THE DEVELOPMENT OF A NEW DSX PROCESS FOR THE SEPARATION OF NICKEL AND COBALT FROM IRON AND ALUMINIUM AND OTHER IMPURITIES

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ABSTRACT

A new synergistic solvent extraction (SSX) system has been developed in CSIRO recently to separate nickel and cobalt from iron and aluminium and other impurities. A new CSIRO DSX process has been created using the new SSX technology to directly recover nickel and cobalt from laterite leach solutions without intermediate precipitation and re-leach steps. This is a significant development for the recovery of nickel and cobalt from laterite leach solutions, especially from heap leaching (HL) and atmospheric leaching (AL) solutions. The new CSIRO DSX process has the following advantages:

- Making the direct recovery of nickel and cobalt from HL, AL and HPAL solutions possible without the removal of iron and aluminium,
- Separation of nickel and cobalt from iron, aluminium and other impurities in low pH to avoid nickel and cobalt losses in neutralisation or precipitation steps,
- Possible savings in capital and operating costs if applied to HPAL processes since the CCD system for neutralisation, precipitation and solid/liquid separation can be simplified,
- All organic reagents are commercially available and in reasonable prices,
- The process flowsheet is much simplified to save capital and operating costs.
- The new CSIRO DSX process can be readily coupled with nickel hydrolysis, electrowinning and hydrogen reduction to obtain different nickel products.

1. INTRODUCTION

The world mineral industry is experiencing an unprecedented interest in nickel-cobalt extraction from laterite ores through high pressure acid leach (HPAL) and subsequent recovery processes. In WA, the Murrin Murrin (Motteram et al., 1996) nickel plant is in operation and the Ravensthorpe nickel plant is being reactivated. In New Caledonia, the Goro nickel plant (Mihaylov et al. 2000) is in the process of commissioning. The HPAL process for these projects is very similar with very high capital investments and high operation costs.

Heap leaching (HL) needs much less capital and operating costs than those for HPAL. However, the separation of nickel and cobalt from iron and aluminium is much more difficult in the HL leach solution than that in the HPAL leach solution. In the later, the concentration of iron and aluminium concentration is in the range of 1-2 g/L (Motteram et al. 1996). When the iron and aluminium are precipitated in the pH range of 4-5, only a small acceptable amount of Ni and Co would be lost due to adsorption because the amount of precipitated solids is small. A typical atmospheric leach (AL) solutions contains about 6 g/L Fe and Al (Liu et al. 2004) and a typical HL solution contains about 25 g/L Fe$^{3+}$ and Fe$^{2+}$ and 3 g/L Al (Diniz 2006). If all iron and
aluminium are precipitated, most nickel and cobalt would be lost in the precipitates.

To separate nickel and cobalt from iron and aluminium has been a long-standing problem. Investigations started from early 1980s using SSX systems consisting of di-nonylnaphthelene sulphonic acid (DNNSA) and N-alkylated bis-picolylamines were tested with very good results (Grinstead 1980, Ginstead and Tsang 1983, Inoue et al. 1997a and 1997b). The metal extraction order was found to be Ni > Co > Fe(III)/Mn/Al/Mg. Nickel was preferably extracted and could be separated from cobalt and iron at pH < 2.0. The separation of cobalt from iron required pH around 2.6. However, no commercialisation of this system has taken place due to poor phase disengagement (Flett 2004).

The solvent extraction of Ni and Co by a synergistic system, containing DNNSA and 2,6-bis-[5-nonylpyrazol-3-yl]pyridine (BNPP) was studied (Zhou and Pesic 1997). In terms of pH50, the system extracted Cu, Ni and Co (<1.0) selectively over Fe, Mn (1.62), Ca (2.47) and Al (3.22) from acidic sulphate solutions as low as pH 0.5. The separation of Ni and Co could be achieved either during loading or stripping because of the difference in extraction and stripping kinetics of the two metals. The system was found to be poisoned by copper and also suffered from slow kinetics of nickel. Preston and du Preez (1998) studied the synergistic solvent extraction of base metals with DNNSA and pyridinecarboxylates. The metal extraction order was found to be Cu > Ni > Al > Co > Ca > Zn > Al > Fe(III) > Mg with 3-pyridinecarboxylates and Cu > Ni > Co > Zn > Al > Fe(III) > Ca > Mg with 2 and 4-pyridinecarboxylates. In four-stage batch counter-current extraction tests, up to 95% Ni was extracted with a co-extraction of up to 19% Ca and 9% Fe. The relative high Ca and Fe co-extraction after 4-stage extraction could be a concern.

A resin-in-pulp process using ion exchange (IX) with Dowex M4195 resin was reported by Duyvesteyn and Omofoma (1997) for the separation of Ni from Co and Fe in laterite leach solutions. The disadvantages of this process are that nickel cannot be completely separated from Fe(III) especially if the concentration of Fe(III) is high, and Co cannot be recovered. This process was improved by reducing all iron from ferric to ferrous state followed by recovering both Ni and Co (Duyvesteyn et al. 2002) at pH 3.0. The resin-in-pulp obviously suffers from resin loss, resulting in high operating costs.

Liu et al. (2002) proposed a two-stage IX strategy with Dowex M4195 resin to recover Ni and Co from laterite leach solutions. In the first stage, Ni and Fe(III) are separated from Co and Fe(II) at pH 1.0-2.5. The eluate is then neutralised to make a mixed hydroxide product (MHP) containing Ni and Fe(III), which is roasted to obtain ferronickel product. In the second stage, after partial iron precipitation, the Co is separated from Fe(II) using the same resin at pH 2.0-3.0. The disadvantages of this process are that Ni and Co are separated from iron and recovered in different stages, which makes the process complicated, and the difficulty of adjusting the pH in IX columns presents a practical problem. The low efficiency of ion exchange process is its biggest
disadvantage, especially when the absorbed metal’s concentration is high such nickel in the range of a few g/L.

The brief literature review shows that the nickel industry needs SX or SSX systems with commercially available reagents to separate nickel and cobalt from iron, aluminium and other impurities in HL, AL and HPAL solutions. The CSIRO SX group developed SSX systems used for its DSX processes to meet this needs. The development of SSX systems and DSX processes for the purification of nickel and cobalt in laterite leach solutions has passed five phases including:

**Phase 1**: SSX system consisting of Versatic 10 and CLX50 for the Bulong DSX process to separate Ni from Ca and to solve its gypsum formation problem in 2000-2001 (Cheng 2000).


The above SSX systems solved the problem for the nickel laterite industry to directly recover nickel and cobalt from leach solutions without intermediate precipitation and re-leach steps from HPAL solutions after iron and aluminium removal. However, they cannot be used for HPAL and HL solutions without iron and aluminium removal. In the other hand, there is no SX system with a single extractant to separate nickel and cobalt from iron and aluminium and the development of such reagents would be very difficult and very expensive. Therefore, the only alternative is to develop SSX systems using commercially available reagents to achieve this goal and to meet the very important and urgent need of the nickel industry.

Recently, the CSIRO SX group has developed new SSX systems and DSX processes, which marked the development of CSIRO DSX processes entering **Phase 6**: new SSX system to separate nickel and cobalt from iron and aluminium and other impurities. This is a significant technology development and will be reported in this paper.
2. **THE CSIRO DSX PROCESSES FOR HL AND AL SOLUTIONS**

As shown above, both heap leach (HL) solution and atmospheric leach (AL) solution contain high concentrations of Fe and Al. In this study, a synthetic solution containing high concentrations of Fe and Al was tested.

2.1. **The new SSX system to separate Ni/Co from Fe/Al**

The new SSX system consists of two reagents in a diluent, and all these reagents are commercially available. The chemical composition of the synthetic leach solution is shown in Table 1. The aqueous solution contained 9 g/L Fe(III) and 3 g/L Al.

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe(III)</th>
<th>Al</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
<td>9.0</td>
<td>3.0</td>
<td>0.4</td>
<td>8.2</td>
<td>0.2</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

2.1.1. **Metal extraction pH isotherms**

Batch tests were conducted to determine the metal extraction pH isotherms with the SSX system and the synthetic laterite leach solution (Fig. 1). It is clear that the metal extraction order in terms of pH\(_{50}\) values is (Table 2):

Cu > Ni > Co > Zn > Mn > Al ~ Mg ~ Fe(III) ~ Ca

Table 2: Metal pH\(_{50}\) values and separation factors over Fe(III) and Al.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe(III)</th>
<th>Al</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH(_{50})</td>
<td>1.3</td>
<td>2.1</td>
<td>&lt;1.0</td>
<td>~2.6</td>
<td>&gt;&gt;2.6</td>
<td>&gt;&gt;2.6</td>
<td>&gt;2.6</td>
<td>&gt;&gt;2.6</td>
<td>&gt;&gt;2.6</td>
<td>&gt;&gt;2.6</td>
</tr>
<tr>
<td>β(_{MF/Fe}^*)</td>
<td>1067</td>
<td>65</td>
<td>6878</td>
<td>66</td>
<td>1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>β(_{MA/Al}^*)</td>
<td>896</td>
<td>55</td>
<td>5776</td>
<td>55</td>
<td>---</td>
<td>1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

\(β_{MF/Fe}^*\) = separation factor of metals over Fe(III) at pH 2.0
\(β_{MA/Al}^*\) = separation factor of metals over Al at pH 2.0

The separation factors of Cu and Ni over Fe(III) and Al are over 5000 and 1000, respectively, indicating that the separation of these two metals from Fe(III) and Al and other impurities are easy and complete. The separation factors of Co over Fe(III) and Al are in the range of 55 – 65, indicating that the separation of Co from Fe and Al is possible, although a number of extraction and scrubbing stages could be needed.

The metal pH isotherms also suggest that the stripping of Ni and Co can be achieved at pH 0.5 or with a free acid concentration of 15 g/L H\(_2\)SO\(_4\). The complete stripping of Cu needs a strip solution with a much higher acidity, probably at pH 0 or with a free acid concentration of 50 g/L H\(_2\)SO\(_4\).

2.1.2. **Metal extraction kinetics**

The metal extraction kinetics with the new SSX system and the synthetic heap leach solution at pH 2.0 are shown in Fig. 2. Within 30 seconds, all copper,
97% nickel, 70% cobalt and 42% zinc were extracted, suggesting very fast extraction kinetics of these metals. The extractions of zinc and other impurities, such as manganese, iron, calcium, magnesium and aluminium were decreased after one minute of mixing, probably caused by the crowding effect of nickel. The metal extraction almost reached equilibrium in 1 minute, again, suggesting very fast extraction kinetics.

2.1.3. Metal stripping kinetics

The stripping kinetics of nickel, cobalt, zinc and copper with a strip solution containing 25 g/L sulphuric acid are shown in Fig. 3. It can be seen that the stripping kinetics of nickel, cobalt and zinc are very fast: within 30 seconds, almost all of these metals were stripped. The stripping of copper was slow: 46% was stripping within 30 seconds and this increased to 47% in 10 minutes, suggesting the acidity was not high enough for its complete stripping. A further test with 100 g/L H₂SO₄ showed that all copper was completely stripped, indicating that an organic bleeding with a strong acidic solution can be used to keep the copper in a low level.

2.2. The DSX process coupled with Ni hydrolysis

A conceptual flowsheet consisting of HL – DSX – Ni hydrolysis is shown in Fig. 4.

- The pH of the HL solution is adjusted to 1.8-2.0 using laterite ores. After S/L separation, the aqueous solution is subjected to extraction with the DSX process to obtain (a) an aqueous raffinate containing almost all the iron, aluminium, arsenic, chromium, manganese, magnesium, calcium and chloride and some zinc (b) a loaded organic solution containing almost all the copper, nickel, cobalt and some zinc and residual iron.
- The organic solution from the extraction step is subjected to scrubbing, resulting in (a) a scrubbed organic solution containing nickel, copper, cobalt and zinc and (b) a loaded scrub liquor containing mainly iron and small amount of cobalt, zinc nickel and copper, which is recycled to the extraction step.
- The scrubbed organic solution is subjected to stripping using a hydrochloride acid from the nickel hydrolysis step, resulting in (a) a loaded strip liquor containing nickel, cobalt, copper and zinc and (b) a stripped organic solution containing almost no metals and is recycled to the extraction step.
- The loaded strip liquor from the DSX circuit enters another SX circuit using tri-octyl- and decyl-amine (Alamine 336) for extraction and water for stripping, resulting in (a) a loaded strip liquor containing all cobalt, copper and zinc, and (b) a raffinate with high concentration of nickel, which is subjected to hydrolysis to obtain NiO product and HCl solution recycled for stripping.
- The loaded strip liquor containing cobalt, copper and zinc is subjected to ion exchange with Purolite S-950 resin using acid for stripping, resulting in (a) a cobalt solution for recovery of pure cobalt product, and (b) a mixed
copper and zinc solution for recovery as a bulk product or further separation for individual products.

2.3. The DSX process coupled with Ni electrowinning

A conceptual flowsheet consisting of HL – DSX – Ni electrowinning (EW) is shown in Fig. 5. Until stripping, all process steps are the same as shown in the above HL-DSX-Hydrolysis flowsheet.

- The scrubbed organic solution is subjected to stripping using a mixture of concentrated sulphuric acid and part of Ni spent electrolyte from the nickel EW step, resulting in (a) a loaded strip liquor containing nickel, cobalt, copper and zinc and (b) a stripped organic solution containing some copper and is recycled to the extraction step.
- An organic bleed is required using relative strong sulphuric acid to keep the copper concentration in the organic solution at a low level. The loaded strip liquor joins the strip solution.
- The loaded strip liquor from the DSX circuit is subjected to another SX circuit using Cyanex 272 for extraction and sulphuric acid for stripping, resulting in (a) a loaded strip liquor containing all cobalt, copper and zinc, and (b) a raffinate with high concentration of nickel, which is subjected to EW to obtain Ni cathodes. Part of the Ni spent electrolyte is recycled to EW after combining with the raffinate from the Cyanex 272 circuit.
- The loaded strip liquor from the Cyanex 272 circuit containing cobalt, copper and zinc is subjected to the same treatment as in the above HL-DSX-Hydrolysis flowsheet.

2.4. The DSX process coupled with Ni hydrogen reduction

A conceptual flowsheet consisting of HL – DSX – Ni hydrogen reduction (HR) is shown in Fig. 6. Until the treatment of the raffinate from the second SX circuit with Cyanex 272, all process steps are the same as shown in the HL-SX-EW flowsheet.

- The raffinate with high concentration of nickel from the Cyanex 272 circuit is subjected to solution making with ammonium sulphate and hydrogen reduction to obtain Ni product.
- The raffinate from the HR enters a small SX circuit using the same SSX system as in the DSX circuit to recover the residual Ni, which is recycled to the HR circuit. The Ni-depleted \((\text{NH}_4)_2\text{SO}_4\) solution is used for solution making for the HR circuit or for making \((\text{NH}_4)_2\text{SO}_4\) product for sale.
- The loaded strip liquor from the Cyanex 272 circuit containing cobalt, copper and zinc is subjected to the same treatment as in the HL-DSX-Hydrolysis flowsheet.

3. THE CSIRO DSX PROCESS FOR HPAL SOLUTIONS

If the new SSX system is used for HPAL solutions, the CCD system for neutralisation, precipitation and solid/liquid separation can be simplified,
suggesting capital and operating savings. The same as for the HL and AL solutions, the DSX process can be coupled with either hydrolysis or electrowinning or hydrogen reduction to obtain different Ni products.

4. THE STABILITY OF THE NEW SSX SYSTEM

The commercial reagents used in the new SSX system are chemically stable individually and confirmed by researchers and industrial users. The combination of the reagents or the SSX system has been stable during the developing period through numerous tests. Although no apparent organic degradation has been noticed, a long turn stability study can be carried out in the future research to confirm this.

5. CONCLUSIONS

The new CSIRO DSX process using the new SSX system has the following advantages:

- Making the direct recovery of nickel and cobalt from HL, AL and HPAL solutions possible,
- Separation of nickel and cobalt from iron, aluminium and other impurities in low pH to avoid nickel and cobalt losses in neutralisation or precipitation steps,
- Possible savings in capital and operating costs if applied to HPAL processes since the CCD system for neutralisation, precipitation and solid/liquid separation can be simplified,
- All organic reagents are commercially available and in reasonable price,
- The process flowsheet is much simplified to save capital costs.
- The new CSIRO DSX process can be readily coupled with nickel hydrolysis, electrowinning and hydrogen reduction to obtain different nickel products.

This new CSIRO DSX process is a significant technology development to separate Ni/Co from Fe/Al and other impurities. It will largely simplify the process flowsheet and to significantly save capital and operating costs.

6. ACKNOWLEDGEMENT

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7. REFERENCES


Fig. 1: Extraction pH isotherms of metals with the novel SSX system and the synthetic laterite heap leach solution.

Fig. 2: Metal extraction kinetics with the novel SSX system and the synthetic laterite heap leach solution.
Fig. 3: Metal stripping kinetics from the loaded SSX system with 25 g/L sulphuric acid solution.
Fig. 4: A conceptual process flowsheet with HL – DSX – Ni hydrolysis.
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