INVESTIGATION OF SELECTIVE LEACHING PROCESS OF NICKEL SILICATE ORE FROM THE DEPOSIT "RUĐINCI"

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Abstract: This paper presents the results of research on the high-temperature sulphuric acid pressure leaching of nickel silicate ore from the deposit "Rudinci". The aim of the research was to determine optimal parameters of the leaching process. As well, the effect of KMnO₄ on iron precipitation and purification of the leach solution was investigated. Beforehand, according to the results of both chemical and mineralogical characterization of the ore "Rudinci", the way of its processing and the leaching agent were chosen and the main chemical reactions of the leaching process were determined.

INTRODUCTION

Nickel production is based on processing of sulphide and oxide ores. Thanks to possibility of their flotation, nickel sulphide ores are less complicated for processing than oxide ores. However, the main world nickel resources are oxide ores. Also, the nickel production from marine nodules consisting of oxide minerals, with about 3% (Cu + Ni + Co), becomes increasingly important [1]. The nickel recovery from the low-grade oxide ores is an actual problem of the nickel metallurgy. The nickel oxide ores are mostly low-grade ores with high content of moisture and useless minerals (SiO₂, MgO, CaO, Al₂O₃, etc.). Many researches indicated the impossibility of the nickel minerals concentration from these ores by physical methods. Therefore, these ores are manufactured directly by both, pyrometallurgical and hydrometallurgical processes. The pyrometallurgical processes demand the considerable energy consumption and mostly used process of them is ferronickel smelting. The ferronickel smelting in a conventional electric-furnace is generally limited by the SiO₂/MgO ratio or iron content in the ore. Operation in the electric-furnace generally requires a SiO₂/MgO ratio not greater than 2 and an iron content of not more than 20% [2].

The hydrometallurgical processes make possible the complex processing of low-grade nickel oxide ores with energy savings. Today's ammonia leaching processes are improvements of the original Caron process started in Cuba [3]. The Caron process involves the reduction of the ores at temperatures between 700 and 800 °C followed by leaching with ammoniacal carbonate solution under aerobic condition. During the time, this process has been modified in order to increase the Ni and Co recoveries from the ores and many variations of the original Caron process exist in the world today. The US Bureau of Mines process [4] and the UOP process [5] use various additives, which include sulphur and chlorides. It is considered that these additives prevent the formation of nickel unsoluble forms during the ore reduction. Valix and Cheung studied the influence of elemental sulphur additions on the nickel laterites reduction and reported that the sulphur presence markedly improved the Ni and Co recoveries from the ores.

The acid pressure leaching process of laterites started in Moa Bay, Cuba, in 1959 [7]. The Moa Bay process includes the sulphuric acid leaching of nickel ores at about 250 °C, the phase separation and the nickel sulphide precipitation by hydrogen sulphide. The temperatures above 200 °C make possible to achieve maximal iron precipitation and good purity of leach solution. A considerable leaching degree of both Ni and Co (93-95 %) may be achieved by applying the Moa Bay process for treatment of nickel laterites. The AMAX process is an improvement of the Moa Bay Process which provides lower sulphuric acid consumption during the leaching. The savings of sulphuric acid is achieved by preliminary roasting of the ore in presence of elemental sulphur.
There are substantial reserves of nickel ores in Serbia. These ores can be divided in three regions: Zapadna Morava region, Sumadija region and Mokra Gora region.

Vučurović [8] studied ammonia leaching process of the nickel silicate ore "Rudinci" from the Zapadna Morava region. He suggested as optimal the ore reduction roasting at 800 °C for 2 hours. Also, he reported that CO was more efficient reduction agent in comparison with H2: the nickel recovery from the ore reduced by CO was about 70 % Ni and from the ore reduced by H2 was 60 % Ni. Addition of 2 % CaCl2 during the reduction by H2 led to the increase of the nickel leaching degree from 60 to 64.5 % Ni.

This paper presents the results of research on the high-temperature sulphuric acid pressure leaching of the nickel silicate ore "Rudinci". The aim of the research was to determine optimal parameters of the leaching process. Besides, the effect of KMnO4 on iron precipitation and purification of the leach solution was investigated.

**CHEMICAL PROCESSES**

Sulphuric acid leaching of nickel ores in autoclave is based on selective dissolution of Ni and Co from the ores. With increase of temperature and pressure, the solubility of nickel and cobalt sulphate increases, while the solubility of aluminium, magnesium and ferric sulphate decreases. In this way the selective dissolution of Ni and Co from the ore can be achieved and the leach solutions with low iron content can be obtained, which makes their further purification easier.

The goethite dissolution occurs by formation of ferric sulphate:

\[
\text{FeOOH} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}
\]  

which immediately hydrolyzes at temperatures above 200 °C by iron precipitation as hematite and arising of sulphuric acid:

\[
2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + 6\text{H}^+
\]  

The reaction given above makes it possible to reduce consumption of sulphuric acid due to its regeneration during iron precipitation. Also, in this way can be achieved a high \([\text{Ni}]/[\text{Fe}]\) ratio in the leach solution because the nickel dissolved by Eq. 3 does not precipitate at these high temperatures.

\[
\text{NiO} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2\text{O}
\]  

The behaviour of aluminium during the leaching is similar to iron, i.e. it first dissolves and then hydrolyzes with precipitation of alunite.

Magnesium oxide from the ore reacts with sulphuric acid with formation of MgSO4 whose solubility decreases when the temperature increases.

**EXPERIMENTAL RESULTS**

**CHEMICAL AND MINERALOGICAL ANALYSIS OF ORE "RUDINCI"**

For experimental studying of nickel silicate ores leaching at high temeperatures and pressures the ore from the deposit "Rudinci" with 1.29 % Ni was used.

In order to investigate in detail the characteristics of the ore, its chemical composition was determined (table 1) and the microphotographs of prepared ore samples were taken.

Table 1. Results of chemical analysis of the ore "Rudinci"

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Al</th>
<th>Mg</th>
<th>Cr</th>
<th>Mn</th>
<th>Ca</th>
<th>Na + K</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>WT, %</td>
<td>1.29</td>
<td>0.045</td>
<td>15.74</td>
<td>2.12</td>
<td>3.04</td>
<td>0.75</td>
<td>0.37</td>
<td>1.00</td>
<td>0.08</td>
<td>25.34</td>
</tr>
</tbody>
</table>
In the Figures 1 and 2 are presented microphotographs of prepared ore samples in need of qualitative characterization and perceiving mutual relations of present minerals. This ore belongs to disintegration crust deposit and the main minerals are garnierite, probably nontronite and nepouite as secondary nickel recipient minerals, and milerite as primarily. Garnierite is an important ore of nickel, consisting essentially of hydrated silicate of magnesium and nickel, perhaps $\text{H}_2\text{(Ni,Mg)}\text{SiO}_4 + \text{water}$, but very variable in composition, particularly as regards the nickel and magnesium, not always homogeneous. Amorphous. Very similar to garnierite is nepouite, but it has crystal structure. XRD and IR analyses are required for precise determination. Chromite, hematite and limonite - goethite are the other minerals in this paragenesis. Average contents of nickel and cobalt in the ore is 1.29% Ni and 0.045% Co.

**DETERMINATION OF OPTIMAL LEACHING PARAMETERS**

The sulphuric acid leaching of the ore "Rudinci" at temperatures below 100 °C and under atmospheric pressure showed that iron conten in the final solutions was from 8 to 10 times greater than nickel content, which complicated purification of the solutions and nickel separation from the solutions. In order to attain a high leaching selectivity, further investigation is aimed to the sulphuric acid leaching of the ore at high temperatures in the autoclave.

From the experimental results the following parameters were determined as optimal for the autoclave leaching process of the ore "Rudinci":

- temperature: 220 – 240 °C,
- leaching time: 120 min,
- phase ratio (S:L): 1 : 1.5,
- initial concentration of $\text{H}_2\text{SO}_4$: 210 – 220 g/l,
- pressure: 2.3 – 3.3 MPa.

These temperatures are sufficient to secure good leaching selectivity and the nickel leaching degree of 95 %Ni. The higher initial concentrations of $\text{H}_2\text{SO}_4$ than optimal cause the considerable increase of iron dissolution, while the nickel leaching degree insignificantly increases, which does not justify growth of initial solution acidity.

Influence of the ore granulometry on the nickel leaching dissolution was studied for three different fractions under following leaching conditions: 220 °C, 120 min, initial concentration of 210 g/l $\text{H}_2\text{SO}_4$ and phase ratio (S:L) of 1 : 1.5. Obtained results are shown in table 2, from where it can be seen that decrease of particles size almost does not effect on the nickel leaching degree. For that reason, the ore granulometery of 100% - 0.833 mm was taken as satisfactory.
Table 2. Effect of ore granulometry on leaching of nickel and iron

<table>
<thead>
<tr>
<th>Ore granulometry</th>
<th>Concentration in leach solution, g/l</th>
<th>Ni leaching degree, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Fe</td>
</tr>
<tr>
<td>100% - 0.833 mm</td>
<td>8.40</td>
<td>3.85</td>
</tr>
<tr>
<td>100% - 0.351 mm</td>
<td>8.52</td>
<td>4.12</td>
</tr>
<tr>
<td>100% - 0.147 mm</td>
<td>8.70</td>
<td>4.00</td>
</tr>
</tbody>
</table>

PURIFICATION OF LEACH SOLUTIONS FROM IRON

The solutions obtained by leaching under optimal conditions contained 8 - 8.5 g/l Ni, 2.0 - 3.9 g/l Fe, 25 - 35 g/l H₂SO₄, 105 - 135 g/l MgSO₄ and 0.06 - 0.10 g/l Co.

To decrease iron content and improve Ni/Fe ratio in the final leach solution, during the leaching KMnO₄ was added as oxidant for Fe²⁺ ions. In experiments where the ore was leached without KMnO₄, the final solutions contained almost equivalent concentrations of Fe²⁺ and Fe³⁺ ions. The addition of KMnO₄ has been an attempt to transform whole soluble iron to ferric form, because at temperatures above 210 °C ferric sulphate hydrolyzes and iron precipitates as hematite (Eq. 2).

The weight of KMnO₄ used in the experiments was 0.5 %wt from the ore mass. The influence of KMnO₄ on Ni/Fe ratio in the final leach solution was studied in a temperature range from 210 to 240 °C and under constant following conditions: leaching time of 120 min, initial concentration of 220 g/l H₂SO₄, ore granulometry of 100% - 0.833 mm and phase ratio (S:L) of 1 : 1.5. The obtained results are presented in Table 3.

Experimental results (table 3) show that oxidation of Fe²⁺ to Fe³⁺ by KMnO₄ improves quality of the leach solutions. However, if the leaching process is carried out at 240 °C, addition of oxidant is not necessary, because the leaching solution with iron content of about 2 g/l is obtained even without KMnO₄ presence at this temperature. The iron content of 2 g/l in leach solutions enables easy and effective their further processing.

Table 3. Influence of KMnO₄ on leaching of nickel and iron

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Fe leaching degree, %</th>
<th>Fe content in solution, g/l</th>
<th>Ni/Fe ratio in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with KMnO₄</td>
<td>without KMnO₄</td>
<td>with KMnO₄</td>
</tr>
<tr>
<td>210</td>
<td>2.46</td>
<td>3.79</td>
<td>2.75</td>
</tr>
<tr>
<td>220</td>
<td>1.90</td>
<td>3.77</td>
<td>2.08</td>
</tr>
<tr>
<td>240</td>
<td>0.92</td>
<td>1.77</td>
<td>1.02</td>
</tr>
</tbody>
</table>

CONCLUSION

This investigation indicates that the sulphuric acid leaching process of the nickel ore "Rudinci" at high temperatures and under high pressures gives satisfactory results with respect to the nickel leaching degree and the leaching selectivity. As optimal leaching conditions were determined following parameters: temperature from 220 to 240 °C, initial concentration of H₂SO₄ from 210 to 220 g/l, leaching time of 120 min, phase ratio (S:L) of 1 : 1.5 and ore granulometry of 100 % -0.833 mm. Under optimal conditions, the nickel leaching degree of about 95 % Ni was achieved and the leach solutions with iron content of 2.0 - 3.9 g/l were obtained. The ore granulometry of 100%-0.833 mm is optimal because the further decrease of the particles size does not influence on the nickel leaching process.
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degree. Addition of KMnO₄ during the leaching has as a result decrease of iron content in the leach solution, which makes further processing of the solution easier.

References