Wells. Dissolution kinetics of dehydroxylated nickeliferous goethite from limonitic lateritic nickel ore. Applied Clay Science,2009:42:615-624.
8. Li J, D Xiong, H Chen, R Wang, Y Liang. Physicochemical factors affecting leaching of laterite ore in hydrochloric acid. Hydrometallurgy,2012:129:14-18.
9. Ma M, H Gao, Y Sun, M Huang. The adsorption and desorption of Ni (II) on Al substituted goethite. Journal of Molecular Liquids,2015:201:30-35.
10. MacCarthy J, J Addai Mensah, A Nosrati. Atmospheric acid leaching of siliceous goethite Ni laterite ore: Effect of solid loading and temperature. Minerals Engineering,2014:69:154-164.
11. McDonald RG, BI Whittington. Atmospheric acid leaching of nickel laterites review Part I. Sulphuric acid technologies. Hydrometallurgy,2008a:91:35-55.
12. McDonald RG, BI Whittington. Atmospheric acid leaching of nickel laterites review. Part II. Chloride and bio-technologies. Hydrometallurgy,2008b:91:56-69.
13. Mudd GM, SM Jowitti. A Detailed Assessment of Global Nickel Resource Trends and Endowments. Economic Geology,2014:109:1813-1841.
14. Ndlovu S, GS Simate, M Gericke. The microbial assisted leaching of nickel laterites using a mixed culture of chemolithotrophic microorganisms. Biohydrometallurgy: a Meeting Point between Microbial Ecology, Metal Recovery Processes and Environmental Remediation,2009:71-73:493-496.
15. Nosrati A, K Quast, DF Xu, W Skinner, DJ Robinson, J Addai Mensah. Agglomeration and column leaching behaviour of nickel laterite ores: Effect of ore mineralogy and particle size distribution. Hydrometallurgy,2014:146:29-39.
16. Radojevuć M, VN Bashkin. Practical Environmental Analysis. The Royal Society of Chemistry, Cambridge, UK, 1999.
17. Sidhu PS, RJ Gilkes, RM Cornelll, AM Posner, JP Quirk. Dissolution of iron-oxides and oxyhydroxides in hydrochloric and perchloric acids. Clays and Clay Minerals, 1981, 29.
18. Singh B, RJ Gilkes. Properties and distribution of iron oxides and their association with minor elements in the soils of south-western Australia. Journal of Soil Science,1992:43:77-98.
19. Watling HR, AD Elliot, HM Fletcher, DJ Robinson, DM Sully. Ore mineralogy of nickel laterites: controls on processing characteristics under simulated heap-leach conditions. Australian Journal of Earth Sciences,2011:58:725-744.
20. Zhang YL, Wang CY, Yang YQ, Yin F, Ma BZ. Pressure nitric acid leaching of alkali-pretreated low-grade limonitic laterite. Rare Metals,2015:34:64-70.