Dissolution Behaviour of Lateritic Nickel Ore in HCl and HCl-C₂H₅OH-H₂O Medias

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Abstract

In this study; HCl ve HCl-C₂H₅OH-H₂O leaching behaviour of the ore sample containing 1.87 %Ni obtained from Karaçam (Eskişehir-Turkey) lateritic deposit that started operation recently was investigated. Acid concentration, temperature and reaction time were investigated as variables by comparison leaching tests and the optimum leaching conditions were determined by Ni,Fe, Co and Mg analyses.

In the HCl leaching experiments 70°C, 8N HCl concentration and a reaction time of 90 minutes were found to be the optimum parameters in the tests repeated for HCl leaching and Ni and Fe contents in the solution phase were found as 97.09% and 97.84% respectively. Leaching experiments were also done using mixed-aqueous HCl-C₂H₅OH-H₂O solvent system that improved interesting results for some different complex ores but no improvements were observed compared to HCl leaching. Bulk (pH:10) and selective (pH:10 and pH:5,5) precipitation tests were performed on the pregnant HCl leach solutions obtained at optimum leaching conditions for the recovery of Ni from solution. Ni and Fe precipitation recoveries from HCl leach solution was found 2.94%. Although the grade of 2.94% Ni obtained for the precipitate from the HCl leach solution was of high grade ore quality. In the selective precipitation tests, after removal of Fe at pH:10, nickel was precipitated at pH:5,5 and the Ni grades of the precipitates obtained from HCl leach solution, was determined as 13.43%.

1. Introduction

In the beneficiation of sulphide nickel ores, mostly pyrometallurgical methods are used. On the other hand, about 39% of lateritic ores are beneficiated by pyrometallurgical, and 61% are beneficiated by hydrometallurgical methods [1]. In laterite beneficiation, the ore properties are of significance; that is to say, limonitic ores are eneficiated by high pressure acid leaching or via the Caron process, nontronitic ores are beneficiated by high pressure acid leaching or heat treatment (smelting), and ores containing serpentine by pyrometallurgical methods [2, 3, 4].

Having complex mineralogies, lateritic nickel deposits that have commercial value mostly do not contain tree nickel minerals; and their nickel content is in the form of being adsorbed on to iron oxide and/or silicate minerals or in the form of a substituent in the structure of these minerals by translocation [5]. For this reason, upgrading their nickel content by classical mineral processing methods does not give satisfactory results; and pyrometallurgical and/or hydrometallurgical methods are used for industrial beneficiation of lateritic nickel deposits [6].

In the beneficiation of lateritic nickel ores with hydrometallurgical methods, mostly the classical sulphuric acid leaching method is used. However, the increase in demand for nickel has led to the search for new processes, such as bacterial leaching methods, also called bioleaching, and the use of organic acids such as oxalic, citric, acetic, and formic acid, as well as hydrochloric, perchloric and hydrofluoric acid leaching [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. In these studies, atmospheric chloride leach processes proposed include the Jaguar process [17, 18].

In accordance with the increase in nickel consumption around the world, the processability of the lateritic nickel deposits in our country has also been considered, and ore production and bulk leaching projects were initiated at the Çaldağ and Gördes deposits. Since the year 2004, approximately 140 million USD has been spent including the research and development studies and Caldag project has now been brought into construction phase. When up and running, the project will provide direct employment to over 500 people [19]. Besides the Çaldağ and Gördes deposits, there is another lateritic nickel ore deposit that has started production, in the Karaçam (Mihalçiçek-Eskişehir) region. Reserve studies in this region have been underway for some time, and as a result of the evaluation of certain areas, it is estimated that there is a reserve of approximately 5 million tons of ore with a grade of over 1% nickel.

In the literature, studies have been reported on the dissolution of lateritic nickel ores in hydrochloric acid media and the extraction of nickel from pregnant solutions; however, there is no study on the beneficiation of the lateritic nickel ore at Karaçam [20, 21, 22, 23, 24, 25].
In this study, after analyzing the physical and chemical properties of the sample taken from the Karaçam ore deposit, the atmospheric hydrochloric acid leaching behaviour of the ore was determined. Then, considering the results of the atmospheric hydrochloric acid leaching tests, comparative experiments were done in order to demonstrate the dissolution behaviour of the ore in a HCl-C2H5OH-H2O medium. Additionally, the subject of nickel recovery through bulk and selective precipitation from pregnant leach solutions obtained under optimum leaching conditions is also examined.

2. Experimental Procedure

The primary objective of the present studies was to determine the behaviour of lateritic nickel ore from the Eskişehir-Mihalçıç-Karaçam deposit in a hydrochloric acid leach under atmospheric conditions, and the leach experiments were repeated using mixed aqueous medias for comparative purposes. In these experimental studies, hydrochloric acid (37%, d:1.19 g/cm3) and de-ionized water were used. Chemical analysis of Ni, Co, Fe, and Mg was carried out with an atomic absorption spectrometer. Solid samples were also analysed by XRD (Rigaku D/max-2200 XRD Diffractometer-CuKα) and TG/DTA (Setaram Labsys Thermal Analyzer, heating rate-air atmosphere at 10°C/minute), and particle size analyses were performed using a Sympatek laser grain size analyzer.

2.1. Characterisation of the ore sample

Approximately 50 kg of sample from the Eskişehir-Mihalçıç-Karaçam deposit was taken from the raw ore and sieved to collect the fraction below 5 mm. The grain size of the raw ore was further reduced by using a roll crusher and the samples to be used in the experiments were prepared by sieving at 0.50 mm. As per the particle size distribution of the sample used in the experiments given in Figure 1, the entire sample passes a particle size of 650 μm, and 80% of the sample passes a particle size of 273 μm.

Figure 1. Particle size distribution curve of the Karaçam ore sample.

The moisture content of the test sample was determined to be 6.69% and the solids density is 2.70 g/cm3. The chemical composition of the sample, as analyzed by atomic adsorption, and its loss on ignition value are shown in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Mg</th>
<th>Loss on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>1.87</td>
<td>0.09</td>
<td>26.77</td>
<td>3.39</td>
<td>11.44</td>
</tr>
</tbody>
</table>

TG/DTA analysis was performed on the ore sample over the 25 to 1000°C temperature range, and the curves are presented in Figure 2. The endothermic peak at about 303°C is indicative of goethite’s transformation to hematite, as per Reaction 1[29].

2FeOOH = Fe2O3 + H2O
(1)

Decomposition of antigorite (serpentine) is indicated by the peak at 630°C (Reaction 2), and following that an exothermic peak indicates forsterite (Mg2SiO4) formation at about 800°C, as per Reaction 3 [30].

Mg3Si2O5(OH)4=Mg3Si2O7+2H2O
(2)

2Mg3Si2O7 = 3Mg2SiO4 + SiO2
(3)

Figure 2. XRD pattern and TG/DTA curve of the Karaçam ore sample.

In all leaching experiments, ore samples used were dried for 2 hours at 105°C. Using a 1/3 w/v solid/liquid ratio, as indicated by preliminary tests, 40 gram sample was leached in 120 ml solvent at different acid concentrations, temperatures and times in a 200 ml pyrex reactor. The leaching experiments were carried out in a pyrex reactor placed in a water bath and the bath temperature was controlled with a thermocouple within a temperature range of ± 0.1°C. The mixed aqueous media leaching experiments were carried out under the same conditions, using a reflux condenser.

3. Results and Discussion

3.1. Hydrochloric acid leaching

Leaching experiments were carried out over the range of...
1-8N hydrochloric acid concentration at a leaching time of 30 minutes, at the 20°C, 45°C, 70°C and 95°C temperature conditions. The results are shown in Figure 3.

In the experiments carried out at 20°C, extraction was found to follow the order of Co>Mg>Ni>Fe. There was an increase in Co, Ni and Fe dissolution over the range of 1-4N HCl concentration; however, there was a steady decrease in Mg dissolution. The highest extractions achieved for Co, Ni, and Fe were 58.74%, 19.32% and 16.59% at 8N HCl concentration, respectively, while the highest value for Mg dissolution (34.47%) was reached at a 1N HCl concentration.

The irregularities in the dissolutions have become more significant at 45°C (Figure 3); decreasing trends in dissolution at 70°C were observed at 3N HCl concentration, increasing dissolutions at higher acid concentrations reached to the values of 100%, 94.37%, 93.03% and 92.85% for Co, Ni, Fe and Mg in 8N HCl concentration. At 95°C, the irregularity have disappeared and all the extraction ratios reached to the close values to each other at the concentration of 8N acid with increasing HCl concentration, which were 98.33%, 100%, 97.75% and 97.72% for Ni, Co, Fe and Mg.

Considering the results of the foregoing experiments, it was decided to investigate the effect of leaching time, considering that there are significant increases in the extractions of the metals when the HCl concentration increases from 6N to 8N at 45°C. The time and the extent of this rapid increase has been explored at a constant temperature of 45°C, carrying out leaching experiments of 30–60–90–120–240 minutes at 6N and 8N HCl concentrations. In the leaching experiments at 6N HCl and at a temperature of 45°C, an increase in dissolution was observed during the first 60 minutes (Co>Mg>Ni>Fe), maintaining the dissolution order as leach time is extended further.

Further leaching experiments were carried out at a temperature of 70°C over the range of 4-8N HCl concentration, with results having been presented in Figure 5. At a temperature of 70°C and a leaching time of 90 minutes at a 4N HCl concentration, there was a rapid increase in Co dissolution, a steady increase in Ni and Mg dissolution, and a slight increase in Fe dissolution. The dissolution trend for all elements decreases between 30–60 minutes. At 70°C and 8N HCl concentrations, the extractions of metals reaches almost completely able to be extracted at the end of the 240 minutes period or leaching in HCl medium, conditions of T=70°C, [HCl]=8N and t=90 were regarded as the optimum Co could be extracted to an extent of 99.31%, Ni extraction was 97.09%, Mg extraction 96.73% and Fe extraction was 97.84%.

Further experiments were conducted over the range of 1-6N HCl concentration at a temperature of 95°C for 30–240 minutes of leaching, and results are presented in Figure 4. In the leaching experiments performed, the dissolution order for all leaching times at a 1N HCl concentration (Figure 3-4) is Mg>Ni>Co>Fe. There was an increase in dissolution of Co with time, but no significant change was observed for Mg, Ni and Fe. Except for some iron in solution at 30 minutes, Fe extraction was negligible. Mg dissolution was the highest, followed by Ni and Co, respectively, at a leach residence time of 240 minutes. Irregular dissolution behaviours were observed when the HCl concentration was increased to 2N. After 240 minutes, the following extractions were achieved: Mg 77.56%, Co 60.52%, Ni 45.39% and Fe 8.04%.

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### Figure 3. Effects of HCl concentration on the dissolution of Ni, Co, Fe and Mg at different leaching temperatures.

### Figure 4. Effect of leaching time on the dissolution of Ni, Co, Fe and Mg at different HCl concentrations at 70°C.

#### 3.2. HCl-C2H5OH-H2O Media Leaching

Hydrochloric acid media experiments gave good results when considering the extraction of nickel and cobalt values. The HCl media was mixed with absolute ethanol in different volumetric amounts (25%, 50% and 75%) for the purpose of improving the extraction values and achieving selectivity. Mixed aqueous (HCl-C2H5OH-H2O) leaching experiments were carried out at different temperatures, acid concentrations, leaching time and ethanol concentrations. Significant Ni, Co, Fe and Mg extraction results are given in Table 2 for mixed aqueous leaching experiments.

### Table 2. Some significant extraction results for HCl and mixed aqueous medias.
3.3. Bulk and Selective Precipitation

As a result of the leaching experiments carried out, the recovery of iron and nickel in the pregnant solution obtained under optimum conditions was studied by precipitation. For this purpose, the pH value was changed by NaOH addition and the recovery of iron and nickel in the dissolved phase by bulk and selective precipitation was investigated.

4. Conclusion

In the acidic leaching experiments carried out in order to determine the dissolution behaviour of Karaçam lateritic nickel ore within the media of HCl and HCl-C₂H₅OH, the acid concentration, temperature, time have been optimized. Within the created atmospheric HCl acid leaching optimum conditions ([HCl]:8N, T:70°C, t:90 minutes), it has been understood that nickel and iron show similar dissolution behaviour, and nickel can be extracted at the value of 97.09% and the iron can be extracted at 97.84%.

Atmospheric acid leaching experiments in HCl-C₂H₅OH-H₂O medias have been carried out for the purpose of improving the results obtained under optimum conditions in HCl media. The amount of ethanol was used in three different volumes (25%, 50%, 75%) in mixed aqueous media. The effect of acid concentration, temperature and leaching time were also determined in the HCl-C₂H₅OH-H₂O medias compared to the HCl media. Primarily, the effects of temperature and acid concentration on the leaching time of the 30 minutes reaction in different ethanol contents were studied and after these experiments leaching time optimization is investigated at 45°C in 6N-8N acid concentrations. As a result of these experiments, when results are compared with HCl media in mixed aquous medias dissolution rates not seen that any improvement and it was determined that the best again HCl media. Atmospheric acid leaching experiments have also been performed in HCl media compared to mixed aquous medias, for the purpose of improving the extraction values in the leaching process and achieving selectivity. And in these experiments, acid concentration, temperature and time are optimized as well as in the case of hydrochloric acid leaching. Optimum conditions ([HCl]:8N, T:70°C, t:90 min) were obtained at a lower acid concentration and temperature. Under these conditions, it was determined that nickel can be extracted at the value of 97.09% and the iron at 97.84%.

Bulk (pH:10) and selective (pH:10 and pH:5.5) precipitation tests were performed on the pregnant HCl leach solutions obtained at optimum leaching conditions for the recovery of Ni from solution. Ni and Fe precipitation recoveries from HCl leach solution was found 2.94%. Although the grade of 2.94% Ni obtained for the precipitate from the HCl leach solution was of high grade ore quality. In the selective precipitation tests, after removal of Fe at pH:10, nickel was precipitated at pH:5.5 and the Ni grades of the precipitates obtained from HCl leach solution, was determined as 13.43%.

As a result of all experiments applicable flowsheet is given in Figure 5.

![Figure 5](image-url) Applicable flowsheet extraction of Ni from ore.

References

Metallurgy Review, 21(6),527-599.