THE LEACHING OF NICKEL LATERITE ORE USING ACIDIC MEDIA AND FERRIC IONS

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ABSTRACT

The influence of sulphuric acid, citric acid and ferric sulphate on the leaching kinetics of nickel laterites has been investigated in this study. Preliminary results showed that sulphuric acid had a higher recovery than citric acid and ferric sulphate of the same concentration. However, a higher recovery of nickel was recorded for samples leached in a mixture of sulphuric acid and citric acid. Due to the apparent formation of basic ferric hydroxy sulphate, ferric sulphate was observed to give lower nickel recoveries. In the presence of ferric sulphate dissolution was seen to increase with sulphuric acid concentration within the range 0.1 - 0.5 M studied indicating the positive effect of sulphuric acid in both ferric sulphate and citric media. The kinetic study indicated that the leaching of nickel laterite is product layer diffusion controlled process for sulphuric acid, citric acid and acidified ferric sulphate.

KEY-WORDS: nickel laterites, sulphuric acid, citric acid, ferric sulphate, leaching kinetics

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1. INTRODUCTION

Nickel laterites account for almost 70% of the world's land based nickel reserves, are mineralogically and chemically complex (unlike the sulphides of nickel), which makes the processing more complex and expensive. Nickel is present in the lateritic ores as minor constituent of other minerals and, therefore, it is not amenable to concentration by any known conventional upgrading system (Valix et al., 2000). Recovery of nickel laterites currently is through conventional methods – pyrometallurgically and hydrometallurgically. It is estimated that there is almost twice as much laterite resources that is amenable to hydrometallurgical processing (limonite, nontronite/smectite) as that amenable to pyrometallurgical processing (saprolite, garnierite).

Recently, interest has been shown in microbial assisted recovery of nickel from laterite ores, because large tonnages of low-grade (<1%) nickel laterites are uneconomical to process, but might become viable if a suitable low-cost, low-energy leaching technique could be developed. The possibility to employ heterotrophic organisms to treat non-sulphidic ores such as nickel laterites has been described by several authors (Bosecker, 1985; Groudev, 1987; Tzeferis et al., 1991; Valix et al, 2000). There are, however, serious disadvantages associated with the use of heterotrophic organisms on industrial scale. For instance the cost of the organic carbon used as energy source makes their application very expensive and unless it can be replaced by inexpensive waste products, it would not be a viable process. An alternative route is the use of the most studied processes in biohydrometallurgy involving the use of chemolithotrophic microorganisms in the leaching of sulphidic ores. These organisms produce strong inorganic acids, primarily sulphuric and nitric, from oxidation of reduced sulphur and nitrogen compounds. However, the use of chemolithotrophic bacteria in recovery of nickel from lateritic ores is currently relatively unexplored, probably because of the lack of the sulphidic content of the ore to produce the required sulphuric acid. If this is to be done successfully then, external dosages of sulphur will need to be added. However to understand a bit more on how this process can be done, it is advisable to first understand the role and effect of acids in the actual leaching process before embarking on a pure economical bioleaching process for the nickel laterite ores as this would subsequently lead to an easier way in designing and optimizing the process. In this regard it is often easier and desirable to first undertake chemical leaching testwork.

Relatively great attention has been paid to the research connected with the recovery of nickel from nickel laterites using organic acids (Mckenzie et al., 1987, Valix et al., 2000; Alibhai et al., 1993). Citric acid has proved to be the most active product of fungal metabolism for nickel laterite extraction. To elucidate the role of the acid produced by the chemolithotrophic bacteria mainly sulphuric acid, it would be helpful and easier to base the chemical behavior of sulphuric acid to the previously well researched citric acid (Tzeferis et al., 1994). As a result, if sulphuric acid is seen to perform better than citric acid it will make it easier to sell the idea of chemolithotrophic leaching of nickel laterite ores over the well established heterotrophic leaching. On the other hand the use of the ferric sulphate as one of the lixiviant will act as a basis for the provision of using ferrous iron or pyrite as a substrate in the bacterial leaching.

This study is thus seen as a preliminary to selecting appropriate conditions for the chemolithotrophic leaching of nickel laterite ores in later stages of research. Determination of the acid conditions i.e. concentration and pH required to maximize nickel extraction will lay a foundation for the subsequent bioleaching studies. In addition a preliminary report of experimental kinetic study of nickel laterites dissolution using sulphuric acid, citric acid and ferric ions will also be given. The basis for the comparison in the leaching kinetics of these acids will help in determining the cost implications of the chemolithotrophic leaching approach.

2. EXPERIMENTAL METHODS

2.1 Ore samples

The nickel laterite ore used in this study was kindly provided by Mintek, South Africa. Table 1 below shows the chemical composition of the sample used in the study. The ore was crushed and the mineral classified into +63-75μm size fraction using standard sieve plates.

Table I: Chemical composition of laterite ore sample

Mineral	SiO_2	Fe_2O_3	Cr_2O_3	Al_2O_3	MgO	NiO	CoO	CaO	MnO	CuO	C	S	P
Mass %	52.79	21.86	0.99	2.5	7.46	1.87	0.25	0.68	1.28	0.01	0.119	0.034	0.064

2.2 Chemical leaching experiments

The chemical leaching tests were performed in 250-ml Erlenmeyer flasks placed in a rotary shaker with analytical grade citric acid, sulphuric acid and ferric sulphate as the lixiviants. In each experiment, 5g of ore was added to 100mls of lixiviant having a specified concentration, pH and temperature of 30°C (Table 2). A pulp density of 5% was maintained as our previous research has shown to give higher recoveries in microbial leaching studies (Olubambi, 2007). To rule out the diffusion control of dissolution, the tests were stirred at a rate ensuring particles hovering ($\geq$ 200 rpm). The solution was sampled every two days and the total concentration of nickel determined by the Varian SpectrAA-55B Atomic Absorption Spectrophotometer (AAS). The pH profiles and redox potentials of the leach solution were measured but not controlled through out the leach period. In one other set of experiments an initial pH similar for all the lixiviants was used but not controlled during the actual experimental run. A pH of 1.0 and 1.5 were selected as these have also been shown to be more conducive for chemolithotrophic bioleaching of ores. The liquid extracted was compensated by the addition of distilled water. The recovery during the leaching of nickel laterites was calculated as a percentage of nickel in the liquid phase to that in the nickel laterite ore.

3. RESULTS AND DISCUSSION

3.1. Effect of initial lixiviant concentration

Table 2 shows the leaching conditions of various chemical tests and nickel recovery. The results show that the dissolution of nickel laterite depends largely on the leaching media.

Table II: solubilisation of nickel by sulphuric acid, citric acid and ferric sulphate

| Leach media	Initial pH	Final pH	Initial redox (mV)	Final redox (mV)	Recovery (%)
0.5 M H$_2$SO$_4$, 0.5 M citric acid	0.36	0.63	421	409	79.6
1M H$_2$SO$_4$	0.25	0.55	425	405	74.4
0.5 M H$_2$SO$_4$	0.39	0.74	421	404	71.9
1 M Citric acid	1.29	1.70	372	350	57.4
0.5 M Fe$_2$(SO$_4$)$_3$, 0.5 M H$_2$SO$_4$	0.33	0.57	426	413	50.3
0.5 M Citric acid	1.45	2.02	358	328	46.6
0.5 M Fe$_2$(SO$_4$)$_3$, 0.1 M H$_2$SO$_4$	0.74	0.96	402	390	37.4
0.5 M Fe$_2$(SO$_4$)$_3$	0.93	1.13	391	381	20.3
Distilled water	5.88	8.39	99	-46	0.5

[a] Extraction values is the average of two separate runs carried out under the same experimental conditions

The initial concentration was fixed at 0.5 M for sulphuric acid representing the leaching conditions expected to prevail during microbial chemolithotrophic leaching without adverse effect on the microorganisms. This was changed to 1M for sulphuric acid and citric acid to further investigate the expected changes in recovery. Although the results showed a significant increase for citric acid, the increase in recovery for sulphuric acid was not very major indicating that the 0.5M could be safely used in bioleaching studies.

The results shown in Table 2 indicate that sulphuric acid is more active than ferric sulphate and citric acid at the same starting concentration. Citric acid is a weaker acid compared to sulphuric acid hence the lower recoveries. The acidity constant of sulphuric acid is $pK_1 = -1.7$; $pK_2 = 1.96$ at 25°C (Perrin, 1982) and that of citric acid is $pK_1 = 3.14$; $pK_2 = 4.77$; $pK_3 = 6.39$ at 20°C (Albert and Sergent, 1962) and the higher the acidity constant the weaker the acid. Even when the concentration of citric acid was doubled to 1M the recovery was still lower than that given by sulphuric acid at 0.5M. However, citric acid solubilised more nickel when mixed with sulphuric acid clearly indicating the positive synergistic effect of sulphuric acid in the leaching process. The results seem to cement the work of other researchers (Alibhai et al., 1993) who noted that hydrogen ions concentration is the main factor affecting chemical leaching.

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The recoveries as shown in Table 2 further suggest that leach rates are highly depended on the initial pH of the solution and the type of lixiviant. When the citric acid and sulphuric acid starting concentrations were doubled the initial pH was lowered and a significant increase in nickel recovery for citric acid was recorded. To understand more on the effect of pH leaching was undertaken at similar starting pH with the different lixiviants (results not shown). In the study, a starting pH of 1.0 and 1.8 were used and the results showed that citric acid produced a higher nickel recovery than sulphuric acid and ferric sulphate of the same initial pH. The higher recovery with citric acid than sulphuric acid can be attributed to the chelating of nickel ions by organic acid at these pHs while H^+ ions in sulphuric acid do not act as chelators. Previous other research has shown that citric acid acts as a chelator of nickel ions at given pH ranges and is more active than sulphuric acid alone (Tzeferis et al., 1994, Mckenzie et al., 1987). However, further test works will be done to investigate the pH ranges for which chelation is most effective for this particular ore.

The negative influence of ferric sulphate on leaching can be attributed to the formation of the insoluble basic ferric hydroxy sulphate layer (equation 1). The insoluble layer causes a mass transfer barrier to mineral-H^+ contact.

$$M^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow MFe_3(SO_4)_2(OH)_{6(s)} + H^+ \qquad (1)$$

Where M = H_3O^+ or K^+ or Na^+
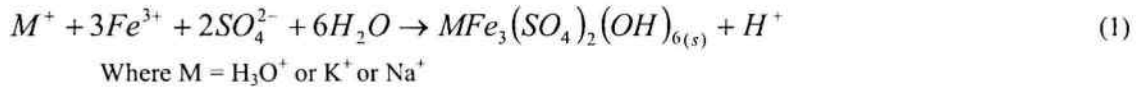
Basic ferric hydroxy sulphate formation depends upon leaching conditions and is favoured by high sulphate contents (Georgiou and Papangelakis, 1998). The gradual increase in pH during leaching in all the tests was caused by the progressive acid dissolution of nickel laterite.

3.2. Kinetic analysis

The reactions of nickel laterite with the lixiviants in this study are heterogeneous. For heterogeneous systems the reaction kinetics is based on the shrinking core model (Levenspiel, 1972; Smith, 1981; Han, 2002). Based on the shrinking core model, the mechanism of the uncatalysed heterogeneous reaction may take place as follows: Initially the reactants diffuse from the bulk of the first phase to the interface between the phases. If an additional layer of solid products and inert material is present at the interface the reactants would have to overcome the resistance of this layer before reaching the surface of the second layer. Then, diffusion of reactants from the interface to the bulk of the second phase takes place. Further, chemical reactions between the reactants in phase one and those in phase two occur. Finally, the products diffuse within the second phase and /or out of phase two into the bulk of phase one (Levenspiel, 1972; Smith, 1981; Han, 2002).

To determine the rate controlling regime, the experimental results at 30°C were plotted in terms of the standard equations of the shrinking core model (figures 1-3). The experimental data were plotted by assuming a mono-sized particle size distribution. The kinetic model for diffusion through the product layer was assumed to control the rate of reaction for nickel laterite with sulphuric acid, citric acid and acidified ferric sulphate in accordance with the kinetic equation $1-3(1-X)^{2/3}+2(1-X) = kt$ where X is the conversion, t is the time in days and k is the apparent reaction rate constant (day^{-1}). The product layer formed during the leaching of the laterite with sulphuric acid and ferric ions is attributed to the possible formation of jarosite from the dissolution of Fe_2O_3 present in the nickel. On the other hand the product layer formed during citric acid leaching could be due to the possible formation of Fe (III) and Fe (II) citrate complexes. Further analysis by XRD will be done to verify these solod products.
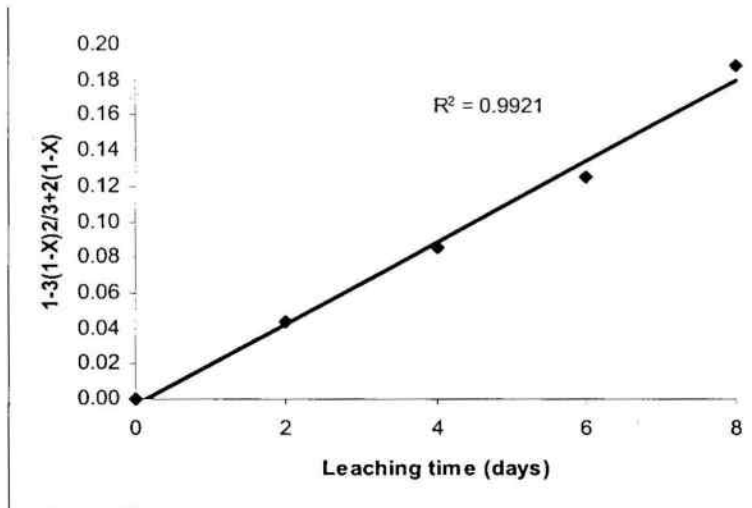
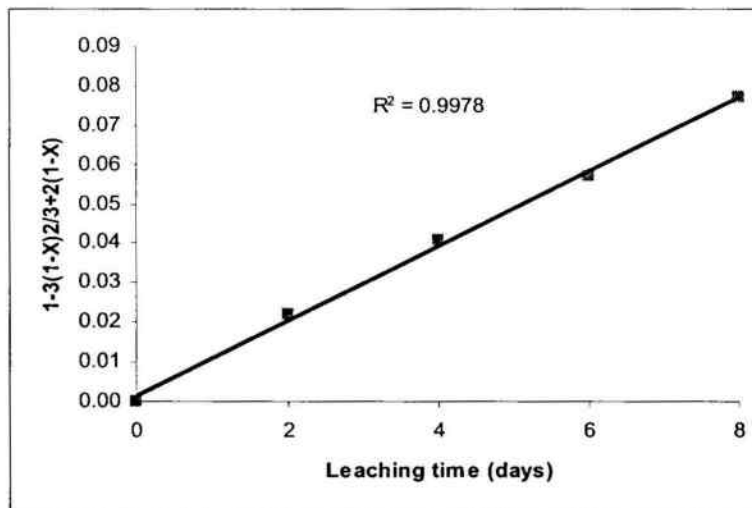Fig 1: Plot of $1-3(1-X)^{2/3}+2(1-X)$ versus time for sulphuric acid

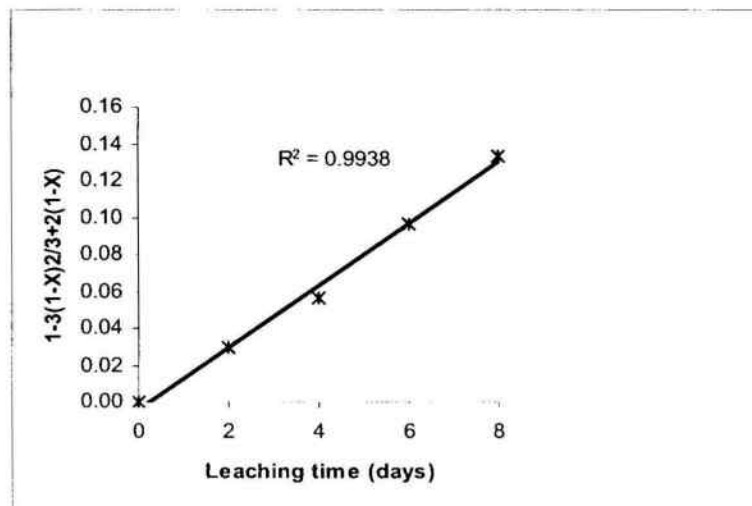Fig 2: Plot of $1-3(1-X)^{2/3}+2(1-X)$ versus time for citric acid

Fig 3: Plot of $1-3(1-X)^{2/3}+2(1-X)$ versus time for acidified ferric sulphate

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4. CONCLUSION AND FUTURE SCOPE OF STUDY

The kinetic analysis indicates that the leaching of nickel laterite is product layer diffusion controlled process for sulphuric acid, citric acid and acidified ferric sulphate. It has been deduced from this study that the dissolution rate of nickel laterite depends largely on the leaching media and the possible effect of chelation at certain pH ranges. The possible formation of basic ferric hydroxy sulphate has a negative effect on leaching of nickel laterites by ferric ions indicating that the addition of pyrite and ferrous sulphate will have to go hand in hand with close monitoring of the pH for this lixiviant to work more efficiently. Combinations of sulphuric acid and citric acid gave a higher extraction than when citric acid was used alone, indicating the positive effect of sulphuric acid on leaching. Although an increase in the concentration of citric acid from 0.5M to 1M had a positive effect on the recovery of nickel, the recovery was still lower than that recorded for sulphuric acid alone at similar concentrations. Taking this into account, the feasibility of the use of chemolithotrophic bacteria for nickel recovery from laterite ores has been clearly demonstrated. However, the possibility of this successfully being conducted will depend on the external dosages of sulphur. Future studies will have to focus on the quantities of sulphur that can be added to the leaching media in order to generate conditions that have been shown to give higher recoveries of nickel in this study. A cost analysis and efficiency comparison between the heterotrophic and the chemolithotrophic route will also be conducted.

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