Nickel and Cobalt Extraction from Caldag Lateritic Nickel Ores by Hydrometallurgical Processes

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Abstract

In that study that we conducted, first atmospheric pressure sulphuric acid leaching was applied to the lateritic nickel ore and the effects of the parameters such as leaching duration, leaching temperature, acid concentration, grain size and pulp density on nickel and cobalt extractions were determined and according to these optimized parameters, with 150 g/l acid concentration, at 80°C leaching temperature and in 120 minutes leaching duration, with 10 % pulp density and 0.074 mm grain size, it was achieved to extract nickel with 69.89% and cobalt with 62.80% efficiencies. Then, by the way of applying of the process of pug-roast-leach, the effect of parameters such as acid amount, roasting temperature, roasting duration, leaching duration and pulp density on nickel and cobalt extractions were determined and according to these optimized parameters, by using sulphuric acid 150 wt % of ore, at 300°C roasting temperature and in 60 minutes roasting duration, in 30 minutes after roasting leaching duration and with 0.125 g/l pulp density, it was achieved to extract nickel with 76.80% and cobalt with 45.75% efficiencies. It has been seen that instead of acid leaching, acid pug-roast-leach process is more effective in nickel extraction from lateritic ores.

1. Introduction

Despite 73% of nickel sources in earth are lateritic, only 44% of the total nickel is being produced from laterites [1]. To meet future demand for nickel, there is an increasing proportion of nickel being extracted from laterite ores [2]. Because of that reason and also dangerous effects of production process from sulfide formed ores on the environment, production of nickel from lateritic ores has become very significant.

Production of nickel from lateritic ores is carried out in three different ways: hydrometallurgical, pyrometallurgical and hydrometallurgical-pyrometallurgical methods according to the magnesium content and the ratio of nickel to iron [3].

In our country, especially in Manisa Caldag region, there are approximately 68.5 million tons of lateritic structured nickel ore, from which nickel can be produced by hydrometallurgical processes, with relatively low magnesium and low nickel / iron ratio [4].

Hydrometallurgical processes that applied to lateritic ores can be investigated in 3 groups as high pressure acid leaching, atmospheric pressure acid leaching and acid pug-roast-leach process which was our main focus point in this project. Nickel production can be achieved economically from ore containing Mg below 4% with high pressure acid leach process. [5] However, studies have been made to apply atmospheric pressure acid leaching due to high cost autoclave requirement of high pressure acid leach. In the atmospheric pressure acid leaching studies that conducted, it was possible to obtain 85% nickel in 40-80 days from the iron-containing ore containing less than 50% [6].

The aim of this study is to determine the optimum parameters of nickel and cobalt production from limonitic formed lateritic nickel ores which have been taken from Manisa Caldag region by the atmospheric pressure sulphuric acid leaching and also acid pug-roast-leaching processes and then, hydroxide precipitation process; to evaluate these hydrometallurgical processes kinetically and to produce these metals most effectively and hereby, to contribute to the development of industrial production processes.

2. Experimental Procedure

On experimental study, 2 different methods have been implemented on nickel ore to take the nickel into the solution. First, atmospheric pressure sulphuric acid leaching process and then acid pug – roast – leach process have been applied to the grinded lateritic nickel ores and leaching efficiencies of these 2 methods were compared. After taking the nickel into the solution, iron removal and mixed hydroxide precipitation processes applied to the pregnant solution that obtained from acid pug - roast – leach process. On Figure 1, flow chart of experimental study has been given.

The results of experiments were obtained with chemical analysis of solutions with Perkin Almer Aanalyst 800 Atomic Absorption Spectroscopy and chemical analysis of
precipitated metal compound powders remained in filters after solid-liquid separation.

**Figure 1. Flow chart of experimental studies**

### 2.1. Atmospheric pressure acid leaching

On leaching experiments, 10 g of lateritic ore, magnetic stirrer (800 rpm), diluted sulphuric acid, filtration system were used and effects of parameters such as leaching duration, leaching temperature, acid concentration, particle size and pulp density on nickel, cobalt and iron leaching efficiencies were investigated and obtained parameters have been optimized.

### 2.2. Acid pug – roast – water leaching

On acid pug – roast - water leaching process, 10 g of lateritic ore, concentrated (% 96-98 purity) sulphuric acid, atmosphere controlled furnace, magnetic stirrer (800 rpm), distilled water and filtration system were used and effects of parameters such as acid/ore ratio, roasting duration, roasting temperature, leaching duration and pulp density on nickel, cobalt and iron leaching efficiencies were investigated and obtained parameters have been optimized.

- **NiO(s) + H₂SO₄(l) → NiSO₄(s) + H₂O(g)** (1)
- **CoO(s) + H₂SO₄(l) → CoSO₄(s) + H₂O(g)** (2)
- **Fe₂O₃(s) + 3H₂SO₄(l) → Fe₂(SO₄)₃(s) + 3H₂O(g)** (3)
- **FeO(s) + H₂SO₄(l) → FeSO₄(s) + H₂O(g)** (4)

The chemistry of roasting process has been shown on the equations above. According to these chemical reactions, water insoluble nickel, cobalt and iron oxides had been converted to water soluble sulphates of these metals during roasting process.

### 2.3. Iron removal process

After nickel, cobalt, iron and low amounts of other metals such as Al, Mg, Mn, Cr, Zn were taken into solution, before the extraction of nickel and cobalt from solution, iron removal process was implemented. To remove the iron by neutralization which is called goethite precipitation process, first, oxidation of ferrous ions to ferric ions has to be provided. Because, the solubility value of ferrous ions’ changes with pH is very close to nickel and cobalt ions’ values as it can be seen on metal hydroxides’ precipitation diagrams. After oxidation, pH was adjusted from 1.0 to 2.5 with addition of NaOH and iron was precipitated. The chemistry of the oxidation and precipitation reactions taking place in this process have been shown on Equations 5-6.

- **2 Fe²⁺SO₄²⁻ + H₂SO₄ + H₂O₂ → Fe²⁺(SO₄)₂²⁻ + 2H₂O** (5)
- **Fe₂(SO₄)₃ + 6NaOH → 3Na₂SO₄ + 2Fe(OH)₃** (6)

### 2.4. Mixed Hydroxide Precipitation Process

After removal of iron from solution, by adjusting the pH value of pregnant solution with 3,33 M NaOH from 2.5 to 7.5, nickel and cobalt hydroxides were precipitated according to the Equation 7-8.

- **NiSO₄ + 2NaOH → Na₂SO₄ + Ni(OH)₂** (7)
- **CoSO₄ + 2NaOH → Na₂SO₄ + Co(OH)₂** (8)

### 3. Results and Discussion

The chemical analysis result of lateritic nickel ore has been given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>Co</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.41</td>
<td>24.94</td>
<td>0.062</td>
<td>4.0</td>
<td>5.88</td>
<td>40.9</td>
</tr>
</tbody>
</table>

**Table 1. Chemical analysis results of lateritic ores**

According to particle size analysis, as it can be seen in Figure 2, average particle size of grinded ore is 27,757 μm.

Atmospheric pressure sulphuric acid leaching process experiments were carried out, the parameters that affects the leaching efficiency were investigated and following results were obtained;
As it can be seen in Figure 3, because nickel and cobalt leaching efficiencies did not increase considerably over 90 minutes of leaching duration, optimum leaching duration was determined as 90 minutes.

As it can be seen in Figure 6, with a decrease of particle size from 100 µm to 74 µm, especially cobalt leaching efficiencies increased significantly. This shows that kinetic principles of cobalt’s leaching is more important than nickel’s. Optimum particle size value was determined as 74 µm.

According to the results of experiments that conducted with different pulp densities, it could be seen that especially over 20 % pulp density value, the leaching efficiencies of nickel and cobalt decreased dramatically. In the scope of industrial production, the pulp density can be changed between 10-20 % according to the conditions of facility. When we consider the importance of nickel metal, we determined 10 % pulp density as optimum value.

Rather than dissolving metal oxides directly with sulfuric acid; acid pugging - roasting - leaching process was carried out experimentally in order to determine how the leaching efficiencies of nickel and cobalt, which are significant metals present in lateritic ores, and iron, as contaminating metal, will be changed when metal oxides are first converted into water soluble metal sulphates and then dissolved in water. The following results were obtained.

As it can be seen in Figure 3, because nickel and cobalt leaching efficiencies did not increase considerably over 90 minutes of leaching duration, optimum leaching duration was determined as 90 minutes.

According to the results seen in Figure 5, increase of the leaching temperature caused increase of the leaching efficiency of nickel, cobalt and iron almost linearly. However, the efficiency of nickel and cobalt did not increase significantly over 80°C while efficiency of iron did. So, 80°C determined as optimum leaching temperature.

According to the results given in Figure 8, 150 % of ore’s weight sulphuric acid (H2SO4) is required theoretically. However, according to the results given above, at least 70 % of ore’s weight concentrated sulphuric acid (H2SO4) is required theoretically. However, according to the results given in Figure 8, 150 % of ore’s weight sulphuric acid is the optimum value for obtaining most efficient leaching process because over this value, the leaching efficiency of nickel and cobalt did not increase significantly while iron’s did.

According to the experiment results shown in Figure 9, the optimum roasting duration value has been determined as 30 minutes due to leaching efficiency of nickel and cobalt did not increase significantly over 30 minutes.
According to the results of experiment, increasing roasting temperature increased the leaching efficiency of both nickel and cobalt significantly up to 300°C. So, this temperature value determined as optimum.

After roasting experiments and process optimizations, in order to see the effect of water leaching duration experiments were carried out and according to the results, 30 minutes was long enough for receiving the metals into solution so 30 minutes determined as optimum duration for water leaching process.

According to the result seen in Figure 12, especially the leaching efficiencies of nickel and cobalt decreased with the increase of pulp density. At 100 g/l pulp density, the efficiencies were the highest but when the pulp density was increased to 125 g/l, leaching efficiency of iron decreased significantly and therefore that value was determined as optimum.

When all the results were evaluated, with the optimum parameters, in acid pug – roast – leach process, the leaching efficiency of nickel was higher and iron was lower than the efficiencies in atmospheric pressure acid leaching. For that reason, nickel extraction processes, which are iron removal and hydroxide precipitation experiments, were carried out on the solution that taken from water leaching step. After all the precipitation processes, it was determined that 88.14 % of iron had been precipitated with 17.18 % nickel loss and 90.81 % of nickel and 75.22 % of cobalt could be precipitated.

4. Conclusion

According to the results obtained; instead of direct sulphuric acid leaching process, with applying of pug-roast-leach process, it has been seen that nickel extractions could be increased by 9.88 %, iron leaching efficiency could be decreased by 8.69 % which would decrease the amount of chemicals required for the oxidation and neutralization. Also, the processes could be completed in 33.33 % less time.

According to these result, it has been seen that the lateritic ores in Manisa-Caldag are utilizable to produce nickel and cobalt effectively. It was clearly seen that Turkey has the necessary and sufficient resources to produce stainless steels, high quality alloyed steels and nickel and cobalt super alloys efficiently.

References