The use of mesophile microorganisms for extracting nickel out of nickel-bearing flotation tailings

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ABSTRACT
The hydrometallurgical routes are being considered as promising alternatives for processing waste and ores with low metal content. Among these routes we can mention the bioleaching process in which microorganisms are used for extracting those metals. That route is increasingly being studied for processing low metal content bearing ores. As such, microorganisms are able to promote the oxidation of sulphide minerals, including the most refractory ones, under atmospheric pressure.

This research work aimed at extracting nickel out of the flotation process tailing, which consisted essentially of silica and iron and magnesium oxides containing calcium (4.5%) and sulphur (3.2%). The sample, which bears 0.32% of nickel, is composed by near 9% of sulphides, such as pyrrhotite (Fe¹⁻S), pentlandite (Fe,Ni)S₈, violarite (FeNi₂S₄) and chalcopyrite (CuFeS₂). Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans microorganisms were used in bioleaching experiments accomplished in bench scale. The parameters monitored during the bioleaching process were pH, redox potential and concentration of metals being released into solution. According to the analytical results more than 50% of the nickel content was extracted. However, it is expected with the continuity of the test work being undertaken a substantial enhancement of the extraction efficiency without disregarding the need of decreasing the acid consumption.
INTRODUCTION

The demand for nickel is growing worldwide, driven by world market of stainless steel that consumes, approximately, 70% of primary nickel (Hewitt, 2007). This increase in consumption imposes the need to extract that metal from low metal content ores and tailings. For that to occur low investment and operating cost processes for extracting nickel are required to make that extraction feasible economically. An alternative is the bio-hydrometallurgical way, more specifically the bioleaching, which enables to reach high metal extraction with low operating cost (Watling, 2008).

The equations below, show how the pentlandite bioremediation process takes place through the mechanism of direct contact where the cells interacts with the surface of sulphide mineral, followed by an enzymatic attack to the components of that mineral being oxidized, such as Fe^{2+} (equation 1).

\[ 8(NiFe)_sS_8 + 141O_2 + 26H_2SO_4 \rightarrow 36NiSO_4 + 18Fe_2(SO_4)_3 + 26H_2O \]  
(1)

The oxidation of the pentlandite by ferric ions is shown in Equation 2.

\[ 2(NiFe)_sS_8 + 18Fe_2(SO_4)_3 \rightarrow 9NiSO_4 + 45FeSO_4 + 16S^0 \]  
(2)

During the chemical oxidation of that mineral, the ferric ion is reduced to ferrous ion (Fe^{2+}). The role of the micro-organisms, in this case, is to oxidize the ferrous ions back to ferric ions, regenerating thus the oxidising agent (equation 3). The elemental sulphur generated during the process is oxidized generating sulphuric acid in the reaction system (equation 4).

\[ 2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \]  
(3)

\[ S^0 + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \]  
(4)
EXPERIMENTAL

Mineral Sample

The mineral sample is a flotation process tailing, which consisted essentially of silica, iron and magnesium oxides with 3.2% of sulphur. The sample, which bears 0.32% of nickel, is composed by near 9% of sulphides, such as pyrrhotite (Fe\(_{1-x}\)S), pentlandite (Fe,Ni)\(_9\)S\(_8\)), violarite ((Fe,Ni)\(_3\)S\(_4\)) and chalcopyrite (CuFeS\(_2\)).

Micro-Organisms and Culture Medium

The microorganisms Acidithiobacillus ferrooxidans (Strain S), Acidithiobacillus thiooxidans (Strain FG01) and Leptospirilum ferrooxidans (Strain ATCC53992) used in this study were cultivated at 30ºC, in orbital stirrer at 150 rpm, using the modified 9K culture medium, with the following composition (Table 1).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>[g.L(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>1.0</td>
</tr>
<tr>
<td>MgSO(_4).7H(_2)O</td>
<td>0.5</td>
</tr>
<tr>
<td>K(_2)HPO(_4)</td>
<td>0.5</td>
</tr>
<tr>
<td>FeSO(_4).7H(_2)O</td>
<td>33.3</td>
</tr>
<tr>
<td>S(^\prime)</td>
<td>10</td>
</tr>
</tbody>
</table>

The pH of the culture medium was adjusted to 1.8 with H\(_2\)SO\(_4\) 5M. Prior to use in the experiment, the consortium consisting of three species of microorganisms was submitted to the adaptation process that occurred through the growth, from successive subcultures, on each new spread, the concentration of soluble source of Fe\(^{2+}\) was decreased and increased the flotation tailing content in the cultivation until a 10% w/v solid/liquid ratio was reached.
Bioleaching Tests

The experiments were accomplished in 100 cm³ Erlenmeyer flasks containing 100 cm³ of MKM culture medium (OLSON, 2003) in a 1:5 dilution and 10 g of nickel-bearing flotation tailing (pulp density of 10% w/v). The culture medium, which composition is shown in Table 2, had its pH adjusted to 1.8 with 5M H₂SO₄ solution.

Table 2. The composition of the culture medium used in the bioleaching tests.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>g.L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.8</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.8</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.08</td>
</tr>
</tbody>
</table>

All of the tests were carried out in triplicate and inoculated with the consortia of A. ferrooxidans (Fe²⁺ and S⁰ oxidizer), L. ferrooxidans (Fe²⁺ oxidizer) and A. thiooxidans (only S⁰ oxidizer), in the order of 10⁶ cells of each culture on each flask. The direct cells counting operation was accomplished in a Thoma’s chamber in optical microscope with phase contrast coupled.

After the inoculation, the Erlenmeyer flasks were incubated in stirring table (New Ethics Incubator 430), at 150 rpm in a temperature of 30± 10°C over 21 days. During the whole test period the redox potential and pH were monitored, being the pH adjusted in the range of 1.6 to 1.8 using a 5M sulphuric acid solution whenever necessary. Non-sterilized samples were used so as to establish experimental conditions close to those while running an industrial scale. The loss of water by evaporation was estimated by the weight loss and compensated by adding water.
Analytical methods

- The nickel concentration in solution was determined by atomic absorption spectrometry in equipment Varian Spectra 50B;
- The pH and redox potential measurements were carried out, directly, in the reaction system using the ANALION AN2000 equipment with a combined glass and platinum electrodes (against Ag/AgCl), respectively;
- Cell counts were accomplished using a Coleman optical microscope coupled to the N200 phase contrast, with the aid of Thoma’s chamber (Plumb, Mcsweeney e Franzmann, 2008; Mousavi et al., 2008).

RESULTS AND DISCUSSION

After 21 days of test 75.22 % of nickel out of the aforementioned tailing were extracted. Figure 1 shows the kinetics of nickel bio-extraction, where we can observe that between the 7th and the 14th day there was an increase in the nickel extraction, showing that it was possible, only with the action of mesophiles microorganisms, to obtain significant extraction of nickel, taking into consideration the experimental conditions used.

Figure 1. Nickel extraction vs. sulphuric acid consumption during the bioleaching tests.
Figure 2 shows the comparison between the biological and the conventional chemical leaching (Control test). In the test where the microbial consortium was not added 27.62% of nickel was extracted in 21 days of test with a H$_2$SO$_4$ consumption of 98.41 kg per ton of tailing. Whereas, in the inoculated test, 75.22% of nickel was extracted, in the same period of time, with H$_2$SO$_4$ consumption of 15.74 kg per ton of tailing.

![Figure 2. Nickel extraction in the inoculated and non-inoculated tests – Comparison between the bioleaching and the conventional chemical leaching.](image)

Figure 3A shows the pH variation during the bioleaching test. The pH was adjusted, whenever necessary, by adding 5M H$_2$SO$_4$ solution so as to decrease that pH down to 1.6. Such pH changes are not suitable for the proper activity of the inoculated microorganisms. Those fluctuations are, on the one hand, due to the ore composition, as it has a big content of acid-consuming minerals species (gangue minerals), and, on the other hand, by the protons (H$^+$) consumption during the bioleaching process.
Figure 3  pH (a) and redox (b) potential variation during the bioleaching tests in stirred flasks

Regarding the redox potential variation (Figure 3b) it was observed, in the control test, that such potential remained lower than that of the inoculated test during almost the whole experiment. In that case, the potential variation is due to the action of sulphuric acid in aerated solution. The microorganisms, in the bioleaching process, were in charge of raising the redox potential, during the first five days of test, to values higher than 650 mV vs. SHE and remained that high until the end of the test (21 days).

CONCLUSIONS
The nickel extraction of 75.22% in the inoculated tests indicate the feasibility of the biotechnological process in dealing with nickel-bearing flotation tailing, being more attractive than the conventional chemical leaching where just 27.62 % of the nickel content was extracted over the same period of time.
REFERENCES


