

DISSOLUTION KINETICS OF NICKEL LATERITE ORE USING DIFFERENT SECONDARY METABOLIC ACIDS

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Abstract - The dissolution kinetics of nickel laterite ore in aqueous acid solutions of three metabolic acids, i.e., citric acid, oxalic acid and acetic acid were investigated in a batch reactor individually. It was determined that experimental data comply with a shrinking core model. The diffusion coefficients for citric acid, oxalic acid and acetic acid were found to be 1.99×10^{-9} cm²/s, 2.59×10^{-8} cm²/s and 1.92×10^{-10} cm²/s respectively. The leaching ability of each acid was observed and it was found that oxalic acid was better than the other two.

Keywords: Dissolution kinetics; Laterite ore; Leaching; *Pseudomonas putida*.

INTRODUCTION

Nickel is a strategic metal of vital importance in many modern industrial and metallurgical applications. In India, the country's requirement of nickel is met through annual imports of about 4,000 tonnes of the metal and its associated products equivalent to about 2.2 million US\$. The underground mining deposits below 65m in depth in chromite mines in the Sukinda Valley in Orissa are the major reserve of India's lateritic deposit, which is estimated to be 65 million tons with 0.15-1.2% nickel content (Sukla and Das, 1987; Kanungo and Jena, 1988). The only significant deposit of lateritic nickel ore in India, which is in the ultra-basic belt of Sukinda, is yet to be commercially exploited.

Nickel is commonly found in iron meteorites as the alloys kamacite and taenite. Nickel ores are of two types (Valix *et al.*, 2001a):

1) Primary sulphide deposits associated with mafic and ultramafic rocks

2) Near-surface laterite deposits formed over olivine-rich host rocks following intense weathering.

The sulphide ores have been the major source of nickel to date; however, the lateritic ores have been estimated to constitute about 73% (Davidson, 2006) of the known nickel reserves of the world. The nickel lateritic ore is normally the overburden (in the present case, it is the overburden of chromite mines), which is nothing but the soil and dust removed in order to access an ore or mineral body. The huge amount of overburden (nearly 8 to 10 times that of the ore) that is generated during chromite mining and dumped nearby has found a very little use so far. With the continuous depletion of high grade nickel sulphide ores, there is the need to win metals from the abundant low grade nickel laterite ores and overburdens as well.

Bioleaching involves the utilization of microorganisms and their metabolic products to dissolve metals from low grade ores. Both autotrophic (Torma and Bosecker, 1982) and

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heterotrophic (Kiel and Schwartz, 1980; Sukla and Panchanadikar, 1983; Munier-Lamy and Berthelein, 1987) microorganisms possess the potential to remove nickel from its ores.

For sulphidic ore leaching, the widely used autotrophic microorganisms are *Acidithiobacillus ferrooxidans* and *Acidothiobacillus thiooxidans*. Bioleaching mechanisms of sulphidic minerals using heterotrophs have received less attention from microbiologists (Kiel and Schwatz, 1980). Among the heterotrophic bacteria, members of the genus *Pseudomonas* have been found to be effective in the leaching of non-sulphidic minerals (Karavaiko et al., 1997).

Utilization of heterotrophic microorganisms for leaching of non-sulphidic ores is a matter of interest nowadays. As non-sulphidic ores do not contain any energy source for the microorganism to utilize, they can be leached out by heterotrophic bacteria and fungi when a carbon source for their energy supply and growth is introduced. The organism utilizes the carbon source and excretes organic acids and compounds with at least two hydrophilic reactive groups (e.g., phenol derivatives) into the culture medium as metabolic products. The secondary metabolites, produced by the heterotrophic organisms from the organic carbon they consume for energy production, interact with the mineral surfaces. In addition to forming several organic acids such as acetic acid, citric, oxalic and α -ketoglutaric acid (Agatzini and Tzeferis, 1997; Castro et al. 2000; Natarajan and Deo, 2001), they also produce exopolysaccharides (Malinovskaya et al., 1990; Welch and Vanderivere, 1995; Welch et al., 1999), amino acids and proteins that can solubilize the metals via a variety of mechanisms (Henderson and Duff, 1963; Avakyan and Robotnova, 1971; Valix et al., 2001b). Organic acids, however, play a central role in the overall process, supplying both protons and metal complexing organic acid anions (Gadd, 1999).

Leaching kinetics plays an important role in the extraction of metals and their compounds in an economical way. Many researchers have studied the dissolution kinetics in hydrometallurgy (Abdel-Aal, 2000; Antonijevi et al., 1997; Ekinci et al., 1998; Liang et al., 2005; Raschman and Fedorockova, 2004). Inorganic acids have been commonly used as leaching reagents in these studies. In addition to these, organic acids are in use for that purpose in recent years (Bakan et al., 2006; Bayrak et al., 2006; Demir et al., 2006; Fred and Fogler, 1998). Ingec et al. (2004) conducted a dissolution kinetics study on smithsonite ore (ore of zinc) with an organic leach reagent in the presence of ultrasound energy and

showed that it had a positive effect on the dissolution rate. In case of nickel, most of the dissolution studies have been done on leaching of spent catalyst (Mulak et al., 2005; Mishra et al., 2008). Mishra et al. (2008) studied the dissolution kinetics of spent catalyst using acidophilic bacteria. Scheckeland Sparks (2001) studied the dissolution kinetics of nickel surface precipitates on clay mineral and oxide surfaces using an array of dissolution agents like EDTA, oxalate, acetyl acetone and HNO_3 .

Ehrlich (2001) proposed a two-reactor leaching process for heterotrophic leaching in which the first reactor would be a generator, where the desired microbes would produce the acids in pure culture under optimal growth conditions. The spent culture solution from this reactor would be bled into a second reactor, where the maintenance of sterile conditions is not required, containing the ore to be leached. He also suggested that the growth of microbes in the second tank might be due to contamination of the ore and it might destroy the acids. This could be controlled by ensuring a very low level of residual nitrogen source in the spent culture medium (a nitrogen source being essential for growth) and by temperature manipulation. In the second reactor, the leaching process becomes a hydrometallurgical process rather than a bio-hydrometallurgical one. Here the dissolution kinetics plays an important role in optimizing the process and making it more economical.

In view of this, the present paper considers the heterotrophic leaching of nickel with a mention of two-tank leaching. The objective of the present study is the theoretical postulation of a shrinking-core model and its adaptation here to propose the dissolution kinetics of laterite ore with secondary metabolic acids in the second stage of a two-tank leaching process.

MATERIALS AND METHODS

Ore Material Source

The nickel ore used for the study was overburden of a chromite mine and was obtained from the major deposits of Sukinda mines, Orissa, India. The sample was collected from the site of Orissa Mines Corporation. After collection, the sample was ground and utilized for the experiment. The particle size distribution or range of particle diameters was calculated by using standard screens/sieves in the size range between $106\mu\text{m}$ to $500\mu\text{m}$. The weight fraction of the ore particles retained by each and every successive screen was noted.

The average particle diameter was calculated as the mass mean diameter (\bar{D}_w), given as:

$$\text{Mass mean diameter } \bar{D}_w = \sum w_i \bar{D}_{pi}$$

where w_i is the weight fraction retained by a particular mesh sieve and \bar{D}_{pi} is the average particle diameter, taken as the arithmetic average of the smallest and largest particle diameters in increment.

Chemical Analysis of Ore

The acidified raw ore overburden was subjected to chemical analysis to determine the percentage of nickel present in the ore. One gram of ore was taken and was added to 50ml of concentrated, hydrochloric acid (HCl) in beakers and then the mixture was heated until the residue turned white. The mixture was cooled and filtered and kept in a clean volumetric flask, which had been rinsed prior with distilled water for several times. The volume was made up to 250ml by adding distilled water. The solution was filtered and diluted 10 times, 100 times and 1000 times for analysis of nickel content by Atomic Absorption Spectrophotometry (AAS). An XRF (X-ray fluorescence) analysis was done to find all the metal constituents present in the laterite ore.

Mineralogical Analysis of Ore

Mineralogical analysis of the nickel laterite samples was done by using a high-resolution synchrotron based X-ray diffractometer (XRD).

Study of Dissolution Kinetics

For the study of dissolution kinetics, experiments were conducted in an in-house designed laboratory scale batch reactor. The batch reactor has a 6 litre capacity and a pulp density of 10 g/L was maintained in the reactor. A 1 M acid concentration was used for the leaching experiments and the experiments were done with three individual acids, namely oxalic acid, citric acid and acetic acid. The temperature of the reactor was maintained at 32°C. A 5ml sample was

collected from the reactor after every 8 h and was centrifuged at 4000 rpm for 5min to remove the ore particles. The supernatant was taken for AAS (Atomic Absorption Spectrophotometric) analysis to determine the nickel concentration.

RESULTS AND DISCUSSION

Mineralogical Analysis of the Ore

The XRD study revealed the presence of goethite, hematite, nickel ferrite, garnierite and quartz in the ore body. The mineralogical studies indicated that there is no separate nickel bearing mineral phase in the lateritic nickel ore. Goethite or hydrated iron oxide is the main iron bearing phase or host that contains most of the nickel oxide in the raw lateritic ore.

Chemical Analysis of the Ore

The chemical analysis of raw lateritic ore has revealed the presence of 0.97% Ni along with some other different metals, as confirmed by the XRF study of nickel ore (Table 1).

Effect of Acids Type on Leaching

Fig. 1 shows the percentage leaching of nickel for different acids at time intervals of 40, 80 and 120 h at a concentration of 1 M. From the figure, it is evident that oxalic acid is the most efficient leaching agent compared to the other two acids (Figure 1). This may be due to the fact that the extent of dissolution is dependent on the acid activity (Tang and Valix, 2006). The pK_a (acid dissociation constant) values of the three acids suggest that oxalic acid has higher acidity.

The pK_a values of the three acids are:

Citric acid	Oxalic acid	Acetic Acid
$pK_{a1}=3.15$	$pK_{a1}=1.27$	$pK_a =4.76$
$pK_{a2}=4.77$	$pK_{a2}=4.28$	
$pK_{a3}=6.40$		

Table 1: Chemical Analysis of Lateritic Ore

Weight Percentage (%)					
Ni	Co	Fe	Cr	Mn	Acid insoluble matter (Al)(g)
0.97	0.032	46.86	4.14	0.37	0.88

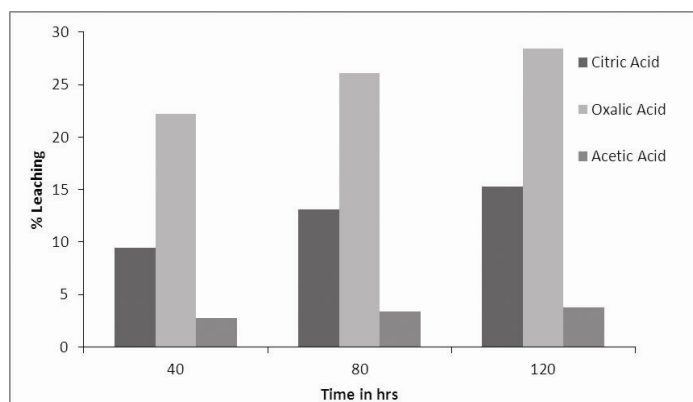
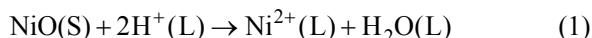


Figure 1: Effect of acid type on nickel leaching.

Dissolution Kinetics of Nickel Oxide Present in Laterite

The reaction between nickel oxide (captive in the goethite core) and organic acids can be written as follows:



The reaction (1) of laterite ore can proceed via the shrinkage of the inner reactive core of the particle with time. Leaching kinetics is controlled either by the diffusional mass transfer of the reactant through a liquid boundary layer or ash layer (unreacted Goethite Structure) or chemical reaction at the ore surface (Levenspiel, 1999). The reaction between nickel oxide (solid) (captive in the goethite core) and organic acids (liquid) was analysed by using a heterogeneous reaction mechanism. The fit of the experimental data to the integral rate equations (Table 2) was tested by using linear regression for three different acids. The calculated regression coefficients for kinetics controlled by different regimes are presented in Table 3. The highest regression coefficients or the best fits for all the experimental results for ore leaching using the different acids were obtained for rate expressions controlled by diffusion through an ash layer. Fig. 2 shows the fit of the experimental data using the integral rate expression governed by ash layer diffusion for a spherical particle. From the slopes of

the best-fit curves of our experimental results to the integral rate expression pertaining to ash layer diffusion control, the apparent rate constants of the reactions between ore particles and organic acids were found. The effective diffusion coefficients for the diffusion of liquid reactants through the ash layer of a spherical ore particle were calculated using the slope of the best fit curves of Fig. 2, the Mass Mean Diameter (\bar{D}_w) of the ore particles, the molar density of nickel oxide, and the stoichiometric coefficient of the reactant nickel oxide in the reaction. The calculated effective diffusion coefficients are as follows:

$$\text{Citric Acid } D_e = 1.98567 \times 10^{-9} \text{ cm}^2/\text{s}$$

$$\text{Oxalic Acid } D_e = 2.5907 \times 10^{-8} \text{ cm}^2/\text{s}$$

$$\text{Acetic Acid } D_e = 1.91904 \times 10^{-10} \text{ cm}^2/\text{s}$$

On the basis of these D_e values, oxalic acid is found to be the prime mover in heterotrophic leaching of nickel laterite ore (Table 2, Table 3, Figure 2). The present study also aimed to establish the activation energies for the above reactions, but, after 5 days, the leaching percentage was so low that the change in temperature did not have a significant effect on nickel leaching. It would be necessary to carry out the experimentation for longer times and change the temperatures much more. A logical consequence of the present exercise was what would be the effect on leaching if the acid concentrations studied were not exactly the concentrations achieved due to microbial activity, which will be the subject of a future study.

Table 2: Conversion-time equations for various shapes of particles in the shrinking core model (Levenspiel, 1999)

Shape of the particle	Film diffusion control	Ash diffusion control	Reaction control
Flat plate			
$\alpha = 1 - \frac{1}{L}$ L=half thickness	$\frac{t}{\tau} = \alpha$ $\tau = \frac{\rho_p L}{bK_1 C_A}$	$\frac{t}{\tau} = \alpha^2$ $\tau = \frac{\rho_p L^2}{2bD_e C_A}$	$\frac{t}{\tau} = \alpha$ $\tau = \frac{\rho_p L}{bK^n C_A}$
Cylinder			
$\alpha = 1 - \left(\frac{r_c}{R}\right)^2$	$\frac{t}{\tau} = \alpha$ $\tau = \frac{\rho_p R}{2bK_1 C_A}$	$\frac{t}{\tau} = \alpha + (1-\alpha)\ln(1-\alpha)$ $\tau = \frac{\rho_p R^2}{4bD_e C_A}$	$\frac{t}{\tau} = \alpha - (1-\alpha)^{1/2}$ $\tau = \frac{\rho_p R}{bK^n C_A}$
Sphere			
$\alpha = 1 - \left(\frac{r_c}{R}\right)^3$	$\frac{t}{\tau} = \alpha$ $\tau = \frac{\rho_p R}{3bK_1 C_A}$	$\frac{t}{\tau} = 1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)$ $\tau = \frac{\rho_p R^2}{6bD_e C_A}$	$\frac{t}{\tau} = 1 - (1-\alpha)^{1/3}$ $\tau = \frac{\rho_p R}{bK^n C_A}$

Table 3: Kinetic equations for different mechanisms and their regression coefficients for linearity

Kinetic Equation	Regression Coefficient		
	Citric Acid	Oxalic Acid	Acetic Acid
Film diffusion control (any shape) and reaction control (flat plate) $\frac{t}{\tau} = \alpha$	0.8924	0.9049	0.8683
Ash layer diffusion control (flat plate) $\frac{t}{\tau} = \alpha^2$	0.976	0.945	0.959
Ash layer diffusion control (cylindrical) $\frac{t}{\tau} = \alpha + (1-\alpha)\ln(1-\alpha)$	0.977	0.949	0.96
Ash layer diffusion control (spherical) $\frac{t}{\tau} = 1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)$	0.9735	0.9542	0.9609
Reaction control (spherical) $\frac{t}{\tau} = 1 - (1-\alpha)^{1/3}$	0.8831	0.928	0.8997
Reaction control (cylindrical) $\frac{t}{\tau} = \alpha - (1-\alpha)^{1/2}$	0.8978	0.912	0.8697
First order reaction $\frac{t}{\tau} = -\ln(1-\alpha)$	0.9032	0.9187	0.871
Second order reaction $\frac{t}{\tau} = \frac{\alpha}{(1-\alpha)}$	0.9135	0.9312	0.8737

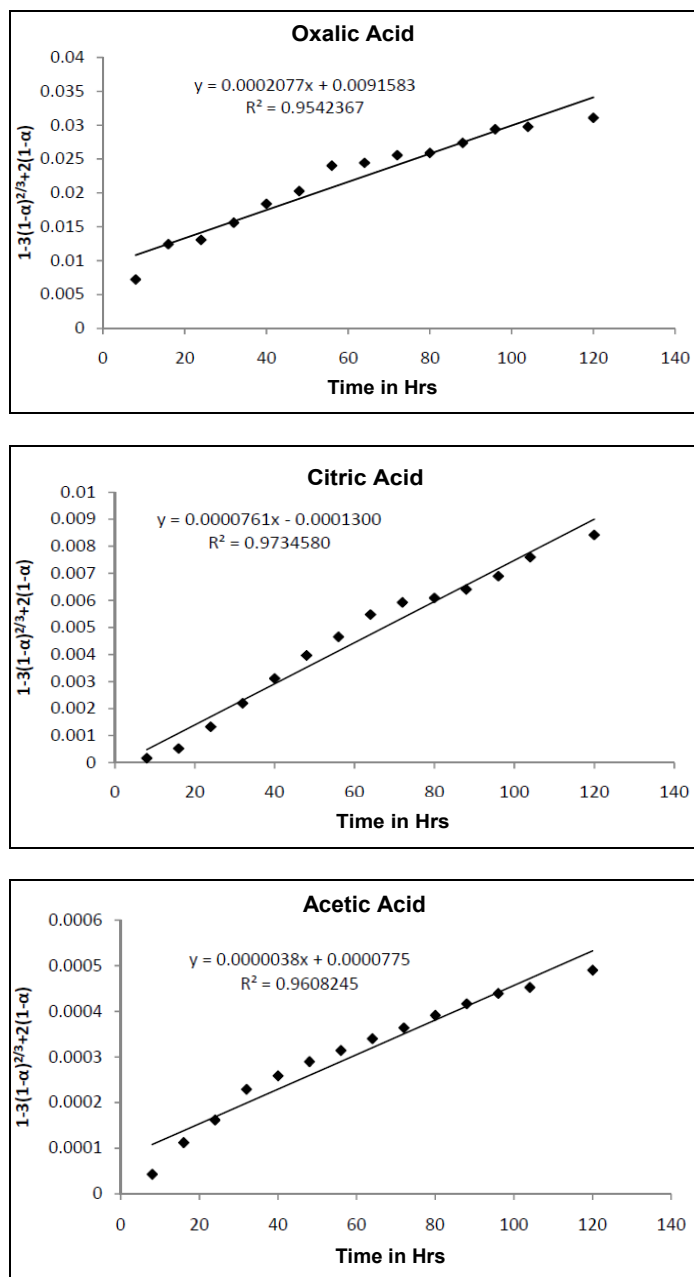


Figure 2: Agreement of experimental data with the ash layer diffusion controlled integral rate expression for oxalic acid, citric acid, acetic acid.

CONCLUSION

The imminent outcome of the present exercise can be summarized as follows:

The mineralogical studies indicated that there was no separate nickel bearing mineral phase in the lateritic nickel ore. Goethite is the main iron bearing

phase or host, which contains most of the nickel in the raw lateritic ore. This study also revealed the presence of hematite, nickel ferrite, garnierite and quartz in laterite ore. The dissolution of lateritic ore particles (captive in the goethite core) with metabolic acids like citric acid, oxalic acid, acetic acid falls under the category of heterogeneous reaction. The

reaction between nickel ore (captive in the goethite core) and organic acids were ash-layer-diffusion controlled. The effective diffusion coefficients for the diffusion of acids through the ash layer of spherical ore particle were also calculated. On the basis of those D_e values, oxalic acid seems to be the best leaching agent.

This study also enabled the authors to conclude that the effective diffusion coefficients of the acids, along with the activation energy profiles, could be immensely useful for developing first principle models for simulation, control and scale-up of such a microbial two-tank leaching process of nickel ore.

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