Hydrometallurgical process for the separation and recovery of nickel from sulphate heap leach liquor of nickeliferrous laterite ores

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Abstract
The Laboratory of Metallurgy of the National Technical University of Athens has developed and patented a novel integrated hydrometallurgical method, suitable to treat low-grade nickel oxide ores efficiently and economically. It involves heap leaching of the ore by dilute sulphuric acid at ambient temperature, purification of the leach liquor and recovery of nickel and cobalt by electrowinning. A typical composition of the pregnant solution produced from heap leaching is the following: Ni²⁺ = 5 g/L, Co²⁺ = 0.3 g/L, Fe³⁺ = 23.0 g/L, Al³⁺ = 6.0 g/L, Cr³⁺ = 1.0 g/L, Mn²⁺ = 1 g/L and Mg²⁺ = 8 g/L. The proposed hydrometallurgical process for nickel recovery from real sulphate heap leach liquors consists of the following six (6) unit operations:

(1) Removal of iron, aluminium and chromium, as easily filterable crystalline basic sulphate salts of the jarosite–alunite type, at atmospheric pressure, by chemical precipitation at pH: 3.5 and 95°C.

(2) Cobalt, manganese and magnesium extraction over nickel by Cyanex 272 at pH: 5.5, T: 40°C, with 20% extractant concentration and stripping of the loaded organic phase at T: 40°C with diluted H₂SO₄ (4 M).

(3) Nickel concentration by solvent extraction using Cyanex 272 at pH: 7.5, T: 40°C, with 10% extractant concentration and stripping of the loaded organic phase by nickel spent electrolyte (55.45 g/L Ni) at T: 40°C with diluted H₂SO₄ (2 M).

(4) Nickel electrowinning from sulphate solutions, using stainless steel as cathode and Pb–8%Sb as anode. The pH of the electrolyte (10 g/L H₃BO₃, 75.95 g/L Ni²⁺ and 130 g/L Na₂SO₄) was adjusted at 3.5 and at 60°C, while the current density was kept constant at 20 mA/cm².

(5) Cobalt and manganese extraction over magnesium by Cyanex 302 at pH: (5.0), T: 40°C, with 20% extractant concentration and stripping of the loaded organic phase at T: 40°C with diluted H₂SO₄ (1 M).

(6) Removal of magnesium by chemical precipitation (as brucite), using Ca(OH)₂ as neutralizing agent, at atmospheric pressure, pH = 10 and 25°C.

1. Introduction

About 60% of the current worldwide production of nickel is derived from sulphide ores and the rest comes from nickel laterites (Sudol, 2005). However, about 70% of the nickel reserves are present in laterite deposits (Dalvi et al., 2004). As a result, there is growing interest in improving the technology for extraction of nickel (and cobalt) from laterites, as the demand for stainless steel continues to grow and the sulphide deposits become depleted (McDonald and Whittington, 2008).

Nickel laterite ores can be broadly characterised as dry-land (e.g. deposits found in Greece, Albania, Western Australia) or tropical (e.g. deposits found in Cuba, New Caledonia, Brazil) (Whittington and Muir, 2000; Krause et al., 1997). Typically the dry-land laterites are less weathered than tropical laterites and contain more clay minerals and less goethite. Since laterite type ores naturally occur close to surface, economical open pit mining techniques are employed to recover the ore after removal of the overburden (Moskalyk and Alfantazi, 2002). Laterite deposits typically occur in layers, ranging from zero to 40 m in depth below the surface.

Greece is the only EU country with extensive but low-grade nickel laterites. They mainly occur as limonitic laterites and, to a
lesser extent, as serpentinic laterites. Nickeliferous limonite is comprised of nickel bearing ferric oxides in deposits formed from ultrabasic rocks. The Greek laterites are unique in the world in that they are sedimentary and have originated by transport and sedimentation of laterite-derived material, generated by weathering of ultramafic rocks (Agatzini et al., 2004). Nickel is usually found as a replacement of magnesium in chlorite and serpentine. In some cases its content in these minerals can be of the order of 5–6% Ni (Mposkos et al., 2000).

The Greek limonitic laterites have been exploited to produce ferronickel via a pyrometallurgical route. This involves pre-reduction of the ore in rotary kilns, reduction smelting in electric furnaces, and upgrading of the raw ferronickel in a converter to the final 20–25% Ni grade (Agatzini et al., 2004). Because of the rising cost of energy, the method is economically marginal when ore with 0.95–1% nickel is treated and is uneconomic for lower grade laterites. Furthermore, direct application of the above pyrometallurgical method to existing serpentinic laterites is not feasible because the slag produced is difficult to melt, resulting in higher energy requirements and poor phases (metal-slag) separation.

The bulk of the work on sulphuric acid leaching of laterites concerns pressure leaching. However, because of the problems encountered during commissioning and operation of the modern Australian plants (Murrin Murrin, Cawse and Bulong), atmospheric pressure leaching has recently received much closer consideration (Harris et al., 2003). Atmospheric leaching at lower temperature avoids the need for expensive autoclaves, in case encountered during commissioning and operation of the modern plants (Murrin Murrin, Cawse and Bulong), atmospheric pressure leaching has recently received much closer consideration. Atmospheric leaching at lower temperature avoids the need for expensive autoclaves.

1.1. The HElas leach LAteliteS (HELLAS) process

The Laboratory of Metallurgy of the National Technical University of Athens has developed and patented a novel integrated hydrometallurgical method, suitable to treat low-grade nickel oxide ores efficiently and economically (Agatzini-Leonardou and Dimaki, 1994, 2001; Agatzini-Leonardou and Karidakis, 2000; Agatzini-Leonardou et al., 2000; Tsakiridis and Agatzini, 2004a, 2004b). The first stage of the so-called “HELLAS” (HELas Leach LAteliteS) method is heap leaching with diluted sulphuric acid. The success of the process is based on the selectivity nickel leaching over iron, as the ores are limonitic and contained significant amounts of low reactivity hematite together with goethite. A typical composition of the pregnant solution produced from heap leaching of Greek low-grade nickeliferous laterites with sulphuric acid is the following: NiSO\textsubscript{4} = 4.8 g/L, CoSO\textsubscript{4} = 0.36 g/L, Fe\textsuperscript{3+} = 23.0 g/L, Al\textsuperscript{3+} = 6.0 g/L, Cr\textsuperscript{3+} = 1.0 g/L, Mn\textsuperscript{2+} = 0.9 g/L and Mg\textsuperscript{2+} = 8 g/L. Most of the iron is present in the hematite rather than the goethite phase, thus making the leaching of nickel under mild conditions feasible, and resulting in low acid consumption and subsequent low iron dissolution. Nickel recoveries of up to 85% can be obtained in less than 40 days with less than 5% iron in solution. The sulphuric acid consumption varies from 10 to 25 kg/kg nickel extracted. The high nickel recoveries are achieved with the recirculation of leaching solution, through one or more heaps, controlling the acidity of the leach liquor between each cycle. Leaching is continued until there is no further increase in the nickel concentration, whereas recirculation occurs until the acidity falls below a pre-determined level (Agatzini-Leonardou and Dimaki, 1994). The main advantages of the above leaching method include both lower capital (cheaper construction materials) and operating costs (lower energy requirement, less maintenance). Today, the development of heap leaching for low-grade nickel laterites is gaining momentum with several trial operations expected to expand to full scale production within the next few years.

This paper describes a hydrometallurgical process for nickel recovery, by electrowinning, from purified sulphate heap liquors (Fig. 1) and presents the results and discussion on precipitation, solvent extraction and electrowinning stages. More specifically, iron, aluminium and chromium can be rejected from the solution, as easily filterable crystalline basic sulphate salts of the jarosite–alunite type, at atmospheric pressure, by chemical precipitation at 95 °C. Cobalt, manganese and magnesium are simultaneously extracted by Cyanex 272, leaving nickel in solution, which is easily concentrated by solvent extraction using Cyanex 272. Nickel from the loaded organic phase is then stripped by nickel spent electrolyte in order to produce a solution suitable for nickel electrowinning.

The loaded Cyanex 272 organic phase is then stripped by diluted sulphuric acid. Subsequently, cobalt and manganese are extracted from magnesium by Cyanex 302. The loaded with cobalt and manganese organic phase is stripped by diluted sulphuric acid.

The resulting solution contains only magnesium, which must also be removed in order for the purified barren solution to be recycled to the heap leaching stage. Magnesium can be removed by hydrolytic precipitation, as easily filterable crystalline precipitate, at ambient temperature, using calcium hydroxide as a neutralizing agent.

The combined stream of cobalt and manganese, after stripping the loaded Cyanex 302, can be treated with diluted NaOH for Co and Mn precipitation as hydroxides. After re-leaching the mixed precipitate with ammonia/ammonium carbonate solution, the manganese remains in the residue. Cobalt can be electrowon or precipitated.

2. Experimental

The leach liquor, which was used during experimentation, had been produced by heap leaching of Greek nickel oxide ore with di-
lute sulphuric acid (1 M). The leach liquor was first pre-neutralized by CaCO₃ to pH = 1.1, at ambient temperature. The average composition of the pregnant solution is given in Table 1.

Metal ions concentration was determined by atomic absorption spectrophotometer (Perkin Elmer 4100). The analysis of Fe (Fe²⁺ and Fe³⁺) was performed with back-titration using potassium dichromate (K₂Cr₂O₇).

The produced precipitates as well as the nickel cathodes were mineralogically analyzed by X-ray diffraction (XRD), using a Bruker D8-Focus diffractometer with nickel-filtered CuKα₁ radiation (=1.5405 Å), 40 kV and 40 mA.

Their morphology was also examined by scanning electron microscopy (SEM) using a Jeol 6380LV Scanning Electron Microscope. Experimental conditions involved 15 kV and 20 kV accelerating voltage. Chemical composition of the samples was carried out by an Oxford INCA Energy Dispersive Spectrometer (EDS) connected to the SEM.

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Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration, g/L</th>
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<tr>
<td>Fe</td>
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</tr>
<tr>
<td>Ni</td>
<td>4.82</td>
</tr>
<tr>
<td>Co</td>
<td>0.36</td>
</tr>
<tr>
<td>Al</td>
<td>6.06</td>
</tr>
<tr>
<td>Cr</td>
<td>0.98</td>
</tr>
<tr>
<td>Mg</td>
<td>7.95</td>
</tr>
<tr>
<td>Mn</td>
<td>0.91</td>
</tr>
<tr>
<td>Na</td>
<td>0.20</td>
</tr>
</tbody>
</table>

2.1. Removal of iron, aluminium and chromium by chemical precipitation

In the first stage, iron, aluminium and chromium were removed as basic sulphate salts of the jarosite–alunite type by chemical precipitation. The runs were conducted in a 5 L, five-necked, round
bottomed split reactor, that was fitted with a glass stirrer, vapour condenser, thermometer and a pH electrode. The solution was placed in the flask and heated to 95 ± 0.5 °C by electrical mantle. The temperature of the liquid was controlled by a Fisons controller and the pH was measured using a Hamilton Chemotrode Bridge 200 combined pH electrode, specially designed for semi-solid and boiling water solutions. The pH of the solution was slowly raised to a pre-determined equilibrium value, in the range 1.1–3.5, by adding CaO pulp (20%). It should be emphasized that, during the precipitation process, the pH increase rate was kept low in order to control supersaturation of iron, aluminium and chromium and to avoid the production of an amorphous precipitate.

2.2. Solvent extraction – stripping processes

The extractant Cyanex 272, registered by Cyanamid Canada, was kindly supplied by the Holland branch of the company, Cytec Holland. The reactive component C\textsubscript{16}H\textsubscript{34}PO\textsubscript{2}H is the bis(2,4,4-trimethylpentyl) phosphinic acid having the following structure (Cyanex 272 Technical Brochure, 1989):

\[
\begin{align*}
\text{R} & = \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2 \\
\text{P} & = \text{O} \\
\end{align*}
\]

where R represents the 2,4,4-trimethylpentyl group. The molecular weight is 290 and the density (24 °C): 0.95 g/cm\textsuperscript{3}.

The extractant Cyanex 302 was also supplied by the Cytec Holland. The reactive component is C\textsubscript{16}H\textsubscript{34}PSOH, having the following structure (Cyanex 302 Technical Brochure, 1993):

\[
\begin{align*}
\text{R} & = \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2 \\
\text{P} & = \text{S} \\
\end{align*}
\]

where R represents the 2,4,4-trimethylpentyl group. The molecular weight is 306 and the density (20 °C): 0.943 g/cm\textsuperscript{3}. Both extractants were used without further purification. The organic diluent Exxsol D-80 was obtained from Exxon Chemical Holland. In all cases, the organic phases were modified with 5% T.B.P.

All batch experiments were conducted in a 500-mL five-necked, round bottomed split reactor, which was fitted with a glass stirrer, a vapour condenser, a thermometer and a pH electrode. The two phases (organic and aqueous) were contacted by rapid stirring and the pH was controlled by small additions of 5 M NaOH, using an automatic titration device. Heating was provided by an electrical mantle and the temperature of the liquid was controlled by a Fisons Scientific Apparatus monitor. Stripping of the loaded organic phases was carried out by diluted sulphuric acid. In case of Ni\textsuperscript{2+}, after nickel concentration by Cyanex 272, stripping was conducted by a synthetic nickel spent electrolyte (55.45 g/L Ni\textsuperscript{2+}), producing a solution suitable for nickel electrowinning. Continuous tests were carried out in a laboratory solvent extraction unit (Bell Engineering Model 282).

2.3. Nickel electrowinning

The electrolytic cell was a 1000 mL double walled pyrex cylinder, which was connected with a thermostat circulating H\textsubscript{2}O as heat exchange fluid. The temperature inside the cell was kept constant, throughout experimentation, at 60 °C. The cap of the cell was circular with guidance holes permitting the symmetrical arrangement of the electrodes. Cathode was made from 316L stainless steel sheet 8 cm long by 10 cm wide, and 1 mm thick. The anode was a Pb–8%Sb plate of the same dimension, placed at a constant distance of 30 mm from the cathode. Working electrodes were prepared by cleaning with acetone in an ultrasonic bath for five minutes, rinsing with deionized water, and drying in an air stream. The deposition tests were made for 3 h at 20 mA/cm\textsuperscript{2}, without agitation. DC power was supplied by a laboratory AFX 530-5A programmable power supply. Synthetic Spent electrolyte was prepared from grade nickel sulphate hexahydrate (NiSO\textsubscript{4} 6H\textsubscript{2}O), boric acid (H\textsubscript{3}BO\textsubscript{3}) and anhydrous sodium sulphate (Na\textsubscript{2}SO\textsubscript{4}) to give the desired concentrations. The electrolyte contained 10 g/L boric acid, 75.95 g/L Ni\textsuperscript{2+} and 130 g/L Na\textsubscript{2}SO\textsubscript{4}. The solution pH was adjusted to 3.5 using diluted NaOH/H\textsubscript{2}SO\textsubscript{4}.

2.4. Removal of magnesium by chemical precipitation

Magnesium was removed by chemical precipitation in order to allow the recycling of the purified barren solution in the leaching stage. The precipitation of gypsum/brucite mixed precipitate was carried out in 5 L, five-necked, round bottomed split reactors at 25 °C, using 1.1 times the stoichiometric quantity of Ca(OH)\textsubscript{2} required to precipitate all of the magnesium. Calcium hydroxide was added in solid form. The reaction time was approximately 2 h. Equilibrium pH was around 10. The precipitate was dried at 80 °C and kept in a desiccator.

3. Results and discussions

3.1. Removal of iron, aluminium and chromium by chemical precipitation

In the framework of the “HEap Leach LAteriteS” (HELLAS), a new process of leach liquors purification was invented relating to the removal of iron, aluminium, and chromium, as the existing methods were not satisfactory. The process relates to the precipitation of the above metals as crystalline, easily filterable chemical precipitates of the jarosite/alunite type, at atmospheric pressure without alkali addition (Agatzini-Leonardou et al., 2000). In the precipitation of iron as jarosite in the zinc industry, the addition of an alkali metal, such as Na\textsuperscript{+}, K\textsuperscript{+} or NH\textsubscript{4}\textsuperscript{+}, has been established (Steinweit, 1971). However, the cost of such reagents is quite high. For this reason, experiments were conducted without adding an alkali metal during iron, aluminium and chromium precipitation from the laterites leach liquors.

The jarosite–alunite group of isostructural minerals is described by the general formula M(Fe\textsubscript{x}Al\textsubscript{y}Cr\textsubscript{z})(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}, in which “M” may be Na\textsuperscript{+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+} or H\textsubscript{3}O\textsuperscript{+} and x + y + z = 3. For x = 3, the formula represents jarosite, whereas for y = 3 it represents alunite. The precipitation occurs according to the following hydrolysis reaction (Dutrizac, 1996):

\[
2[Fe_2(SO_4)_{3}]_{[aq]} + [Al_2(SO_4)_3]_{[aq]} + M_2SO_4 + 12H_2O 
\rightarrow 2MFe_2Al(SO_4)_2(OH)_{6(\alpha)} + 6H_2SO_4
\]
Experimentation consisted of six runs, duplicated, aiming to determine the optimum pH value at which maximum iron, aluminium and chromium precipitation occurs with minimum nickel and cobalt losses. The corresponding results of iron, aluminium and chromium simultaneous precipitation are presented in Table 2 and in Fig. 2. All precipitates settled down quickly and were easily filtered. High percentages of iron, aluminium and chromium removal were achieved at the experimental conditions used. At pH = 3.5, 99.9% of iron, 98.9% of aluminium and 99.1% of chromium were precipitated with only 3.5% nickel and 2.0% cobalt losses, which were determined by analyzing the precipitates. The increase of nickel and cobalt losses with pH is also apparent in Fig. 3. It is believed that the losses are due to absorption but an investigation is in progress to reveal the mechanism. It is, thus, concluded that iron, aluminium and chromium precipitation could be efficiently precipitated as basic sulphate salts of the jarosite–alunite type at a pH value around 3.5 and 95 °C. At this pH, the residual iron, aluminium and chromium concentrations are 30 ppm, 200 ppm and 50 ppm, correspondingly.

The X-ray diffraction data of the above mixed precipitate, after drying at 110 °C, using CaO pulp as neutralizing agent, is shown in Fig. 4. The main mineralogical phases were bassanite (CaSO₄ 0.5H₂O), hydronium jarosite ([H₂O]Fe₃(SO₄)₂(OH)₆) and alunite ([H₂O]Al₃(SO₄)₂(OH)₁₆). The main peaks, which correspond to CaSO₄ 0.5H₂O, were sharper and with higher intensity, compared to those of jarosite–alunite, whose peaks displayed lower intensity and higher peak width. The above differences were attributed to the differences in grain size and degrees of crystallinity of the two main products. Specifically, the main peaks of jarosite–alunite phases characterise a finer crystallized material with no well-developed crystals, whereas the main peaks of bassanite reveal a well-crystallized compound. The detection of small quantities of SiO₂ was attributed to its presence in the neutralizing agent. Mineralogical phases of chromium were not detected, probably because of their low content in the mixed precipitate.

Scanning electron microscopy with X-ray energy dispersive analysis (EDS) was performed to gain further knowledge of the mineralogical species contained in the mixed precipitate and their morphology. The evaluation was carried out by secondary and backscattered electrons (BSE) mode. The jarosite–alunite particles appeared as spherical fine-grained particles, dispersed among crystals of bassannite. As shown in Fig. 5a, jarosite–alunite precipitate was in the form of aggregates of fine crystallites. The aggregates
had an irregular shape and size of about 10–20 μm. On the other hand, bassanite consisted of prismatic crystals of 10–30 μm in length and 5–10 μm in diameter (Fig. 5b).

The application of the Toxicity Characteristic Leaching Procedure (TCLP) test (USEPA, method 1311, 1994) has shown the jarosite–alunite precipitate to be environmentally stable and safe to be rejected in a tailings pond. However, the above mixed precipitate is now regarded either as a potentially useful material for replacing the gypsum in cement production (Katsioti et al., 2005), or as a raw material (as a source of iron) for Portland cement clinker production (Tsakiridis et al., 2005). It should be emphasized that the above precipitate, coming from the treatment of nickel oxide ores, does not contain hazardous elements such as Cd, As, or Hg, in contrast with the jarosite precipitate produced during the hydrometallurgical extraction of zinc from sulphide ores.

3.2. Solvent extraction – stripping processes

After the removal of iron, aluminium and chromium, as easily filterable crystalline basic sulphate salts of the jarosite–alunite type, by chemical precipitation, the leach liquor contains 0.33 g/L of Co2+, 3.64 g/L of Ni2+, 0.76 g/L of Mn2+ and 5.85 g/L of Mg2+. The residual iron, aluminium and chromium (30 ppm, 200 ppm and 50 ppm, correspondingly) were totally removed by neutralization at pH: 5, at ambient temperature, with diluted NaOH (5 M). The factors studied and their levels for cobalt, manganese and magnesium extraction over nickel and for nickel concentration over Co2+, Mn2+ and Mg2+ from sulphate solutions, in the presence of Ni2+. Nickel co-extraction did not ex-
ceed 0.3%, under the present experimental conditions. This nickel could be easily scrubbed out.

As Cyanex 272 proved to be an efficient extractant for the simultaneous extraction of cobalt and magnesium in the presence of nickel from sulphate solutions, a McCabe–Thiele diagram was constructed for Co\(^{2+}\), Mn\(^{2+}\) and Mg\(^{2+}\) with the above reagent and the number of counter-current stages required was predicted. Cobalt, manganese and magnesium extraction isotherms were determined at the following conditions: Cyanex 272 concentration: 20%, pH: 5.5 and \(T\): 40 °C. These conditions were found to be optimum using statistical analysis of experiments. McCabe–Thiele diagrams indicated two stages for cobalt and manganese and three stages for magnesium extraction, at a phase ratio A/O = 2.0 (Fig. 6).

Table 4
Results of solvent extraction by Cyanex 272 and Cyanex 302.

<table>
<thead>
<tr>
<th>Treatment code</th>
<th>Co(^{2+}), Mn(^{2+}) and Mg(^{2+}) extraction over Ni(^{2+}) by Cyanex 272</th>
<th>Ni(^{2+}) concentration by Cyanex 272</th>
<th>Co(^{2+}) and Mn(^{2+}) extraction over Mg(^{2+}) by Cyanex 302</th>
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<tbody>
<tr>
<td></td>
<td>% Co extraction</td>
<td>% Mn extraction</td>
<td>% Mg extraction</td>
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</tr>
<tr>
<td>A</td>
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Table 5
Minimum and maximum levels of variables. Stripping of loaded Cyanex 272 10 and Cyanex 302.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Variables</th>
<th>Co(^{2+}), Mn(^{2+}) and Mg(^{2+}) stripping from Cyanex 272</th>
<th>Ni(^{2+}) stripping from Cyanex 272</th>
<th>Co(^{2+}) and Mn(^{2+}) stripping from Cyanex 302</th>
<th>Units measured</th>
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<tr>
<td>A</td>
<td>H(_2)SO(_4) concentration</td>
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<td>3.0</td>
<td>High</td>
<td>4.0</td>
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<tr>
<td>B</td>
<td>Temperature</td>
<td>Low</td>
<td>25</td>
<td>High</td>
<td>40</td>
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</table>

Table 6
Results of metals stripping from the loaded Cyanex 272 and Cyanex 302.

<table>
<thead>
<tr>
<th>Treatment code</th>
<th>Co(^{2+}), Mn(^{2+}) and Mg(^{2+}) stripping from Cyanex 272</th>
<th>Ni(^{2+}) stripping from Cyanex 272</th>
<th>Co(^{2+}) and Mn(^{2+}) stripping from Cyanex 302</th>
<th>% Co stripping</th>
<th>% Mn stripping</th>
<th>% Mg stripping</th>
<th>% Ni stripping</th>
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<td>99.25</td>
<td>99.13</td>
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Fig. 6. McCabe–Thiele diagrams for Co\(^{2+}\), Mn\(^{2+}\) and Mg\(^{2+}\) extraction by Cyanex 272.
As the Table 6 shows, high percentages of Co²⁺, Mn²⁺, and Mg²⁺ stripping from the organic phase were obtained in all cases. This proves the strippability of Cyanex 272 by diluted sulphuric acid. The McCabe–Thiele diagram for cobalt, manganese and magnesium stripping, by diluted sulphuric acid, from the loaded Cyanex 272 organic phase indicated two stages requirement for cobalt and manganese recovery and three for magnesium (Fig. 7), at: H₂SO₄: 4 M, T: 40 °C and phase ratio O/A = 2.0.

3.2.2. Ni²⁺ concentration by Cyanex 272

The data presented in Table 4 show that nickel could be efficiently extracted by Cyanex 272 in order to be concentrated for the electrowinning stage. Nickel extraction isotherm was determined at the following conditions: Cyanex 272 concentration: 10%, pH: 7.5 and T: 40 °C. These conditions were found to be optimum using statistical analysis of experiments. The McCabe–Thiele diagrams indicated two stages for nickel extraction, at a phase ratio A/O = 2.4 (Fig. 8).

The McCabe–Thiele diagram for nickel stripping, by synthetic nickel spent electrolyte (55.45 g/L Ni²⁺), from the loaded organic phase indicated three stages requirement (Fig. 9), at: H₂SO₄: 2.0 M, T: 40 °C and phase ratio O/A = 2.4.

3.2.3. Co²⁺ and Mn²⁺ recovery over Mg²⁺ by Cyanex 302

Cobalt and manganese could be extracted in the organic phase by Cyanex 302, in the presence of magnesium (Table 4). Magnesium co-extraction reached 0.05%, under the present experimental conditions and it was easily scrubbed out. Cobalt and manganese extraction, by Cyanex 302, isotherms were determined at the following conditions: Cyanex 302 concentration: 20%, pH: 5.0 and T: 40 °C. These conditions were found to be optimum using statistical analysis of experiments. The McCabe–Thiele diagrams indicated two stages for cobalt and manganese extraction, at a phase ratio A/O = 2.0 (Fig. 10).

Cobalt and manganese were efficiently stripped from the loaded Cyanex 302 by diluted sulphuric acid (Table 6) and the McCabe–
Thiele diagram indicated two stages requirement for cobalt and manganese recovery (Fig. 11), at: H₂SO₄: 1 M, T: 40 °C and phase ratio O/A: 2.0.

3.2.4. Continuous counter-current test

The operating conditions for the simultaneous extraction of cobalt, manganese and magnesium, from nickel sulphate solution, by Cyanex 272, as well as their stripping by diluted sulphuric acid were:

- Solvent: 20% (v/v) Cyanex 272 in Exxsol D-80 with 5%TBP
- Aqueous phase: 0.33 g/L Co, 3.64 g/L Ni, 0.76 g/L Mn and 5.85 g/L Mg, pH = 5.5
- Extraction stages: 3
- Stripping stages: 3
- Temperature: 40 °C
- Strip feed: Diluted sulphuric acid (H₂SO₄: 4 M)
- Flow rate (mL/min) = aqueous feed: 20.57; solvent feed: 10.29; strip feed: 5.15

At those conditions, cobalt, manganese and magnesium extraction by Cyanex 272, in the presence of Ni²⁺, reached 99.6%, 99.7% and 99.2%, respectively.

The corresponding operating conditions for the extraction of cobalt and manganese, from magnesium sulphate solution, by Cyanex 302, as well as for cobalt and manganese stripping by diluted sulphuric acid were:

- Solvent: 20% (v/v) Cyanex 302 in Exxsol D-80 with 5%TBP
- Aqueous phase: 1.31 g/L Co, 3.0 g/L Mn, 22.6 g/L Mg, pH = 5.0
- Extraction stages: 2
- Stripping stages: 2
- Temperature: 40 °C
- Strip feed: Diluted sulphuric acid (H₂SO₄: 0.5 M)
- Flow rate (mL/min) = aqueous feed: 20.57; solvent feed: 10.29; strip feed: 5.15

At those conditions, cobalt and manganese extraction by Cyanex 302, in the presence of Mg²⁺, reached 99.5% and 99.6%, respectively.

The operating conditions for the extraction-concentration of nickel from sulphate solution by Cyanex 272, as well as nickel stripping by nickel spent electrolyte acid, were:

- Solvent: 10% (v/v) Cyanex 272 in Exxsol D-80 with 5%TBP
- Aqueous phase: 3.6 g/L Ni, pH = 7.5
- Extraction stages: 2
- Stripping stages: 3
- Temperature: 40 °C
- Strip feed: Ni²⁺ spent electrolyte (55.45 g/L) – H₂SO₄: 2 M solution
- Flow rate (mL/min) = aqueous feed: 20.57; solvent feed: 8.57; strip feed: 3.57

At those conditions, nickel extraction by Cyanex 272 reached 99.5%. Nickel stripping by nickel spent electrolyte reached 99.4% (75.95 g/L of Ni: 55.45 g/L nickel spent electrolyte and 20.5 g/L for nickel electrowinning).

3.3. Nickel electrowinning

As it was mentioned above the electrolyte contained 10 g/L H₃BO₃, 75.95 g/L Ni²⁺ and 130 g/L Na₂SO₄ (solution pH: 3.5). The deposition tests were made for 3 h at 20 mA/cm², while the tem-
perature was kept constant, at 60 °C. At those conditions, flat and ductile nickel deposits could be produced.

The orientation of the nickel deposits was examined using XRD analysis and a typical pattern is given in Fig. 12. The XRD spectra showed the presence of five peaks, as maximum, associated with the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystallographic planes of nickel. As expected, this peak distribution indicates that the crystals have a face-centred cubic lattice (fcc). Relative to the random crystal orientation of nickel powder, the deposits produced in this work had a (2 2 0) preferred orientation. This crystal structure has also been identified by other authors using similar conditions (Holm and O’Keefe, 2000; Alfantazi and Shakshouki, 2002).

The surface morphology of the deposits was examined by scanning electron microscopy. Fig. 13 shows micrographs for the nickel obtained from 75.95 g/L Ni²⁺ at 20 mA/cm² and 60 °C. The microstructures of the examined deposits were similar and consisted of large, sharply faceted crystals with distinct grain boundary separations. The crystal size ranged from a few micrometers to 10 mm. The crystal facets appeared to be rough and textured. EDS spectra of all deposits examined only displayed the bands associated with Ni and centred at 0.85 keV (L band), at 7.47 keV (Ka band) and 8.26 keV (Kb band). This confirms the high purity of recovered Ni, free of heavy metals impurities, such as Pb which may result from anode corrosion, and without contamination of sulphur from the baths.

3.4. Removal of magnesium by chemical precipitation

Under the experimental conditions applied, the chemical precipitation of magnesium with the use of Ca(OH)₂ was a very quick process resulting in 99% magnesium removal. The chemical analysis of the produced gypsum/brucite mixed precipitate is given in Table 7. The main mineralogical phases of the mixed precipitate (Fig. 14) were gypsum (CaSO₄·2H₂O) and brucite (Mg(OH)₂). The main peaks, which correspond to CaSO₄·2H₂O, were sharper and with higher intensity, compared with those of Mg(OH)₂, whose peaks displayed lower intensity and higher peak width. The above differences were also attributed to the dif-

<table>
<thead>
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<th>Oxides</th>
<th>% Content</th>
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<tr>
<td>CaO</td>
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<tr>
<td>MgO</td>
<td>18.97</td>
</tr>
<tr>
<td>SO₃</td>
<td>31.29</td>
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<tr>
<td>LOI (1000 °C)</td>
<td>23.80</td>
</tr>
</tbody>
</table>

Table 7
Chemical analysis of gypsum/brucite mixed precipitate.

Fig. 12. Representative XRD spectra for electrodeposited nickel at the current density of 20 mA/cm².

Fig. 13. SEM micrographs of nickel deposits from electrolyte containing 75.95 g/L of Ni²⁺ (pH: 3.5) at 20 mA/cm² and 60 °C.
ferences in grain size and degrees of crystallinity of the two main products. The detection of CaCO$_3$ (and Ca(OH)$_2$) could be attributed to the partial carbonation of calcium hydroxide that had not been consumed during precipitation. The above conclusions were also confirmed by electron microscopic observations. The mixture generally consists of 20–30% non-fibrous magnesium hydroxide, 60–70% gypsum. As shown in Fig. 15, magnesium hydroxide was in the form of aggregates of fine crystallites. The aggregates had an irregular shape and a homogeneous size of about 10 μm (longest dimension). On the other hand, gypsum consisted of needle-like crystals of 5–15 μm in length and 1–3 μm in diameter.

![Fig. 14. Mineralogical phases of the gypsum/brucite mixed precipitate.](image1)

(a) Brucite agglomerate among gypsum crystals  
(b) Needle-like crystals of CaSO$_4$·2H$_2$O

![Composition of the above marked spots](image2)

**Fig. 15.** Micrographs of the gypsum/brucite mixed precipitate.
The above solid product, which was crystalline and easily filterable, was natural white and it presented good properties (particle size, whiteness, specific surface BET, oil adsorption, solubility in water, specific conductivity, pH, weight loss at 105 °C, weight loss at 1000 °C, specific gravity) to be used as filler in polymers, such as in high-density polyethylene, in low-density polyethylene and in PVC (Agatzini-Leonardou and Karidakis, 2000). Furthermore, the mixed precipitate was proved to be quite effective as an additive in cement, replacing gypsum (Agatzini-Leonardou et al., 2005).

4. Conclusions

Based on the data presented in this paper, a complete hydrometallurgical process for nickel recovery, by electrowinning, from real sulphate heap leach liquors, is suggested. The process comprises of several stages: The conclusions from the testwork for each stage are presented below:

1. Iron, aluminium and chromium were precipitated by 99.9%, 98.9% and 99.1%, respectively at 95 °C and pH = 3.5, as easily filterable crystalline basic sulphate salts of the jarosite–alunite type. Nickel and cobalt losses reached 3.5% and 2%, respectively.

2. Cobalt, manganese and magnesium were extracted over nickel by Cyanex 272. The loaded with cobalt, manganese and magnesium organic phase was stripped with diluted sulphuric acid.

3. Nickel concentration was carried out by solvent extraction. The loaded with nickel Cyanex 272 was stripped with nickelspent electrolyte in order to produce a solution suitable for nickel electrowinning. Nickel electrowinning was carried out at constant current density of 20 mA/cm², using stainless steel as cathode and Pb–8%Sb as anode.

4. Cobalt and manganese were extracted over magnesium by Cyanex 302. The loaded with cobalt and manganese organic phase was stripped with diluted sulphuric acid.

5. Magnesium was removed by chemical precipitation, at ambient temperature, as mixed precipitate composed of well-crystallized gypsum (CaSO₄·2H₂O) and aggregates of fine crystallites of brucite (Mg(OH)₂).

References


Sudol, E., 2005. The thunder from down under: everything you wanted to know about laterites but were afraid to ask. Canadian Mining Journal. August, 2005.


