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Leaching of Low- Grade Nickel Ores by Fungi Metabolic Acids

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ABSTRACT

This study was designed to investigate the nature of nickel and cobalt dissolution from limonite and weathered saprolite ores. Chemical leaching was conducted using 1 to 3M of citric, lactic and malic acids. These tests aimed to mimic metal dissolution achieved using heterotrophic or fungi organism and their corresponding metabolic products. The results in this study was able to demonstrate the effect of secondary reaction or adsorption, pulp density and the potential hampering effect of acid neutralizing minerals and acid activity or strength on metal dissolution. Nickel and cobalt dissolution were also found to be dependent on the nature of the host minerals and amenability of these gangue minerals to dehydroxylate as a result of acid attack.

INTRODUCTION

At least 130 million tonnes of nickel are contained in global land-based resources. These contain an average of 1 to 3.5 percent nickel and in some cases more. About 60% are in the laterite form and 40% are in sulphide deposits ([1]). While nickel is the key product of interest, cobalt is extracted as the principle by-product from the ores. Escalating mining costs and diminishing sulphide reserves have pushed the demand for nickel laterite ores. In addition, laterite ores are available in vast quantities, have lower environmental impact and impose lower mining cost ([2]).

Commercial nickel laterite processing routes such as high pressure acid leaching, the Caron process, ferronickel and nickel matte smelting are energy intensive and have costly operations ([3]). There is therefore a need to implement alternative technologies to address the economic and environmental issues associated with laterite ore processing. Bioleaching is one such technology that has been gaining interest in recent years. The bioleaching of mineral oxides is based on the use of heterotrophic or fungi organisms and their metabolic products in dissolving metals. The incentive for green technologies, such as bioleaching processes, have been cultivated because of new government regulations and research policies that aim to address the ecological impacts of mineral processing ([4]). Previous studies have shown that laterite ores are amenable to leaching with the organic acid excreted by heterotrophic organisms ([5, 6, 7, 8]). The commercial application of the process has however been less successful due to process inefficiencies including poor metal recoveries.

Attempts have been made to elucidate the dissolution behavior of the laterite minerals in the bioleaching process. These studies demonstrate the chemical

leaching behavior of nickel laterite minerals as a function of types of acids, particle size, pulp density, temperature, period of leaching (<u>3, 5, 6, 7, 9, 10, 11</u>). Most researchers suggest that citric acid is the most effective for nickel extraction in comparison to other metabolic acids. Others suggest that oxalic acid is the most effective in leaching laterite minerals (<u>10</u>). The lack of consistency among researchers in regard to the effectiveness of these metabolic acids suggest that further work is required to clarify this aspect of the process. Comparisons of the leaching properties of the acids have been based on similar concentrations of acids. The hydronium ions present in solution are expected to assist in the attack of OH^- groups in mineral gangue and should facilitate metal dissolution. Assessment of the effectiveness of the acids should therefore be based on comparisons of hydronium ion concentrations. Poor dissolution of nickel from limonite in comparison to the saprolitic minerals was also commonly observed among these investigations. However this observed phenomena appears lacking.

This study investigated the nature of the dissolution behavior of nickel and cobalt from limonite and saprolite ores using citric, malic and lactic acids. Oxalic acid was omitted from this study because of its tendency to form very stable precipitates during the leaching process (<u>8</u>). This study systematically investigated the role and selectivity of these metabolic acids by taking into account the effect of acid strength in metal dissolution. In addition, the effects of electrosorption, pulp density, and mineralogy on metal extraction were also examined.

EXPERIMENTAL SECTION

Ore Materials

The laterite ores used in this study are limonite and weathered saprolite from New Caledonia. Limonite minerals consist mainly of goethite, while weathered saprolite is characterized by its rich magnesium silicate content. These ores were milled to an average size of 64µm. The chemical analyses of these ores are shown in Table 1. These compositions are typical of commercial grade nickel laterite ores.

Table 1. Chemical analyses of limonite and weathered saprolite ores.

Ore Type	Al (wt%)	Co (wt%)	Cr (wt%)	Cu (wt%)	Fe (wt%)	Mg (wt%)	Mn (wt%)	Ni (wt%)	Zn (wt%)
Limonite	2.14	0.25	0.78	0.044	39.5	2.85	1.07	1.66	0.14
Weathered Saprolite	0.46	0.11	0.089	0.030	11.24	10.64	0.17	3.62	0.034

Zeta Potential

The Malvern Zetasizer was used to measure the ore gangue surface charge. These data were used to establish the potential electrochemical adsorption of metals on the gangue matrix during leaching. Samples were prepared by suspending finely ground ore particles (~mean diameter 1-2µm) in 0.1M $NaNO_3$ for 24 hours. The

solution pH was adjusted using HCl and NaOH. The zeta potential of the minerals was then measured as a function of solution pH.

Chemical Leaching

Analytical grade reagents of citric, malic and lactic acids were used in preparing acid concentrations of 1 to 3M. These acids were used in chemical leaching tests that mimicked metal dissolution achieved by heterotrophic micro-organisms and their metabolic products. Leaching tests were conducted using pulp densities comprising of 2, 3.5, 5, 7.5 and 10 (w/v)%. The slurries were shaken at the rate of 120rpm in a thermally controlled environment where temperature was fixed of 30ºC. The pH of each slurry was monitored using pH-mV-temp meter (TPS WP-80D) The extent of leaching was monitored by taking sub-samples of the slurry and measuring the dissolved metals by Varian Vista AX CCD Inductively couple plasma atomic emission spectrometry (ICP-AES) using standard procedures.

Mineralogical Analyses

Mineralogical analysis of the raw and leached ore residues were carried out using synchrotron-based X-ray powder diffraction in the Australian National Beamline Facility at the Photon Factory in Japan. This facility was accessed through the Australian Synchrotron Research Program. The procedure included loading the ore in a 0.3 mm glass capillary tube. The capillary tube was placed and aligned in front of the X-ray beam using a goniometer. Studies were conducted in vacuum with a gauge pressure of 1 torr. The X-ray wavelength of 1.1 Å and a current of 400 mA were used.

RESULTS AND DISCUSSION

Surface Charge of Laterite Minerals.

The magnitude of the zeta potential is synonymous to the relative charge on the surface of the particle. When the zeta potential is positive, the net particle charge around the diffuse layer of the particle is generally considered positive. A negative zeta potential indicates a negatively charged particle. Zeta potential varies as a function of solution pH. A zeta potential will be positive at low pH and negative at high pH. There is a point where this plot passes through a zero zeta potential. This point is called the isoelectric point. The point zero charge (pH_{IEP})of the ore gangue obtained at various periods of leaching are summarized in Table 2.

Table 2. PH_{IEP} of laterite ore minerals ([3])

Ore Type	pH_{IEP}
Limonite	6.6
Weathered Saprolite	3.8

PH_{IEP} values give an indication of the likely charge of the particle with pH and provide a useful indication of optimum conditions for adsorption to occur. Martell

([12](#)) suggested that positively charged nickel ($NiH_2C_{it}^+$, $NiHM_{al}^+$, and NiL_{ac}^+,) cobalt ($CoH_2C_{it}^+$, $CoHF_{al}^+$, and CoL_{ac}^+) and iron complexes ($FeH_2C_{it}^{2+}$, $FeHM_{al}^{2+}$, and FeL_{ac}^{2+}) occur predominantly at pH below 3. The citric acid ligand is $H_2C_{it}^{-1}$ ($HO_2C.CH_2.C(OH)(CO_2H).CH_2.CO_2^{-1}$), the dl-malic ligand is HM_{al}^{-1} ($HO_2C.CH_2.CH(OH).CO_2^{-1}$), and the lactic acid ligand is L_{ac}^{-1} ($CH_3.CHOH.CO_2^{-1}$). The electrosorption mechanism suggests positively charged metal complexes would be effectively adsorbed onto a negatively charged particle. pH higher than the isoelectric points of the gangue, as shown in Table 2, should promote the adsorption of nickel, cobalt and iron complexes. Figure 1a suggests the amount of nickel adsorbed onto the ore gangue increases as solution pH increases beyond the respective isoelectric points of 6.6 and 3.8 for limonite and weathered saprolite respectively. Figure 1a shows adsorption of nickel complexes on weathered saprolite gangue increased from 0.3g Ni/ g ore at pH 3 to 1.1g nickel/ g ore at pH 4.2. Similarly, adsorption on limonite gangue increased from 1.2 g Ni/ g ore at pH 4.2 to 2.6g Ni/ g ore at pH 7.7. These results confirm leaching at solution pH higher than the isoelectric point results in greater electrosorption effect resulting in lower metal recoveries. Figure 1b shows the relative quantity of nickel removed from solution by adsorption can be significant particularly at high solution pH.
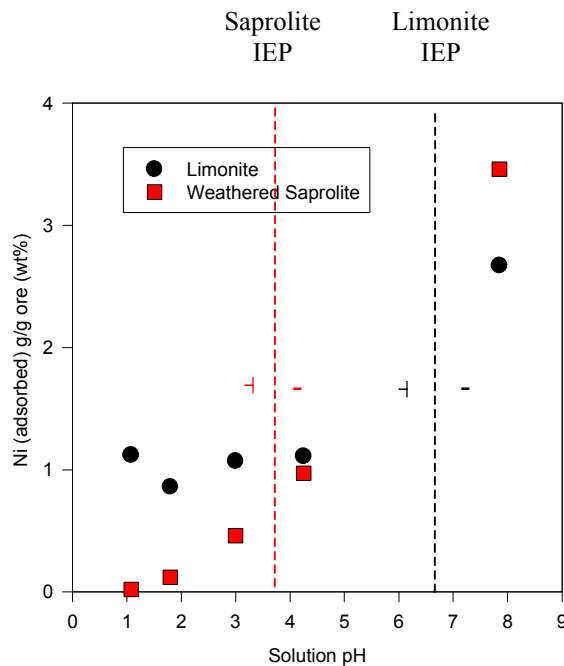

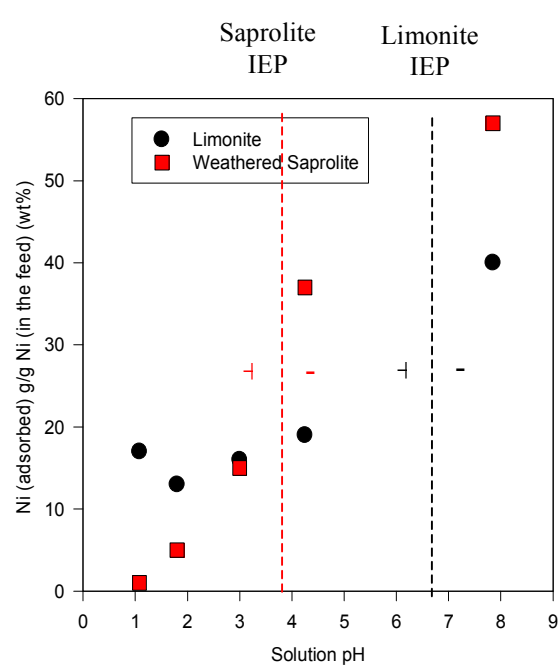**Figure 1a. Nickel adsorption onto the ore gangue as a function of solution pH.**

Figure 1b. Percentage nickel removed from solution by adsorption onto the gangue as a function of solution pH.

Table 3 compares the nickel and cobalt recoveries from limonite and weathered saprolite leached at solution pH below and above the isoelectric points of the mineral gangue. As shown, although there appears to be little difference in the

recoveries of cobalt when leaching was conducted at solution pH above the pH_{IEP} of the mineral gangue, nickel recoveries were reduced by almost 40%. This is consistent with the expected nickel loss by adsorption shown in Figure 1b, which is quite significant for metal extraction process. These results emphasises the relative importance in controlling this phenomenon.

It was also observed from these results that cobalt recoveries from limonite are consistently higher than nickel recovered from limonite ore. The opposite is true for weathered saprolite, where nickel recoveries are higher than cobalt. We propose that the relative selectivity of nickel and cobalt could be associated with the host minerals that contain these metals in these particular ores. This will be examined further in the latter part of this paper.

Table 3. Effect of secondary reaction (adsorption) on nickel and cobalt recoveries from limonite and weathered saprolite using citric acid after 8 days of leaching.

Type of Ore	PH_{IEP}	PH Above PH_{IEP}			PH Below PH_{IEP}		
		Solution pH	Ni (wt%)	Co (wt%)	Solution pH	Ni (wt%)	Co (wt%)
Limonite	2.5	2.6	16	58	1.58	27.3	55.1
Weathered Saprolite	2.0	3.3	38	34	1.94	67.3	33.6

Effect of Acid Activity and Type of Acids

To investigate the relative effectiveness of the various metabolic acids, metal dissolutions were related to the acid activities. The action of the hydrogen ion enables metals to dissolve in solution and should therefore be used as a basis for assessing the effectiveness of the acids. The acid activity is defined in this study as the concentration of hydronium ions (H+ or H_3O^+) present in solution. Acids (HA) dissociate in water to form the hydronium ion (H^+) and the anion (A^-) as follows:

$$HA \leftrightarrow H+ + A-,$$ (1)

 The H+ concentration is dictated by the acid dissociation constant (Ka) which is a specific type of equilibrium constant that indicates the extent of dissociation of hydrogen ions from an acid. Strong acids dissociate practically completely in solution and consequently have large acidity constants while weak acids do not fully dissociate and generally have acidity constants far less than 1. The dissociation constants of the various acids used in this study are shown in Table 4.

Table 4. Dissociation constants of citric, malic and lactic acid (13).

Type of Acid	Step	Temperature °C	pKa
Citric	1	20	3.14
	2	20	4.77
	3	20	6.39
Malic	1	25	3.4
	2	25	5.11
Lactic	1	20	3.85

As shown in Table 4, the relative strength of the acids as suggested by the dissociation constant is citric, malic then lactic acid. To confirm this order, the hydrogen activities of the leaching solutions were estimated from the measured pH prior to leaching by:

$$H^+(mole/litre) = 10^{-(pH)}$$

(2)

The extent of nickel and cobalt dissolution from limonite and weathered saprolite were related to the corresponding acid activities in Figures 2 and 3 respectively.
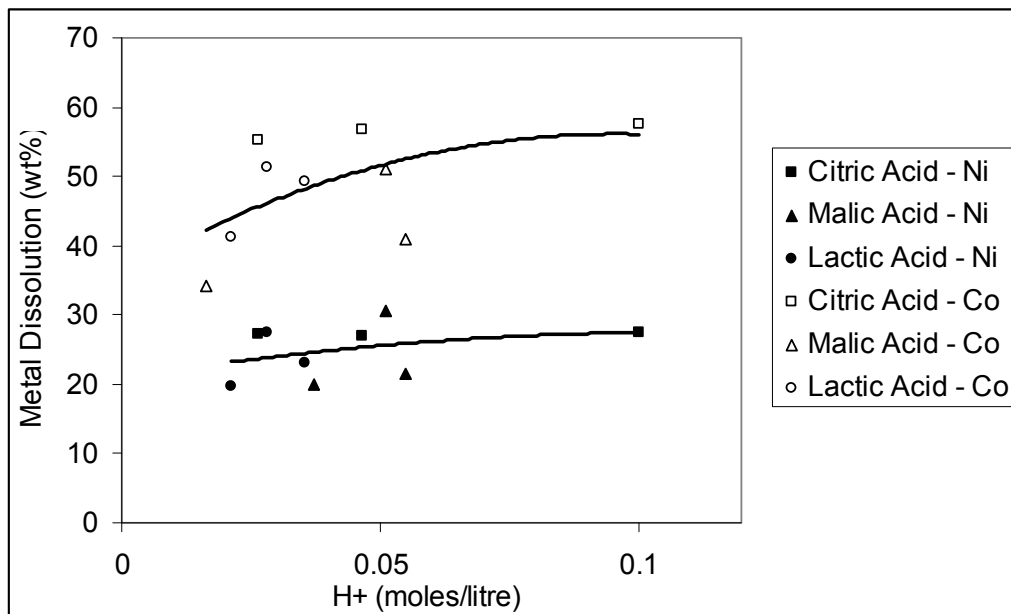
Figure 2. Nickel and cobalt dissolved from limonite after 8 days of leaching with citric, malic and lactic acid as a function of acid activity.
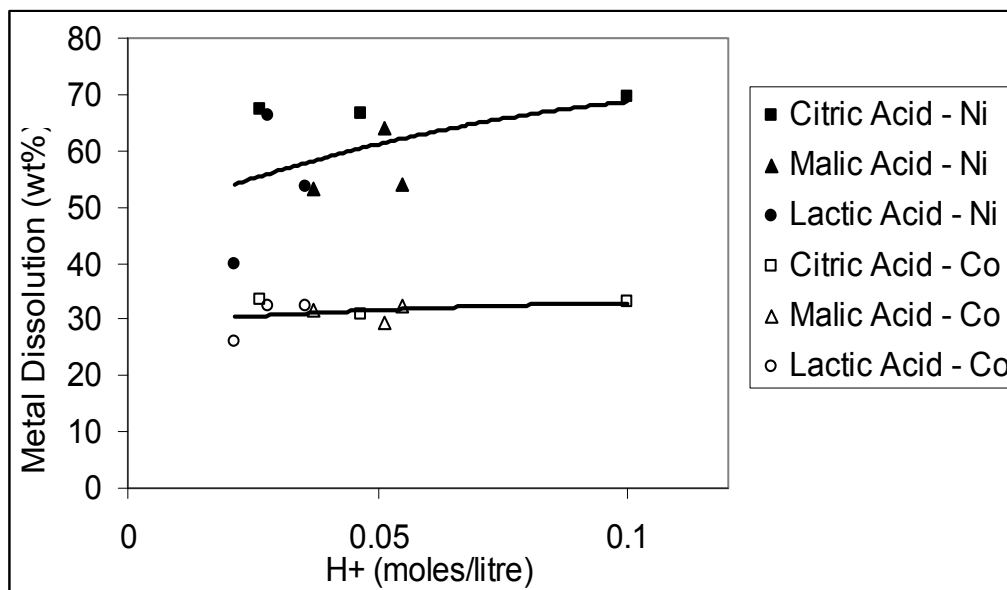
Figure 3. Nickel and cobalt dissolved from weathered saprolite after 8 days of leaching with citric, malic and lactic acid as a function of acid activity.

Although there is some scatter in the data, Figures 2 and 3 suggest that the extent of metal dissolution is independent of the type of acids but rather nickel and cobalt dissolution are dependent on the hydronium ion concentrations. The effectiveness of citric acid in dissolving nickel and cobalt is associated with the strength of this acid or its ability to dissociate in solution. Optimum dissolutions of both metals were achieved at an acid activity of 0.1 moles/litre. A consistent optimal acid activity for dissolving both nickel and cobalt is of importance for practical application. In addition since several metabolic acids are produced by the fungi, the independence of metal dissolution from the types of acids is also of an advantage as it removes the need to produce a specific type of acid to optimise the extent of leaching. The difference in selectivity observed for nickel and cobalt from limonite and weathered saprolite ores is proposed to be associated with the reactivity of the host gangue in these ores. This aspect will be elucidated further in the later section of this paper.

Effect of Pulp Density

Figures 4 and 5 show the effect of pulp density on nickel and cobalt dissolution from limonite and weathered ores saprolite respectively. Leaching was conducted using 3M acid for 8 days.
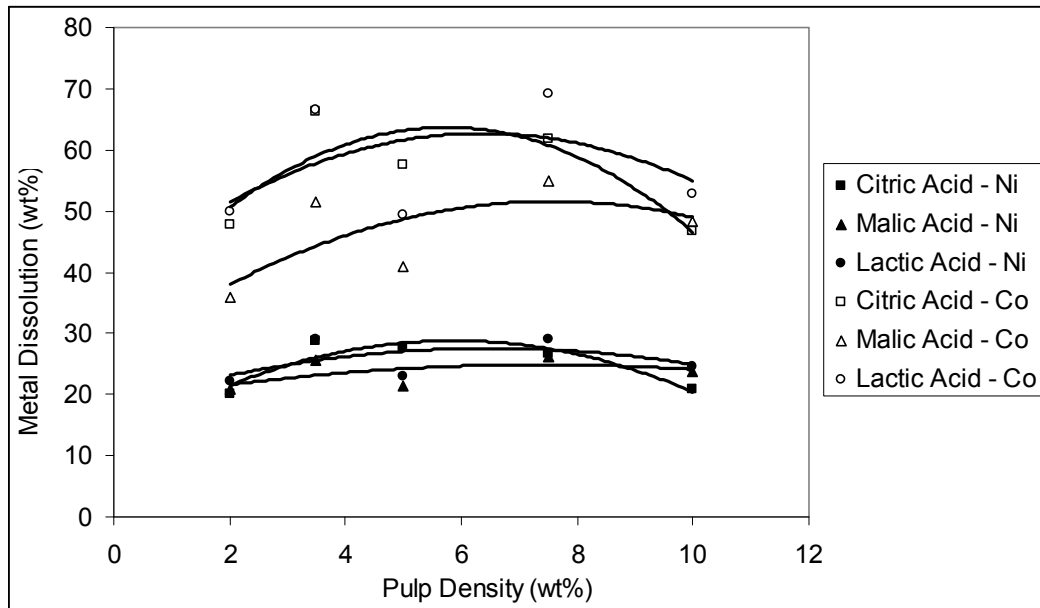
Figure 4. Nickel and cobalt recovery from limonite as a function of pulp density after 8 days of leaching.
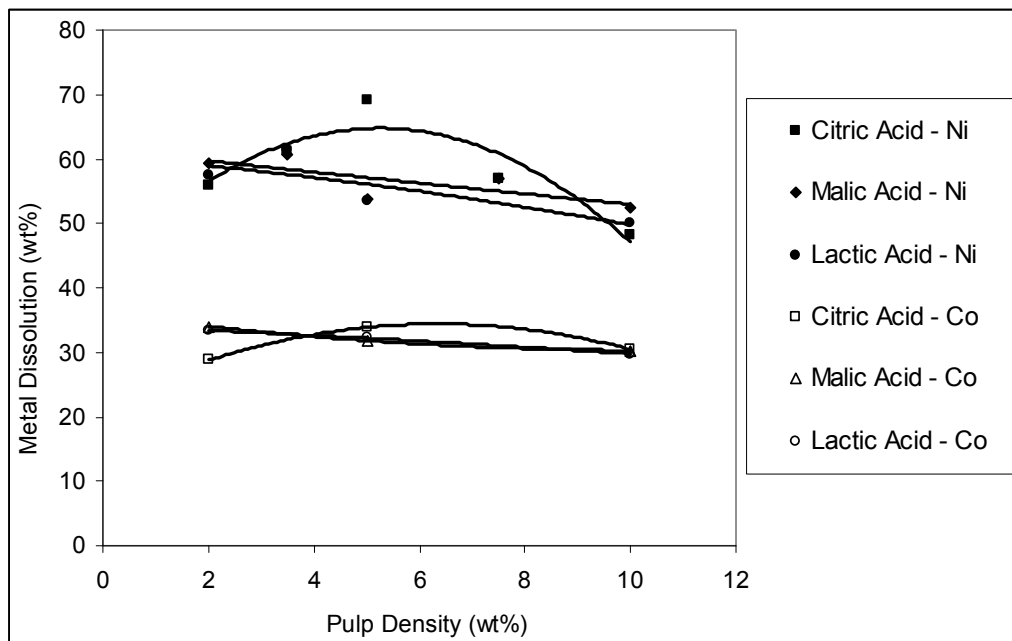

Figure 5. Nickel and cobalt recovery from weathered saprolite as a function of pulp density after 8 days of leaching.

Optimal nickel and cobalt dissolution in limonite as shown in Figure 4 occurs at a pulp density of 7.5wt%. Additional reduction in ore load did not improve metal recovery. Weathered saprolite in Figure 5 was however shown to have optimal recoveries at lower pulp densities (2- 5.8 wt%). This suggests that limonite is more amenable to acid attack at higher ore loading and this could be associated with its lower content of acid neutralising magnesium minerals often present in high quantities in saprolite ores (see Table 1). As shown in Table 3, weathered saprolite,

for the same loading ratio achieves a higher pH compared to limonite. Consumption of acids by the gangue minerals has a significant implication to the economics of processing laterite ores by any form of acid leaching process.

## Mineralogical Analysis of Laterite Gangue

The mineralogical contribution to the variation in recovery was established by examining the raw ores and leached residues using optical microscopy and synchrotron-based X-ray diffraction. Low energy X-ray diffraction was unsuccessful in providing resolution for minor phases, particularly of the leached residues which comprised of a mixture of amorphous and minor crystalline phases. Synchrotron diffraction provided high resolution diffraction information, allowing the complex leached residue phases to be resolved. Figures 6 (a to c) and 7 (a to c) demonstrate the synchrotron X-ray diffraction results of raw and leached limonite and weathered saprolite residues respectively. These minerals were leached with 1M acids at 25 °C. The sub-labels a, b and c represent XRD patterns of citric, dl-malic and lactic acid leached mineral residues.

The only notable change in the limonite minerals (see Figures 6a, 6b and 6c) is the disappearance of the serpentine peak at 2Ө of 8.6. The lack of change in the goethite peaks suggest that the main constraint in leaching metals from limonite ore with organic acids appear to be related to the inability of organic acids to dehydrate this mineral gangue. This is associated with the fact that goethite will not dehydroxylate to hematite until it is heated to 130ºC ([14]). The lower nickel recovery from limonite (see Figures 2 and 3) suggests that nickel is associated with the goethite phase, whereas cobalt, which appears to dissolve easily is hosted by the serpentine minerals. The use of low temperature, 30ºC, in this chemical leaching process hampered the required mineral dehydroxylation that allows nickel dissolution in this bioleaching process. This study shows that nickel and cobalt in this bioleaching process require the host minerals to be converted to reactive or dehydroxylated phases.

Figure 7(a-c) shows the susceptibility of weathered saprolite gangue (hydro magnesium silicate minerals) to organic acids. With the mineral residues produced by leaching with citric acid (see Figure 7a), the serpentine signals, at 2Ө of 8.6, labeled S weakened with leaching. This was followed by the formation of broad peaks at 2Ө of 15.0 and diminishing quartz peak (labeled Q) at 2Ө of 18.9. The development of broad peaks and the eventual loss of mineral signals with leaching reflect the dehydration of magnesium hydrosilicate mineral to form an amorphous magnesium silicate phase ([15], [16]). Amorphous structures are more unstable in comparison to crystalline phases and consequently are more amenable to acid attack. This is consistent with a previous study on the effect of citric acid leaching in laterite minerals ([11]). A similar pattern of behavior was observed with mineral residues of weathered saprolite produced by dl-malic and lactic acid leaching (see Figure 7b and 7c). Dl-malic and lactic acids do not appear to have significant effects on the serpentine peak at 2Ө of 8.6, as this peak remained strong with leaching. This peak is associated with three serpentine phases, lizardite, antigorite and

chrysotile. Other serpentine peaks, however, at 2Ө of 20.9, 32.5 and 35.2 have in contrast diminished with both dl-malic and lactic acid leaching. These peaks are associated primarily with the lizardite and antigorite forms of serpentine. As suggested above, citric acid is relatively a stronger acid in comparison to dl-malic and lactic acids. This implies the chrysotile phase is refractory to dl-malic and lactic acid at the concentration (1 M) used in generating these mineral residues. Figures 2 and 3 would suggest that if the concentrations of dl-malic and lactic acids were consistent with 1M citric acid, then similar dehydroxylation would be achieved. The formation of broad peaks with malic and lactic acid leaching further confirms the amenability of the serpentine (lizardite and antigorite) minerals to acid attack.

Correlation of the observed mineral transformation in Figures 7(a to c) with the nickel and cobalt dissolution in Figure 2 and 3, suggest the association of nickel and cobalt to the gangue within this ore. The greater dissolution of nickel from weathered saprolite suggest that this metal is hosted by the serpentine minerals and the poorer dissolution of cobalt suggest that this mineral may be partially incorporated within the goethite matrix.
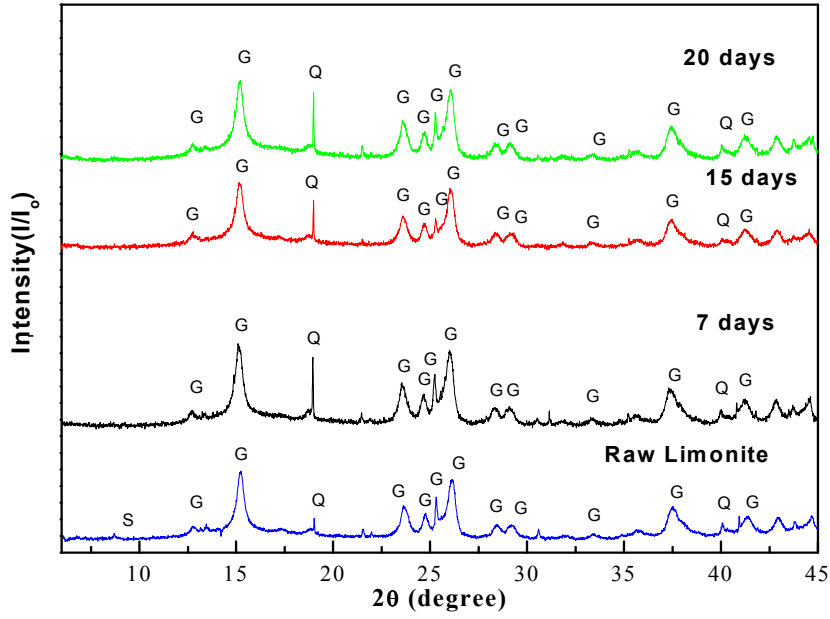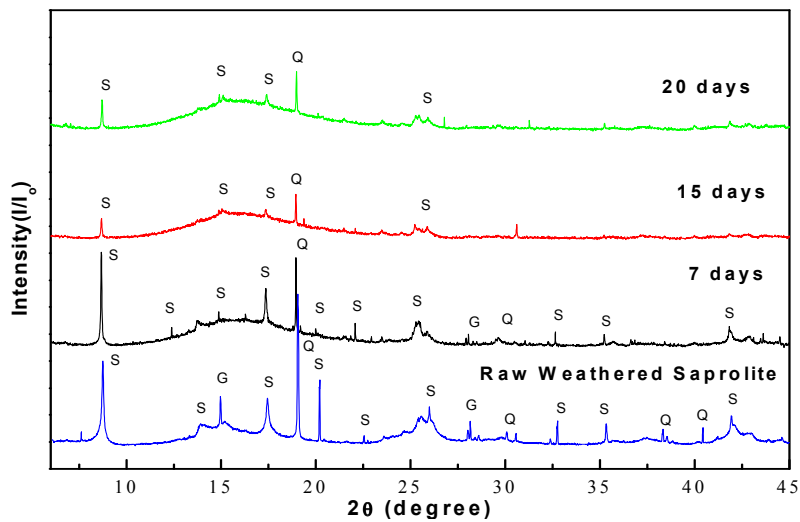
(a)
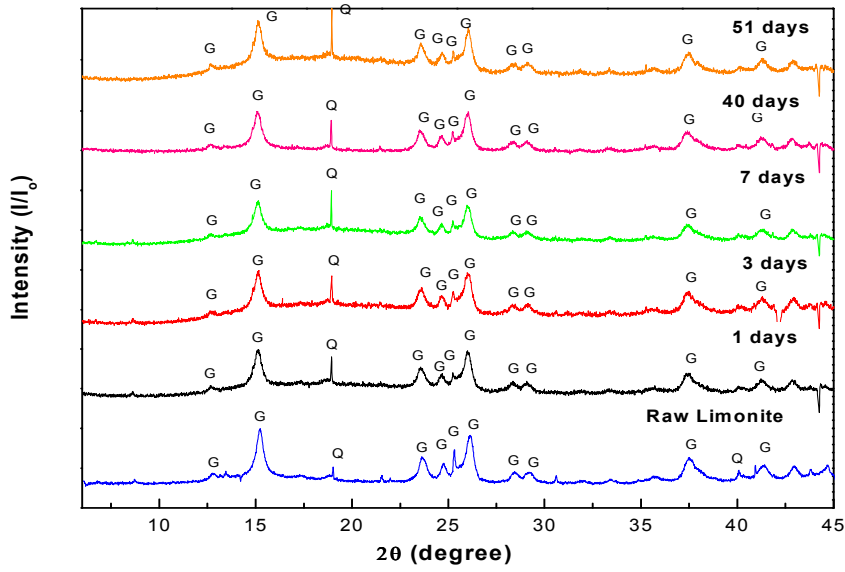
(b)
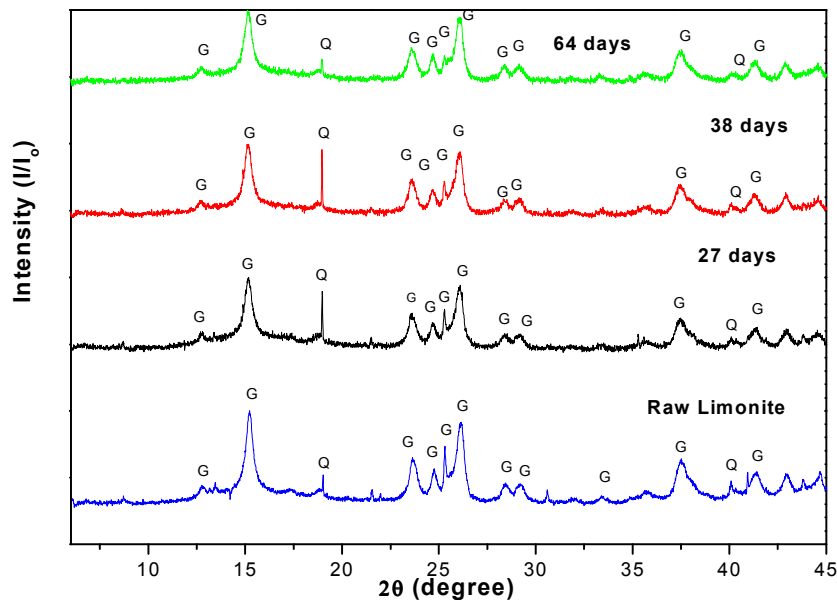
(c)

Figure 6. X-ray diffraction pattern of limonite residues leached with 1M a) citric, b) dl-malic and c) lactic acids as a function of time. (G: goethite, S:serpentine, Q:quartz).
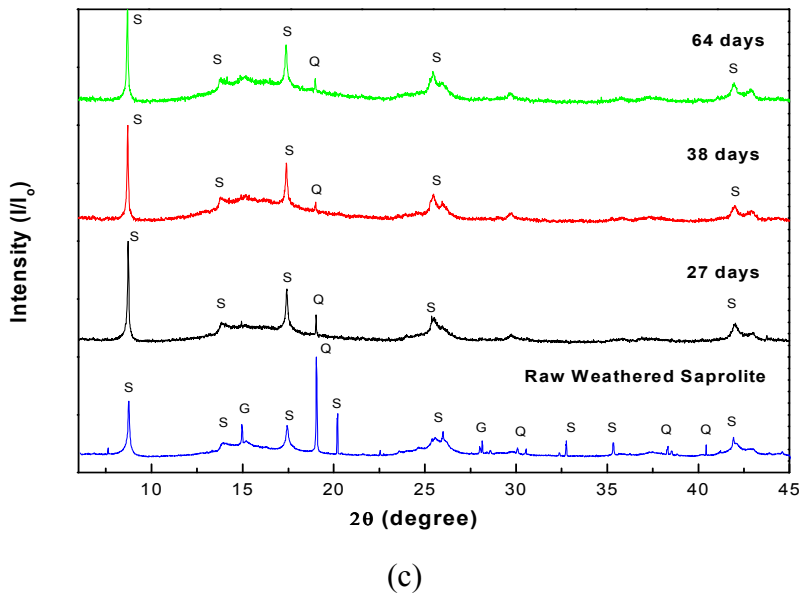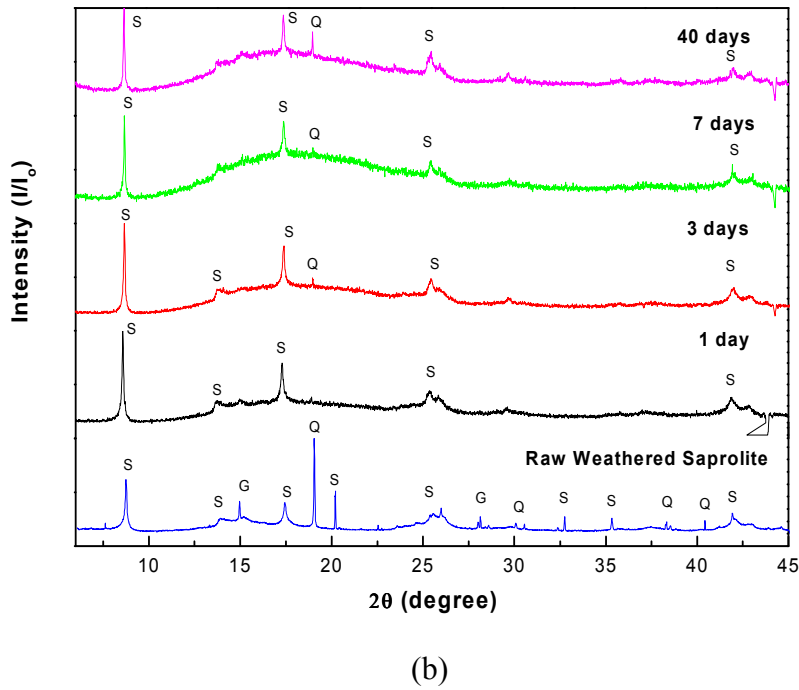

(a)

(b)

(c)

Figure 7. X-ray diffraction pattern of weathered saprolite minerals leached with 1M a) citric, b) dl-malic and c) lactic acids as a function of time. (G: goethite, S:serpentine, Q:quartz).

CONCLUSIONS

The susceptibility of laterite minerals to metabolic acids is dependent on secondary reaction by adsorption, acid activity, pulp density and the capability of the acids to dehydroxylate the main gangue phase, the goethite and garnierite lattice.

The effect of electrosorption was minimised by adjusting the slurry pH such that it was maintained below the pH_{IEP} of ore gangue. Reducing the electrosorption effect can improve nickel recovery by 200%, although this phenomenon appears to have less effect on cobalt dissolution

This study has shown that leaching efficiency is dependent on hydronium concentration rather than acid type. The hydronium concentration is dictated by the strength of the acids or their ability to dissociate in solution. It appears the order of acid strength is citric, malic and lactic acid. The greater efficiency of leaching achieved in citric acid resulted from its ability to dissociate in solution. Comparison of the effectiveness of acids in dissolving metals based on acid concentrations can lead to misleading correlations.

The optimal pulp density for limonite was 7.5wt% and for weathered saprolite was lower at 2-5.8wt%. The lower optimal solid to liquid loading ratio for weathered saprolite is associated with its higher content of acid neutralising magnesium minerals.

The ores are found to be more amenable to acid attack when the mineral phases dehydroxylate, rendering them susceptible to metals liberation. The association of nickel and cobalt with the gangue minerals therefore have a significant implication in the ability of these metals to dissolve. In weathered saprolite, greater susceptibility of nickel to dissolve in comparison to cobalt suggests that nickel is associated with the more reactive serpentine phases, whereas cobalt may be partially hosted by goethite. Similarly the greater cobalt dissolution relative to nickel from limonite would suggest that Co is associated with serpentine minerals and nickel with goethite.

The development of an environmentally friendly, energy conserving and economical bioprocessing of nickel laterite is essential in the sustainability of the nickel industry. This study illustrates that the phase transformation and the interaction of acid with the laterite minerals during organic acid leaching are complex systems and complete elucidation of this process entails further research. The usefulness of synchrotron-based X-ray diffraction in tracing these minerals transformations was demonstrated in this investigation and suggests the importance of such powerful tools in mineral processing studies.

ACKNOWLEDGEMENT

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KEY WORDS

Fungi, Biological, Leaching, Organic acid, Metabolic acid, Limonite, Laterite, Saprolite