Kinetics of high pressure leaching of nickel lateritic ores

S. Stopić and B. Friedrich
IME Process Metallurgy and Metal Recycling
Intzestrasse 3
Aachen, Germany D-52072
ssstopic@ime-aachen.de

N. Anastasijević
Outokumpu Technology GmbH
Ludwig-Erhard Strasse 21
Oberursel, Germany, D-61440

ABSTRACT

The extraction of nickel from Serbian and Western Australian lateritic ore by sulphuric pressure acid leaching (PAL) has been studied. The following parameters were tested: stirring rate, acid to ore ratio, reaction time, pressure and temperature. These studies were performed with ore samples from the Rudjinci, Serbia and Silcrete, Australia, both belonging to the laterite-silicate group of deposits. An increase of the reaction temperature and the stirring speed at a fixed acid/ore ratio showed a positive influence on nickel extraction. The decrease of the oxidation potential with time correlated with the increase in Fe(II) in solution and nickel extraction as the reaction went to completion for both ores. The target values of 95 % Ni extraction and 60 % Co extraction were attained in 5 min at 250°C for the Serbian silicate ore, at an agitation rate of 1500 rpm, 10 % solids, and acid/ore ratio of 0.40. Under similar conditions only 60 % Ni, but 69 % Co could be extracted from the Australian Silcrete ore due to different mineralogy. The nickel extraction was shown follow a diffusion-controlled reaction model.
INTRODUCTION

As a result of the high nickel production costs associated with traditional pyrometallurgical techniques and the depletion of high-grade sulphide ores, renewed interest has been developed concerning the production of the nickel and cobalt by high pressure acid leaching (PAL) of nickel laterites. More than one third of the world nickel is produced from laterite ores (1) which account for two thirds of the world nickel resources. It is expected that increasing amounts of nickel will be produced from laterites since low cost open pit mining techniques are employed to recover the ore after removal of the overburden. The laterite ore consists of fresh saprolite, limonite and nontronite. These ores represent the various layers in the laterite bedrock. The limonite consists mainly of goethite, FeO(OH), which continues to a nontronite rich zone. Saprolite is the next layer, which is distinguished by its rich magnesium silicate content.

PAL is the current widely accepted process for greenfields nickel laterite projects. The extension of the process from tropical limonites to Western Australian laterites is a new approach, and as such the behaviour of the different minerals in tropical and arid laterites during leaching is widely examined. Tindall and Muir (2) conducted a fundamental investigation of the PAL technique using synthetic goethite as a model ore. It was found that goethite transforms to hematite by a dissolution and reprecipitation mechanism. The leaching rate was dependent on the acid concentration, the slurry oxidation potential, and the type of cations in the solution. It was also confirmed that the nontronite (silicate ore) reacted more promptly than iron oxides.

Rubisov and Papangelakis (3) have developed a comprehensive model including the kinetics of Co, Fe, Al, Mn and Ni dissolution in the temperature range from 230°C to 270°C. The resulting model is capable of predicting the Ni extraction and the concentration of major impurities during autoclave operation for a variety of process conditions and feed compositions. The model was validated with data from a continuous mini plant provided by INCO Technical Services during its process development campaigns.

Arroyo et al. (4) proposed an improved method to predict leaching of the nickel from the high-magnesium fraction by processing the limonite fraction of the ore. The pressure leach slurry, or solution, is then contacted with the magnesium fraction of the ore to dissolve most of the nickel contained in the high-magnesium ore fraction while dissolving only a small portion of the iron.

Because of the large presence of nickel laterites in the South-East Europe there is a need for a study of leaching under high pressures (5). The aim of this paper is to compare nickel laterite leaching from chemically different deposits in Rudjinci, Serbia and Silcrete, Australia with the use of sulphuric acid pressure leaching. The investigated parameters were reaction time, temperature, stirring speed at a fixed acid/ore ratio. This study also focuses on the influence of stirring on the kinetics of the leaching process.
EXPERIMENTAL

Materials

Table I presents the elemental analysis of the ore samples from “Rudjinci”, Serbia and “Silcrete”, Australia. Facilities did not allow detailed quantitative XRD and mineralogical analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Rudjinci (wt %)</th>
<th>Silcrete (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>25.33</td>
<td>17.40</td>
</tr>
<tr>
<td>Fe</td>
<td>14.90</td>
<td>26.42</td>
</tr>
<tr>
<td>Al</td>
<td>2.12</td>
<td>4.16</td>
</tr>
<tr>
<td>Cr</td>
<td>1.30</td>
<td>0.67</td>
</tr>
<tr>
<td>Ni</td>
<td>1.13</td>
<td>0.78</td>
</tr>
<tr>
<td>Co</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>3.22</td>
<td>1.70</td>
</tr>
<tr>
<td>Mn</td>
<td>0.37</td>
<td>0.25</td>
</tr>
<tr>
<td>Na</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>K</td>
<td>0.04</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The Rudjinci deposits are located near Vrnjacka Banja (about 200 km southern from Belgrade, Serbia) and are the most abundant ones in Serbia. The ore has a low level of Ni and Co but high level of SiO₂. The Rudjinci nickel ore deposits belong to a group of exogenous nickel deposits, a subgroup of laterite-silicate deposits. This ore belongs to disintegration crust deposit and the main minerals are garnierite, probably nontronite, as the secondary nickel recipient mineral, and millerite as the primary nickel mineral (6). The Silcrete deposit, in Western Australia belongs to a laterite limonite ore, but with higher percentages of iron and smaller content of SiO₂.

Equipment

High pressure leaching conditions tests were performed in a 2 L autoclave, manufactured by the Autoclave Engineers, USA, under similar conditions to previously published work (7,8). The temperature was controlled within ± 1°C, manipulating both an electrical heating mantle and a water-cooling system. A titanium-made impeller that was magnetically driven provided agitation. The agitation speed ranged from 250 to 2000 rpm. The autoclave was equipped with an acid injection device and a system capable to withdraw samples. This allowed exact monitoring of the reaction starting point. A certain amount of laterite was mixed with a pre-calculated amount of deionised water and placed in the autoclave. The slurry was then heated up to a fixed temperature under continuous agitation. Upon temperature stabilisation, a certain amount of the concentrated sulphuric
acid (96 wt %) corresponding to the required acid/ore ratios was injected into the autoclave under pressure using the injection device. The acid/ore ratio was typically between 0.24 and 0.50 g H₂SO₄ per g of dry ore. Using the sampling system 20 mL of suspension was periodically withdrawn through a dip tube and then rapidly cooled. After the end of experiments, solution aliquots were filtered and analysed in order to determine Ni, Co, Mg, Al, Fe and Si by ICP spectrophotometer. Eh measurements were taken using a Pt electrode with an Ag/AgCl reference electrode. pH measurements used a universal pH probe. The experiments were performed at 100, 170, 200, 230, and 250°C for up to 60 min. The equilibrium vapour pressure ranged from 1 to 40 bar.

RESULTS AND DISCUSSION

Kinetics of Nickel Dissolution

The reaction temperature has a positive influence on nickel extraction. As shown in Figure 1 a temperature of 200°C apparently does not provide the driving force needed for rapid nickel extraction from the Rudjinci ore. However the increased temperatures of 230°C and 250°C gave final extraction values of 82 and 86 % Ni.

Figure 1 – Nickel Dissolution Kinetics 200-250°C - Rudjinci Ore
(10% solids, a/o=0.4, 250 rpm)

Similar one-hour leaching tests were performed with the Silcrete ore in the temperature range of 100°C to 250°C as shown in Figure 2. An increased temperature led again to a higher nickel extraction but in this case only 70 % Ni can be extracted.
Most likely the different leaching efficiency could be related to the different mineralogy of the limonite and silicate ores. According to Whittington and Muir (9) the different content of Fe, Al, Mg, and Si can cause changes in acid consumption and leaching efficiency. They reported that acid consumption required for high Ni (95%) and Co (> 90%) extraction depends mainly on the concentration of Mg, Al and FeCO$_3$ (siderite) in the ore. The acid consumption for the Australian limonite amounted between 0.2 and 0.6 kg/kg ore in the temperature range of 245-250°C. For the silicate laterite ore an acid consumption of 0.4 kg/kg ore in the temperature range 235-250°C was expected, but higher levels of acid addition were not tested in this work.

For both types of ore it was observed that the increase of nickel extraction was accompanied by a decrease of the oxidation potential as shown in Fig. 3.
This could be a suitable measurement for process control. We propose that Eh is directly correlated with increased Fe(II) relative to Fe (III) concentration as the iron oxide minerals (goethite and magnetite) react and transform to jarosite and hematite. At low Eh, Fe$^{2+}$ facilitates the electron transfer into the iron oxide lattice, which promotes the breakdown of the iron oxide lattice by the sulphuric acid (3).

The free acid concentration decreased in both cases during leaching as shown in Figure 4. The initial concentration of sulphuric acid amounted to 40 g/L. However, the hydrolytic precipitation of iron and aluminium regenerates acid, eventually leading to a stabilized acid concentration of about 20 g/L. The free acid concentration is slightly lower after leaching of the Rudjinci ore, due to the higher consumption of the sulphuric acid, related to the higher Mg content of the ore.

![Figure 4 - Comparison of free Acidity and Ni extraction during PAL](T = 250°C, 10 % solids, a/o=0.4, 250 rpm)

Rubisov et al (10) examined the effect of free acid on nickel extraction from a limonite and saprolite ore and found that nickel extraction increased with free acid concentration but differed with ore type. Similar results were reported by Whittington et. al.(11), who found that the nickel extraction increased by about 10% when the free acid levels increased from 20 g/L to 60 g/L. Thus the results shown in Figure 4 are consistent with other work.

**Agitation Speed and Leach Selectivity**

Leaching tests of limonitic laterites conducted by Georgiou and Papangelakis (12) at agitation rates between 450 and 650 rpm demonstrated that the agitation rate had a negligible effect on nickel dissolution. Chou et al. (13) showed that the nickel extraction is independent of agitation after a brief initial mixing period. In his experiments, two axial turbines provided mixing between 50 and 600 rpm. However, they reported that Sobol attained high leaching rates and complete conversion in shorter time due to the...
more rapid mixing conditions under high-pressure circumstances. Tindall and Muir (2) had the same opinion for the agitation range of 130 and 410 rpm. Kuxmann and Landau (14) found that an agitation rate of 800 rpm is needed to prevent the solid particles from settling on the bottom of the autoclave. They concluded that an agitation rate above 800 rpm does not influence extraction of nickel.

For proper comparison of the mixing regimes one needs to calculate the Reynolds number. Unfortunately, there are no data in the literature about the influence of agitation speeds above 800 rpm under high pressure leaching conditions for Ni-Co laterites. Since the reaction mechanism of the leach process is strongly dependent on the local conditions surrounding the ore particle in the autoclave, we consider that turbulent flow will also influence the metal dissolution kinetics. It is expected that under increased mass transfer rate the retention time for leaching and the thickness of the boundary layer will decrease. Thus, leaching tests of the Rudjinci ore, as presented in Figures 5a, 5b and 5c were conducted with stirring speeds of 250, 875 and 1500 rpm at 250°C.

Figure 5 - Effect of Stirring Speed on Metal Dissolution Kinetics
(Rudjinci Ore, T = 250°C, 10% solids, a/o=0.4)
It can be seen that the increased agitation rate has a positive influence on nickel extraction. The agitation rate of 875 rpm leads to the final nickel extraction value of 99% in 60 min at 250°C. Besides the positive mass transfer influence of agitation speed, the settling of the solid particles to the bottom of the autoclave was also avoided. This fact was confirmed by simulating the mixing conditions under atmospheric pressure in a glass model.

The target value of 95% nickel extraction was attained in 5 min at 250°C, but with an agitation rate of 1500 rpm. We assume that under high-pressure conditions the high agitation rate could also cause a decrease in particle size by disintegration of agglomerated goethite particles. Apparently, the increased surface generated by "disintegration" of particles during leaching provides additional nucleating sites for hydrolysis of aluminium, dissolved during the initial stages of leaching. The mean particle size was determined after and before leaching using the Software "Sympatec Helos" from Germany based upon a particle size distribution analysis.

![Figure 6 - Change of Mean Particle Size during Leaching of Silcrete Ore](image)

The mean size of ore particles decreased at 100°C and 250°C due to intensive mixing and disintegration of particles. The increased size of particles at 250°C using the stirring speed of 1000 rpm is probably due to the formation and growth of crystalline jarosite and hematite.

Different models describing fluid-solid reactions were tested (15). It was finally found that Equation (1), which nominally describes a diffusion-controlled reaction model of Jander type, gives a reasonable fit to our data as shown in Figure 7:

\[ (1 - (1 - X)^{1/3})^2 = k \cdot t \]  

where X is the nickel extraction, k is the apparent rate constant and t is the reaction time.
We assume that diffusion of sulphuric acid through the hematite and SiO$_2$ layer is the rate-controlling step. The influence of stirring speed on the Ni and Co extraction from Silcrete ore at 250°C and 10% solids in solution is shown in Figures 8 and 9.

The increased agitation rate has a positive influence on nickel and cobalt extraction in all cases due to the disintegration of agglomerated goethite particles. The measurement of specific area, particle size analysis and particle morphology have confirmed that the extraction of metals was improved by intensive agitation.

The different kinetics models were tested in order to describe this leaching process. It was finally found that equation (1) gives a good fit to data for the Silcrete ore in the temperature range between 230°C and 250°C as shown in Figure 10. Again we assume that the diffusion of sulphuric acid through the layer of alunite/jarosite or hematite and SiO$_2$ is the rate-controlling step.
Sulphuric acid pressure leaching using a 2L titanium autoclave was employed for two lateritic Ni ores from Rudjinci, Serbia and Silcrete, Australia. The following summarise the findings.

1) Nickel recoveries were high in the temperature range between 230 and 250°C, indicating that nickel readily extracts from the Rudjinci ore as long as there is sufficient acid concentration (a/o= 0.4), agitation rate (1000 rpm), temperature (T = 250°C) and time (t = 60 min). The target value of 95 % nickel extraction was attained in 5 min at 250°C for the Serbian silicate ore, upon raising the agitation rate to 1500 rpm with 10 % solids.

2) One hour leaching tests of Silcrete ore under similar conditions showed that about 70 % Ni can be extracted within 60 min at an agitation speed of 250 rpm, rising to 80% Ni extraction in 15 mins at 2000 rpm. We assume that the positive influence of the agitation rate is a consequence of improved mass transfer and a disintegration of agglomerated goethite particles due to the intense mixing. The nickel and cobalt extractions were shown to follow a diffusion reaction model in the temperature range between 230°C and 250°C.

3) The H₂SO₄ concentration initially drops very fast and essentially remains constant at about 20 g/L with both ores. Other work (not reported here) indicated that an increase of acid-to-ore ratio from 0.4 to 0.5 and increase in free acidity improved the nickel and cobalt extraction.

4) The decrease of the oxidation potential in time can be related to the increase of Fe(II) relative to Fe(III) in solution as the transformation of iron oxide minerals and nickel extraction goes to completion.
5) Further studies are necessary to investigate the impact of morphology and mineralogy in order to understand better the mechanism of the mass transfer analysis and the explanation of the positive effect of the stirring speed.

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REFERENCES


