Dissolution kinetics of chromite overburden by using mineral acids

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Abstract−Two different mineral acids were used to determine the kinetics of dissolution of Ni and Fe from chromite overburden. Various leaching parameters were studied such as acid concentration, pulp density, temperature and particle size. Both Fe and Ni dissolution followed 1st order irreversible kinetics. The activation energy was also measured. Unified rate equations were established for Ni and Fe dissolution for two different mineral acids, HCl and H_2SO_4. The dissolution reaction was observed to follow diffusion control-dense-constant size spherical particles.

Key words: Nickel Overburden, Kinetics, Activation Energy, Rate Equation

INTRODUCTION

Nickel ore are of two types such as sulphide and oxides. So far sulphide ores are the main sources of commercial recovery of nickel. But with the gradual depletion of high grade ores and stricter enforcement of environmental pollution legislation with reference to SO_2 emission to the atmosphere, alternative sources need to be exploited for the supply of the nickel. The most abundant source of nickel is lateritic nickel ore which constitutes about 85% of the known reserve of the said metal. It is anticipated that future world nickel supplies would be from lateritic nickel ores. Since the lateritic contains no identifiable nickel minerals, beneficiation is ruled out. The ores are directly subjected to pyrotechniques such as ferro and matte smelting or pyro-hydro combined technique such as reduction roasting followed by leaching. Apart from these, interest has been created to use different acids which include both mineral and organic acids to recover metal values from lateritic ore [1-5]. The bulk of the work related to lateritic nickel ore is concerned with sulphuric acid pressure leaching. However, due to problems related to pressure leaching, atmospheric leaching has recently received much closer consideration [6-8].

India does not have either primary sulphide nickel ore or the secondary oxide or silicate type having more than 1.5% nickel content. In India, nickel ferrous ultramatic rocks are available carrying variable amounts of the metals. The most important source of ultramatic rocks is available in Sukinda, Orissa. It is reported [9] that during the mining of chromite in the Sukinda valley, a large quantity of overburden material is generated which on average yields 10 tons for every ton of chromite mineral. It is estimated that the annual generation of overburden is around 6-7 million tons. The overburden contains on average 0.5% Ni. Our laboratory is actively engaged to develop a feasible process to recover Ni from the overburden. This communication is a part of our systematic effort to extract Ni values from chromite overburden by using mineral acids as a lixiviant.

EXPERIMENTAL

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The raw overburden was collected from Sukinda, Orissa. It was a reddish-brown, clay-like solid. The typical chemical analyses show Ni 0.9, Fe 54.2, and Cr 3.7 (values in percentage).

Leaching studies were carried out using roasted overburden. The overburden was initially sieved to different sieve fractions and then roasted to 450 °C for 2 hours. The roasted mass was leached either in shake flasks or 40 liter stirred reactor. Two different mineral acids such as HCl and H_2SO_4 were used as lixiviant. All chemicals used were of chemical pure grade. Metal ions were analyzed by using a 372 Perkin Elmer atomic adsorption spectrophotometer.

RESULTS AND DISCUSSION

1. Physico-chemical Characterization

The microscopic studies of the overburden show the presence of goethite, limonite, chromite, quartz and hematite. Limonite and hematite grains are very fine. Chromite grains have irregular outline. Fine quartz is non-uniformly distributed in the overburden. The TGA-DTA analysis shows an endothermic peak at 330 °C, showing the presence of goethite. The XRD-pattern of overburden shows the peak of goethite, hematite, quartz and chromite. No separate nickel-bearing mineral phase was identified. The overburden samples were roasted to different temperatures to find the temperature of conversion from goethite to hematite. From XRD, it was observed that complete conversion of goethite to hematite took place at 400 °C. Therefore, for leaching purposes the overburden was roasted to 400 °C.

2. Leaching Studies

2-1. Shake Flask Studies

For leaching purposes, two different mineral acids of HCl and H_2SO_4 were used. Various parameters were studied such as acid concentration, pulp density, particle size and temperature.

2-2. Acid Concentration

The acid concentration was varied from 1 to 4 M for both HCl and H_2SO_4 and the results are shown in Figs. 1 and 2. It was observed that the percentage of leaching for Ni and Fe increased progressively with time and acid concentration. The percentage of Ni and Fe leaching was more in the case of H_2SO_4 compared to HCl. The percentage of Ni leaching was higher compared to Fe in H_2SO_4 medium.
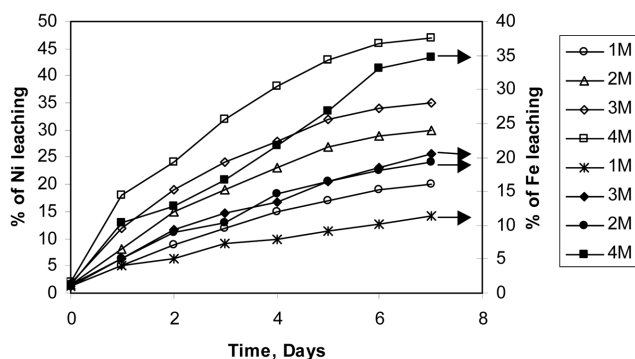
2-3. Pulp Density

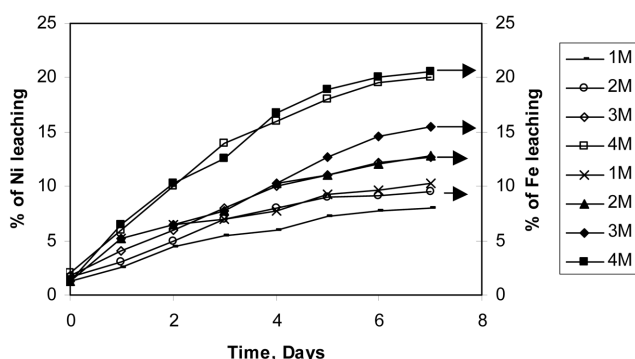Fig. 1. Percentage of Ni and Fe leaching in H_2SO_4 medium.

Fig. 2. Percentage of Ni and Fe leaching in HCl medium, (Condition; Particle Size-87.5 microns, Temperature-30 °C, Pulp Density-10%).
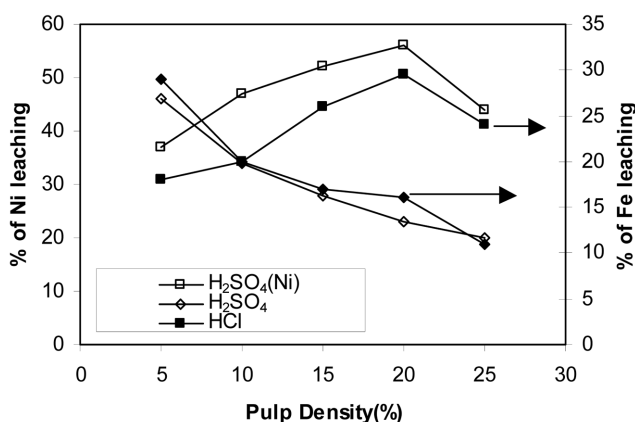

Fig. 3. Percentage of Ni and Fe leaching for different pulp density (Condition; Particle Size-87.5 microns, Temperature-30 °C, Acid Concentration-4 M).

The pulp density was varied from 5 to 25%, keeping the initial acid concentration at 4 M. The percentage of Ni and Fe leaching increased with increase of pulp density up to 20% and thereafter decreased as shown in Fig. 3, whereas Fe leaching efficiency decreased with increase of pulp density. The decrease of percentage leaching with the increase of pulp density may be due to either insufficient availability of acid and/or insufficient mixing at higher pulp density. The lack of availability of acid of higher pulp density can be ruled out as the acid utilization in no cases crossed beyond 30%.
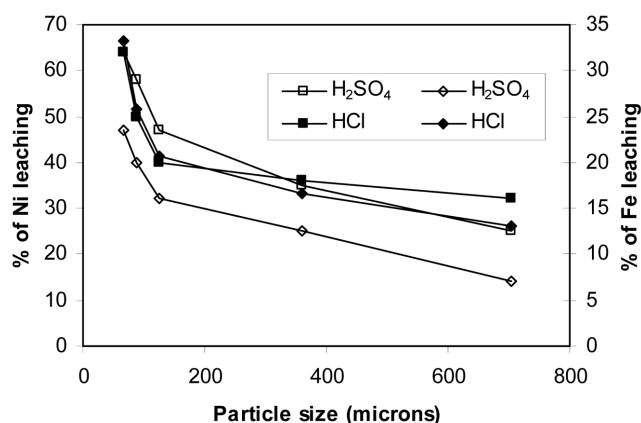

Fig. 4. Percentage of Ni and Fe leaching for different pulp density (Condition; Pulp Density-10%, Temperature-30 °C, Acid Concentration-4 M).

2-4. Particle Size

The roasted overburden was sieved to different fractions. Leaching studies were carried out by using different particle sizes varying from 67.5 to 703.1 micron, keeping pulp density and acid concentration at 10% and 4 M, respectively. The results are shown in Fig. 4. Both extraction efficiency of Ni and Fe increased with the decrease of particle size, as lower particle size always favors higher leaching efficiency, as lixiviant is directly accessible. The nickel extraction efficiency in the case of H_2SO_4 medium was higher than Fe.

2-5. Temperature

The leaching temperature was varied from 30 to 70 °C in order to evaluate its effect on the leaching efficiency. The leaching conditions were 10% Pulp density, acid concentration 4 M and particle size-87.5 microns. The leaching efficiency increased with increase of temperature. The activation energy was calculated to be 30.84 kJ/mol and 24.67 kJ/mol for HCl and H_2SO_4, respectively, for Ni dissolution. The activation energy for Fe leaching was calculated to be 22.69 kJ/mol and 34.02 kJ/mol, respectively, for HCl and H_2SO_4 medium, respectively.

2-6. Evaluation of Rate Equation

In order to evaluate the rate kinetics the leaching data was fitted to the 1st order irreversible rate equation by plotting $Ln(1-\alpha)$ versus t, where α and t are fraction reacted and time, respectively. The slope gives the specific reaction rate. Table 1 shows the specific reaction rate and correlation coefficient for different leaching parameters. From the coefficient of determination values, it can be concluded that dissolution of Ni and Fe follow 1st order irreversible kinetics.

The leaching kinetics depends on parameters like acid concentration, particle size, pulp density, and temperature. Therefore, the rate equation can be written as

$$Rate = -dc/dt = k \text{ (acid concentration)}^{n1}(\text{Particle size})^{n2}(\text{pulp density})^{n3} \quad (1)$$

Where C=Concentration of Fe and Ni.

By converting Eq. (1) to logarithmic form.

$$Log(Rate) = LogK + n_1 Log(\text{acid concentration}) + n_2 Log(\text{Particle size}) + n_3 Log(\text{Pulp density}) \quad (2)$$

For determining the rate order, experimental data obtained was

Table 1. Kinetic data for different parameters

Parameter	k, min⁻¹	R^2	n	R^2	Parameter	k, min⁻¹	R^2	n	R^2
H_2SO_4 medium					HCl medium				
Ni leaching					Ni leaching				
Acid concentration					Acid concentration				
1 M	0.0307	0.98	2.8	0.9	1 M	0.0102	0.96	3.6	0.87
2 M	0.0498	0.97			2 M	0.0126	0.93		
3 M	0.0584	0.95			3 M	0.0173	0.98		
4 M	0.0875	0.96			4 M	0.0297	0.95		
Pulp density (%)					Pulp density (%)				
5	0.0704	0.98	0.3	0.99	5	0.028	0.96	0.31	0.87
10	0.0875	0.96			10	0.0297	0.95		
15	0.0967	0.96			15	0.0382	0.86		
20	0.1063	0.96			20	0.0425	0.86		
Particle size (microns)					Particle size (microns)				
703	0.0305	0.87	0.6	0.94	703	0.0257	0.97	0.2	0.8
360	0.0659	0.97			360	0.028	0.97		
125	0.0875	0.96			125	0.0297	0.95		
87.5	0.1151	0.96			87.5	0.0355	0.93		
67.5	0.1336	0.96			67.5	0.0469	0.85		
Fe leaching					Fe leaching				
Acid concentration					Acid concentration				
1 M	0.0187	0.97	3.15	0.88	1 M	0.012	0.9	3.48	0.88
2 M	0.029	0.98			2 M	0.017	0.95		
3 M	0.395	0.99			3 M	0.022	0.98		
4 M	0.0589	0.99			4 M	0.0317	0.95		
Pulp density (%)					Pulp density (%)				
5	0.0837	0.95	0.7	0.99	5	0.0472	0.97	0.63	0.93
10	0.0589	0.99			10	0.0317	0.95		
15	0.0432	0.98			15	0.0251	0.95		
20	0.0345	0.97			20	0.0237	0.89		
25	0.029	0.96			25	0.0152	0.96		
Particle size (microns)					Particle size (microns)				
703	0.0192	0.98	0.6	0.94	703	0.0164	0.95	0.5	0.97
360	0.042	0.99			360	0.022	0.95		
125	0.0589	0.99			125	0.0317	0.97		
87.5	0.0729	0.98			87.5	0.0408	0.9		
67.5	0.0889	0.99			67.5	0.054	0.91		

arranged to fit into Eq. (2). For this purpose, only one parameter was varied, keeping all other parameters constant. Since specific rate is proportional to rate of reaction, to evaluate the rate order, the respective specific rate was plotted against the leaching parameters. The coefficient of determination along with the different n values are shown in Table 1. Utilizing the n values, the rate equation for dissolution reactions for Ni and Fe can be written as:

In H_2SO_4 Medium

$$\log(\text{rate of Ni dissolution}) = 7.35 + 24.67/RT$$
$$+2.8 \text{ Log (acid concentration)} - 0.6 \text{ Log(Particle size)}$$
$$+0.3 \text{ Log(Pulp density)} \tag{3}$$

$$\log(\text{rate of Fe dissolution}) = 0.86 + 34.02/RT$$
$$+3.15 \text{ Log(acid concentration)} - 0.6 \text{ Log(Particle size)}$$
$$-0.7 \text{ Log(Pulp density)} \tag{4}$$

In HCl Medium

$$\log(\text{rate of Ni dissolution}) = 8.94 + 30.84/RT$$
$$+3.6 \text{ Log(acid concentration)} + 0.2 \text{ Log(Particle size)}$$
$$+0.31 \text{ Log(Pulp density)} \tag{5}$$

$$\log(\text{rate of Fe dissolution}) = 5.578 + 22.69/RT$$
$$+3.48 \text{ Log(acid concentration)} - 0.5 \text{ Log(Particle size)}$$
$$-0.63 \text{ Log(Pulp density)} \tag{6}$$

2-7. Dissolution Model

Some attempts have also been initiated to fit the leaching data by using five different models [10-12] as shown below:
Chemical reaction control-dense-flat plate particles

$$\alpha = Kt \tag{7}$$

Film diffusion control-dense-shrinking spheres

$$1-(1-\alpha)^{2/3}=Kt \tag{8}$$

Chemical reaction control-dense-large-shrinking sphere

$$1-(1-\alpha)^{1/2}=Kt \tag{9}$$

Chemical reaction control-dense-constant size

$$1-(1-\alpha)^{1/3}=Kt \tag{10}$$

Ash diffusion control-dense-constant size-spherical particles

$$1-3(1-\alpha)^{2/3}+2(1-\alpha)=Kt \tag{11}$$

Using all the equations, it was found that both Ni and Fe dissolution followed the pattern described by Eq. (11) (figure not shown).

2-8. Large Scale Batch Dissolution

From small-scale studies it can be concluded that the efficiency of H_2SO_4 is higher in terms of Ni dissolution compared to HCl. Therefore, it is thought worthwhile to carry out a leaching test in a 40 L capacity stirred reactor. The leaching conditions were acid concentration 4 M, pulp density 10%, particle size-67.5 microns and temperature-30 $^{\circ}$C. It was observed that the efficiency of leaching was greater compared to shake flask. The increase of efficiency may be due to proper mixing between lixiviant and ore particle. In 7 days, about 72% Ni leaching could be observed.

CONCLUSIONS

1. H_2SO_4 is a better lixiviant compared to HCl.

2. Higher acid concentration and lower particle size improve the leaching kinetics.

3. In H_2SO_4 medium, the efficiency of Ni leaching is higher than that of Fe.

4. The Ni leaching efficiency increases with increase of density up to 20%.

5. Leaching kinetics follows a 1st order irreversible rate equation.

6. The dissolution process follows diffusion control-dense-constant size-spherical spheres model.

6. Leaching in 40 liter reactors shows recovery of Ni around 72% in 7 days.

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