HYDROMETALLURGICAL PROCESSING OF NICKEL LATERITES- A BRIEF OVERVIEW ON THE USE OF SOLVENT EXTRACTION AND NICKEL/COBALT PROJECT FOR THE SEPARATION AND PURIFICATION OF NICKEL AND COBALT

NİKEL LATERİTLERİN HİDROMETALURJİK İŞLEMI-NİKEL VE KOBALT AYIRIM VE SAFLAŞTIRMASI İÇİN SOLVENT EKSTRAKSİYON KULLANIMI VE NİKEL KOBALT PROJELERİNE KISA BİR BAKIŞ

Sait Kursunoglu,* , Muammer Kaya**

* Abdullah Gul University, Department of Materials Science & Nanotechnology Engineering, Kayseri, TURKEY
** Eskisehir Osmangazi University, Department of Mining Engineering, Division of Mineral Processing, Eskisehir, TURKEY

ABSTRACT

In this study, a brief overview of the solvent extraction (SX) application for the separation and purification of nickel and cobalt in hydrometallurgical processing of laterite nickel ores is presented. This paper consists of two parts: firstly, the SX of nickel and cobalt from sulphate leach solutions is described; and secondly, the development of hydrometallurgical plants for the processing of laterite nickel ores that involve solvent extraction technique is discussed. The most important extractants are shortly given in the first part of the study. It is seen that the extraction and separation of nickel and cobalt from the impure leach solution of laterite nickel ores can be performed by either using a single extractant system that is called as a direct solvent extraction (DSX) or a mixture of two or more extractant which is known as a synergistic solvent extraction system (SSX). Mixed sulphide precipitation (MSP) and mixed hydroxide precipitation (MHP) processes are mentioned. This paper is also addressed advantage and disadvantages of each extraction system. It is shown that capital investment expenditure, operational investment expenditure and mineralogical content are the most important factors that can affect the selection of the appropriate hydrometallurgical process for lateritic nickel ore.

ÖZ


Anahtar Sözcükler:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Keywords:
Laterit,
Nikel,
Kobalt,
Saflaştırma,
Solvent ekstraksiyon.

Geliş Tarihi / Received : 21 December / Aralık 2018
Kabul Tarihi / Accepted : 11 March / Mart 2019

Derleme / Review

Keyword:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Geliş Tarihi / Received : 21 December / Aralık 2018
Kabul Tarihi / Accepted : 11 March / Mart 2019

Anahtar Sözcükler:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Keywords:
Laterite,
Nikel,
Kobalt,
Saflaştırma,
Solvent ekstraksiyon.

Geliş Tarihi / Received : 21 December / Aralık 2018
Kabul Tarihi / Accepted : 11 March / Mart 2019

Anahtar Sözcükler:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Keywords:
Laterite,
Nikel,
Kobalt,
Saflaştırma,
Solvent ekstraksiyon.

Geliş Tarihi / Received : 21 December / Aralık 2018
Kabul Tarihi / Accepted : 11 March / Mart 2019

Anahtar Sözcükler:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Keywords:
Laterite,
Nikel,
Kobalt,
Saflaştırma,
Solvent ekstraksiyon.

Geliş Tarihi / Received : 21 December / Aralık 2018
Kabul Tarihi / Accepted : 11 March / Mart 2019

Anahtar Sözcükler:
Laterite,
Nickel,
Cobalt,
Purification,
Solvent extraction.

Keywords:
Laterite,
Nikel,
Kobalt,
Saflaştırma,
Solvent ekstraksiyon.
INTRODUCTION

High pressure acid leaching (HPAL) using sulphuric acid as lixiviant, including its variant such as the enhanced pressure acid leaching (EPAL) process, is currently the only leaching technology that is in industrial operation for laterite nickel ores to date as the last Caron process operation in Yabulu, Australia, was closed in the early 2016. There are three downstream routes that have been commercialised for recovering the nickel and cobalt from the leach liquor namely mixed sulphide precipitation (MSP), mixed hydroxide precipitation (MHP) and direct solvent extraction (DSX) (Motteram et al., 1996; Manson et al., 1997; Mihaylov et al., 2000; Donegan, 2006). Each has its own advantages and disadvantages. The MSP route has been in commercial operation for more than 55 years and is now the most used technique to recover the nickel and cobalt as a filter cake of mixed nickel and cobalt sulphides separating them from manganese, magnesium and calcium. It has been used at Moa Bay (Cuba), Murrin Murrin (Australia), Coral Bay (Philippines), Ambatovy (Madagascar) and Taganito (Philippines). The MHP route has been used at Cawse (Australia), Ravenstorphe (Australia) and Ramu (Papua New Guinea). This process is simpler to operate than the MSP process but it has poor selectivity against manganese compared to the MSP process. This process therefore is unsuitable for treating feed liquor with high manganese content. The DSX route is the newest addition among the three and has now been used in two commercial operations: Bulong (Australia) and Goro (New Caledonia). This process circumvents the need of intermediate precipitation of the nickel and cobalt and therefore, this approach offers a potential economic advantage over the two intermediate precipitation processes.

Extraction of nickel and cobalt from pregnant leach solutions (PLS) have been investigated using different aqueous media such as sulphate, nitrate and chloride. Most efforts have been implemented to extract nickel and cobalt from sulphate leach solution. The most deleterious impurities are Mg, Ca, Mn, Zn, Al, Fe, Cu etc. These impurities are also dissolved into leach solution along with Ni and Co during the leaching process. Partial neutralization is carried out to remove these impurities from PLS before solvent extraction. Limestone, lime, and calcite oxide are used as neutralization agent in this stage. Fe, Al, Cr are precipitated from PLS in order to obtain nickel and cobalt rich solution at pH between 4.5 and 5.5 since the hydrolysis of the three metals can occur in this pH range.

SX has become one of the most important separation process in hydrometallurgy. This process occurs in at least two steps called extraction and stripping. The extraction step covers mixing the leaching solution with an organic phase that contains at least one extractant to extract the metals of interest into the organic phase separating them from the unwanted metals. The separation of the nickel and cobalt can be achieved by preferential extraction of cobalt over nickel, leaving the nickel in the raffinate with Mn, Mg, Ca for further purification or by extraction both nickel and cobalt leaving majority of the impurity in the raffinate, i.e. the aqueous phase resulted from the extraction process. Clearly, additional SX circuit for the separation of the nickel and cobalt is required for the latter. The extracted metals are then stripped from the loaded organic phase back into aqueous phase by using mineral acids.

Extraction of nickel and cobalt from laterite leach solution can be carried out by using a single extractant system or by using a mixture of two or more extractant known as synergistic solvent extraction (SSX) system. The former is achieved by using a commercially available organic extractant. To avoid re-leaching, DSX process has been developed and applied to industrial scale. SSX process is usually carried out using a commercial available extractant with addition of a new extractant that is synthesized by researchers in the laboratory. Most researchers have tried to find out a new extractant to separate nickel and cobalt more effectively than those of commercially available extractants. Although there are some improvements using this new extractant to separate nickel and cobalt, none has been commercially available (Cheng, 2006). Therefore, it is not practical to use these extractants in industrial scale. A number of synergist, containing oximes and pyridines have been investigated as synergist in solvent extraction to separate selectively nickel and cobalt from PLS. Although
these synergistic systems are highly promising to be used in SX but instability of these synergists in the presence of two or more organic is a major disadvantage. The main objective of this study is to point out the extraction and separation of nickel and cobalt from laterite sulphate leach solution and the presentation of the recent developments of nickel/cobalt project.

1. EXTRACTION OF NICKEL AND COBALT FROM SULPHATE LEACH SOLUTION

The solvent extraction recovery of nickel and cobalt from leach solutions are being practised on a commercial scale at a number of locations. Sulphate, chloride and mixed sulphate-chloride systems are operational. Extraction of organophosphorus acid group have been intensively investigated in recent years to the commercial separation of nickel and cobalt in weakly acidic sulphate media. Early work at Eldorado Nuclear Ltd. In Canada and CANMET resulted in the development of a proprietary process utilising di (2-ethylexyl) phosphoric acid (D2EHPA) (Preston, 1982). The poor cobalt-nickel selectivity is seen by using D2EHPA as extractant. Although the cobalt-nickel selectivity exhibited by PC 88A (2-ethylhexylphosphonic acid, 2-ethylhexyl ester) is better than D2EHPA, both of these organophosphorus reagents are active calcium extractants. This is deleterious in sulphate circuits where the formation of gypsum cruds can lead to serious solvent losses. The American Cyanamid Co. developed a new, selective cobalt extractant; dialkyl phosphinic acid (Cyanex 272). The most significant advantages of this reagent are that it has high cobalt-nickel selectivity and the ability of calcium rejection (Rickelton et al., 1984). Cyanex 272 is a member of one of three groups of organophosphorus compounds. The groups contain phosphoric (6, 7, 15), phosphonic (8, 12, 13, 14, 15) and phosphinic (15, 16, 17, 18) acid derivatives. The major difference between the compounds is that the hydrocarbon group (R) is directly bonded to the phosphorus atom in the Cyanex 272. Both hydrocarbons are bonded to the phosphorous through an oxygen atom in the phosphoric acid, whereas phosphonic acids demonstrate one R-O-P and one R-P bond. It has been reported that cobalt-nickel separation selectivity increases in the order phosphoric "(D2EHPA) < phosphonic (PC 88A) < phosphinic (Cyanex 272)". The extraction order of the metals is summarised as follows (Rickelton et al., 1984):

- D2EHPA: Zn> Ca> Cu> Mg> Co> Ni
- PC 88A: Zn> Cu> Ca> Co> Mg> Ni
- Cyanex 272: Zn> Cu> Co> Mg> Ca> Ni

It has been reported that the extraction order of D2EHPA as a function of pH50 is Zn2+> Ca2+> Mn2+> Cu2+> Co2+> Ni2+> Mg2+. Extraction isotherms from solution containing seven different elements show that the separation of zinc and calcium from other elements is not difficult and the separation of copper and manganese from cobalt and nickel is possible. A hydrochloric acid stripping is necessary to prevent gypsum precipitation and iron poisoning of D2EHPA (Cheng, 2000). The extraction characteristic of base metals Mn, Cu, Co and Ni has been studied using the extractant PC 88A alone. The extraction order of these metals is established as Mn2+> Cu2+> Ni2+> Co2+> Ni2+ when the loading of the metal in the organic phase is low. The extraction order of the metals is changed on the loading high as Cu2+> Mn2+> Co2+> Ni2+ (Thakur, 1998). Complexes of cobalt (II) with organophosphorus acids are tetrahedral, while the nickel (II) complexes octahedral symmetry. The extracted complexes proposed by Cyanex 272 are found as a form of Co (HA2) in agreements with findings (Tait, 1993). The extraction and separation of aluminium from cobalt, nickel and magnesium sulphate solutions has been investigated using Cyanex 272 as extractant. The number of stages is essential to do both extraction and stripping process of aluminium. Two stage of extraction and three stage of stripping are applied for aluminium extraction and separation (Tsakiridis and Agatzini, 2005).

Much study has been conducted in the field of solvent extraction to develop extractants which are selective for one of the metal ions. The more general route is the extraction of cobalt (II), leaving nickel (II) in the aqueous phase. Cyanamid has introduced two thiophosphinic acid extractants (Cyanex 301 bis (2, 4, 4-trimethylpentyl) dithiophosphinic acid) and Cyanex 302 bis(2, 4, 4-trimethylpentyl) monothiophosphinic acid).
These two extractant differ with respect to the anionic donor atom that facilitates extraction. Dithiophosphoric acids are monomeric, whereas monothiophosphoric acids are usually dimeric (Tait, 1993).

Cyanex 301 is the most effective extractants for cobalt (II) and nickel (II), although their separation with this reagent is strongly dependent on pH. Since Cyanex 301 consists of only sulphur donor atoms, it tends to form stable complexes with transitional metal ions than Cyanex 302 that contains oxygen donor atoms. Therefore, Cyanex 301 is more effective extractant than Cyanex 302 at lower pH values. Cyanex 301 has a similar structure to Cyanex 272, with two oxygen atoms replaced by sulphur, however their chemical properties are different. The affinity of metal cations is different due to sulphur and oxygen atom differences in the two extractant bond. This leads to in a different order of metal selectivity for the two extractant. It has been found that Cyanex 301 strongly extracts Ni and Co at low level pH<2. This is the major advantages of Cyanex 301 compared to other extractants that require expensive base addition to control of pH during extraction process. A low level of pH advances the phase-separation rate and decreases soluble loses of the extractant. Furthermore, Cyanex 301 dose not extract Mn in the operating pH range. However, the major disadvantages of Cyanex 301 is that it extracts cobalt at low pH that means it requires a strong acid and an elevated temperature at stripping. The other disadvantages of Cyanex 301 is that relatively small concentrations of ferric iron (20-50 mg/L) present in aqueous feed solution results in significant oxidation of the Cyanex 301 (Mihaylov et al., 2000). The simultaneous extraction and separation of Co (II) and Ni (II) from manganese and magnesium sulphate solutions has been performed using Cyanex 301, diluted in Exxsol D-80. The stripping of loaded organic phase has been carried out using hydrochloric acid solution. The extraction mechanism has suggested that Cyanex 301 acts as a cationic liquid exchanger. It is an acidic extractant by the formation of what appears to be the CoA$_2^+$ and NiA$_2$$(H_2O)_2^+$. Two stage of extraction and three stage of stripping have required (Tsakiridis and Agatzini, 2004a). The extraction process Works best in a fairly narrow pH range, about pH 4-5. As is usual with SX process, the organic extractants produce H$^+$ ions during extraction as given Eq.1. It is important to keep an optimum pH during extraction. This can be achieved by adding a neutralisation agent during extraction to match acid production or pre-neutralising the organic phase before extraction, to reach the pre-determined desired pH of the emulsion at the end of extraction, that is, "saponification" (Jones et al., 2010).

$$\text{M}^{2+}_{(\text{aq})} + 2\text{RH}_{(\text{org})} \rightarrow \text{MR}_2^{(\text{org})} + 2\text{H}^+_{(\text{aq})}$$

Extraction of nickel and cobalt from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272 in kerosene has been performed. The percentage extraction of metal ions increases with increasing equilibrium pH. The pH values, at which the extraction of nickel and cobalt are achieved, is highest NaCyanex 272 and lowest for NaD2EHPA. The separation factor is pH sensitive and is highest with NaCyanex 272 indicating that the sodium salt of the phosphinic acid is the best extractant for nickel-cobalt separation. The composition of extracted species for cobalt and nickel is reported as Co(HA$_2^+$)$_2$ and Ni(HA$_2^+$)$_2$ using NaD2EHPA. The extraction mechanism of cobalt is described as follows (Devi et al., 1994; Devi et al., 1998; Sahu et al., 2004).

$$\text{Na}^+_{(\text{aq})} + \frac{1}{2}(\text{HA})_2^{(\text{org})} \leftrightarrow \text{NaA}_{(\text{org})} + \text{H}^+_{(\text{aq})}$$

The sodium ions in the extractant is replaced by cobalt ion according to following reaction:

$$2\text{NaA}_{(\text{org})} + \text{Co}^{2+}_{(\text{aq})} \rightarrow \text{CoA}_2^{(\text{org})} + 2\text{Na}^+_{(\text{aq})}$$

Once the sodium ions are replaced, extraction of cobalt takes place by the following reaction:

$$\text{Co}^{2+}_{(\text{aq})} + 2(\text{HA})_2^{(\text{org})} \rightarrow \text{CoA}_2(\text{HA})_2^{(\text{org})} + 2\text{H}^+_{(\text{aq})}$$

It has been reported the solvent extraction behaviour of solution of neodecanoic acid (Versatic 10) acid in xylene towards a large number of metal cations. The order of metal extraction decreases through the series Ni$^{2+}$> Co$^{3+}$> Ca$^{2+}$> Mg$^{2+}$ using Versatic 10 in one stage single metal extraction. The pH$_{50}$ values are Ni:6.34, Co:6.55, Ca:7.42, Mg: 8.11 (Preston, 1985). Cobalt and nickel are simultaneously extracted by Versatic 10, leaving magnesium and
calcium in the solution. The loaded organic phase is stripped by a synthetic nickel sulphate solution simulating real electrolyte. Subsequently, cobalt is separated from nickel by Cyanex 272. The loaded with cobalt organic phase is stripped by a synthetic cobalt spent electrolyte (Tsakiridis and Agatzini, 2004b). It has been found that the extracted complexes proposed by Versatic 10 are CoA22HA and NiA42HA (Tsakiridis and Agatzini, 2004b). These results are consisted with the findings (Preston, 1985).

Preston and du Preez (1998) has studied SSX of base metals with di-nonylnaphthelene sulphonic acid (DNNSA) and pyridinecarboxylates. The metal extraction order is determined as Cu> Ni> Co> Ca> Zn> Al> Fe(III)> Mg with 3-pyridinecarboxylates and Cu> Ni> Co> Zn> Al> Fe(III)> Ca> Mg with 2 and 4-pyridine carboxylates. The extraction and separation of nickel and cobalt from calcium, magnesium and manganese using synergistic mixture of carboxylic acid have been reported. Addition of certain viable synergists to commercially available tertiary branched carboxylic acid like Versatic 10 or neodecanoic acid (Exxon) create a large synergistic shifts in the pH50 values for nickel, and small antagonistic shifts in the extraction of calcium. The order of extraction for this system is Cu> Ni> Co> Ca> Zn> Al> Fe(III)> Mg with 3-pyridinecarboxylates and Cu> Ni> Co> Zn> Al> Fe(III)> Ca> Mg with 2 and 4-pyridine carboxylates. The extraction and separation of nickel and cobalt from calcium, magnesium and manganese using synergistic mixture of carboxylic acid like Versatic 10 or neodecanoic acid (Exxon) create a large synergistic shifts in the pH50 values for nickel, and small antagonistic shifts in the extraction of calcium. The order of extraction for this system is Cu> Ni> Co> Ca> Zn> Al> Fe(III)> Mg with 3-pyridinecarboxylates and Cu> Ni> Co> Zn> Al> Fe(III)> Ca> Mg with 2 and 4-pyridine carboxylates.

The extraction and separation of nickel and cobalt from sulphate leach solution has been reported using synergistic systems consisting of carboxylic acid and aliphatic hydroxoxime (LIX 63). Aliphatic alpha-hydroxoxime with the active component 5,8-diethyl-7-hydroxododec-6-one oxime is improved the synergistic solvent extraction research on the recovery of copper, nickel and cobalt. The combination of LIX 63 with Versatic 10 acid exhibits significant synergistic shifts for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts for calcium and magnesium. The extraction and stripping kinetics of cobalt, copper, zinc, and manganese are fast and the extraction and stripping kinetics of nickel are slow with the Versatic 10 and LIX 63 synergistic system. LIX 63 demonstrates the role of an extractant and Versatic 10 a synergist for cobalt. The metal extraction sequence is Cu> Ni> Co> Zn> Mn in the Versatic 10 and LIX 63 synergistic system when the LIX 63 concentration is lower than 0.3 M. The cobalt pH isotherm is located lower than that of nickel and metal extraction order changes to Cu> Co> Ni> Zn> Mn when 0.5 M Versatic 10 and 0.35 M LIX 63 system is used (Cheng, 2006).

The extraction of nickel and cobalt from laterite leach solution has been investigated using 4PC (n-decyl-4-pyridinecarboxylate ester) as synergist and Versatic 10 as extractant in Shellsol D70. The SSX system consisting of 0.5 M Versatic 10 and 1.0 M 4PC in Shellsol D70 performs the best among the system tested containing 4PC. Fast nickel and cobalt stripping kinetics are observed but the manganese stripping kinetics are very slow. The SSX system containing 0.5 M Versatic 10, 0.45 M LIX 63 and 1.0 M TBP (tri-n-butyl phosphate) results in much better than the SSX system containing 0.5 M Versatic 10, 1.0 M 4PC in terms of both manganese and calcium behaviour in extraction, scrubbing and stripping (Cheng et al., 2010a; Cheng et al., 2010b).

Solvent extraction and separation of nickel and cobalt in a typical synthetic lateritic leach solution with hydroxamic acids LIX 1104, LIX 1104SM and the mixture of LIX 1104 and Versatic 10 has been reported. LIX 1104 is highly selective for Zn, Co and Ni over Mn, Mg and Ca, with their pH50 differences over manganese being 2.2, 1.9 and 1.8 units, respectively. In comparison, the pH isotherms of Zn, Ni, Co and Mn with LIX 1104SM are shifted to a higher range, however the pH50 differences all exceed 2 pH units, indicating ready separation of these valuable metal from Mn, Mg, and Ca. The laterite leach
solution shows the following extraction order: Cu >> Zn >> Ni~Co >> Mn >> Mg~Ca both LIX 1104 and LIX 1104SM extractants. The LIX 1104 and LIX 1104SM systems is potentially applicable for the separation of Fe/Cu/Zn/Co/Ni from Mn/Mg/Ca by extraction and the separation of Zn/Co/Ni from Fe/Cu/ by selective stripping (Zhang et al., 2012).

The purification of nickel sulphate by SSX with mixture of Cyanex 272 with Versatic 10 has been performed using a multicomponent aqueous sulphuric acid solution with metal ion concentration similar to high pressure acid leaching liquors, after iron removal step. The multicomponent aqueous solution is selectively purified with respect to zinc, copper, manganese and cobalt using (20% v/v) of Cyanex 272 at pH~3.9. Cyanex 272 proves ineffective in separation of calcium and magnesium from nickel sulphate solution. The mixture of Cyanex 272 and Versatic 10 exhibits a suitable separation of calcium and magnesium from nickel sulphate solution at pH of 5.1 (Guimaraes et al., 2014).

The recovery of nickel and cobalt from leach solution of lateritic nickel ore using a synergistic system consisting of Versatic 10 and Acorga CLX 50 has been investigated. The synergistic solvent extraction system can effectively recover nickel and cobalt and separate them from manganese, calcium and magnesium. Over 99% of Ni and Co are extracted from the synthetic leach solution at pH 6.3 an A:O ratio of 1:1. More than 80 % of the manganese is rejected to the raffinate. No phase separation problem or crud formation is observed, indicating good performance of the SSX system (Cheng et al., 2015).

A two-sequential solvent extraction circuits to extract and separate the nickel and cobalt from Caldag lateritic leach solution was carried out. The nickel (98%) and manganese (94%) were simultaneously extracted using 20% Versatic 10 and 5 % TBP dissolved in ShellSol 2046 at pH 7.2 in the first extraction circuit. The cobalt (96%) and manganese (98%) were extracted using 15% Cyanex 272 and 5% TBP in ShellSol 2046 at pH

<table>
<thead>
<tr>
<th>Cyanex extractant</th>
<th>Chemical formula</th>
<th>Specific gravity</th>
<th>Solubility in water (mg/L)</th>
<th>Use (actual and potential)</th>
</tr>
</thead>
<tbody>
<tr>
<td>272</td>
<td>((C_8H_{17})_2P(O)OH)</td>
<td>0.92</td>
<td>16</td>
<td>Separation of Co from Ni, rare earth separation, zinc extraction</td>
</tr>
<tr>
<td>301</td>
<td>((C_8H_{17})_2P(S)SH)</td>
<td>0.95</td>
<td>7</td>
<td>Selectively extract many heavy metals from alkali and alkali earth metals and manganese</td>
</tr>
<tr>
<td>302</td>
<td>((C_8H_{17})_2P(S)OH)</td>
<td>0.93</td>
<td>3</td>
<td>Similar to Cyanex 272 in performance except that extraction takes place at lower pH and Co is separated from Mn.</td>
</tr>
<tr>
<td>921</td>
<td>((C_8H_{17})_3PO)</td>
<td>0.88</td>
<td>&lt;5</td>
<td>Recovery of uranium from wet-process phosphoric acid, recovery of acetic acid from aqueous effluents</td>
</tr>
<tr>
<td>923</td>
<td>(R_3PO)</td>
<td>0.88</td>
<td>10</td>
<td>Recovery of carboxylic acids, phenol and ethanol from effluent streams, separation of Nb from Ta, removal of As, Sb and Bi from copper electrolytes, extraction of mineral acids</td>
</tr>
<tr>
<td>471X</td>
<td>((C_8H_{17})_3PS)</td>
<td>0.91</td>
<td>3</td>
<td>Selectively recovers silver, separates Pd from Pt, extracts mercury and gold</td>
</tr>
</tbody>
</table>

Table 1. Major Cyanex solvent extraction reagents (Flett, 2004; Flett, 2005)
5.0 in the second circuit. The loaded organic was contacted with a cobalt salt solution containing 20 g/L of cobalt. A two-stage scrubbing of this loaded organic with the cobalt-containing solution displaced the co-extracted manganese, magnesium, calcium and nickel with cobalt. The manganese (93%) was scrubbed out from the loaded organic along with all other impurities. 94% of the nickel and 91% of the cobalt were totally separated from the feed solution (Kursunoglu et al., 2017). Table 1 shows major Cyanex solvent extraction reagent. Table 2 shows brief descriptions of solvent extraction reagents.

2. DEVELOPMENTS OF NICKEL PROJECTS

2.1. Cawse Nickel Project

The Cawse Nickel Project, which is owned by Centaur Mining and Exploration Limited (Centaur), is located 50 km north-west of Kalgoorlie. There are two basic lateritic leaching options that met the criteria. Pressure acid leaching and reduction roast-ammonia leaching are alternatives. The former is selected as an appropriate process. In this project, three options are considered for producing end products. These are DSX to produce nickel and cobalt metal, precipitation of a mixed sulphide and precipitation of a hydroxide intermediate followed by a selective ammoniacal re-leach, solvent extraction and electrowinning (EW) of nickel on cathode. DSX route is rejected due to the high manganese content in the cobalt rich ore. The sulphide route is also rejected because of the high capital expenditure for hydrogen and hydrogen sulphide production facilities. For these reasons, precipitation of a hydroxide intermediate followed by ammoniacal re-leaching, solvent extraction and EW are chosen for this project. Purification of lateritic leach solution is performed using aeration of the solution at pH 3 to 6 to achieve oxidation of ferrous iron (Fe^{2+}) to produce ferric (Fe^{3+}) hydrate. Almost complete iron precipitation is achieved by neutralization with lime stone to pH 3.5. The initial neutralization is carried out prior to Counter Current Decantation (CCD). Some cobalt and nickel is also precipitated as the pH is raised in the subsequent iron removal stage. Magnesia is used as precipitate instead of lime to prevent gypsum contamination. The extraction of nickel and cobalt from ammoniacal leach solution is conducted using an oxime extractant (LIX 84I). Three extraction stage and four strip stage are applied for a plant configuration. Co-extracted copper is separated off the barren organic by contacting with strong acid solution. The alternative approach of extracting the cobalt before the nickel was investigated. Cyanex 272, DEHPA and Versatic acid were tried but the results were not pursued. Figure 1 shows proposed flow sheet for Cawse Nickel Project (Flett, 2004; Flett, 2005; Manson et al, 1997).

2.2. Murrin Murrin Nickel/Cobalt Project

Anaconda Nickel NL was listed on the Australian Stock Exchange in March 1994 with the single purpose of defining a minimum of 50 million tonnes of lateritic nickel/cobalt resources thought to exist at Murrin Murrin, located 60 km to the east of Leonora in the North Eastern Goldfields of Western Australia. The prefeasibility study was performed on the lateritic nickel ore for the three main process routes to obtain metal product. These process routes are DSX from neutralised leach solution followed by EW, hydroxide or carbonate precipitation from leach solution followed by re-dissolution and refining to metals and mixed sulphide precipitation of nickel and cobalt from leach solution followed by re-dissolution and metal refining. The MSP route is determined as the best one in this project. DSX route is rejected due to operating risk associated with no break point between the acid leach and refining section. The hydroxide precipitation route is ruled out due to co-precipitation of metals at given pH levels and apparent difficulty in re-dissolution of precipitates for refining. Recovery of nickel and cobalt requires neutralisation of the free acid. Neutralisation to a high pH range, of between 3.5 and 4.0, with aeration, is considered to promote precipitation of most of the iron, chromium, and aluminium as their respective hydroxides. Two alkaline neutralisation reagents (magnesite and calcrete) that close to Murrin mine site, are used. The use of magnesite offers several advantages over calcrete, including a lower weight of waste solids for disposal. However, the reactivity of the various available magnesites proves lower
<table>
<thead>
<tr>
<th>Class of extractant</th>
<th>Type</th>
<th>Examples</th>
<th>Manufacturers</th>
<th>Commercial uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid extractant</td>
<td>Carboxylic acids</td>
<td>Naphthenic acids, Versatic acids</td>
<td>Shell Chemical Co.</td>
<td>Copper/nickel separation, nickel extraction, yttrium recovery</td>
</tr>
<tr>
<td></td>
<td>Alkyl phosphoric acids</td>
<td>Dialkyl phosphoric acids and sulphur analogues</td>
<td>Daihachi Chemical Industry Co Ltd (DP-8R, DP-10R, TR-83, MSP-8); Bayer AG (BaySolvex D2EHPA pure); Albright&amp;Wilson Americas (DEHPA).</td>
<td>Uranium extraction, rare earth extraction, cobalt/nickel separation, cobalt/nickel separation, zinc extraction etc.</td>
</tr>
<tr>
<td></td>
<td>Alkyl phosphonic acids</td>
<td>2-ethylhexyl phosphonic acid 2-ethylhexyl ester and sulphur analogues</td>
<td>Daihachi Chemical Industry Co Ltd (PC-88A); Albright&amp;Wilson Americas (Ionquest 801), Tianjin Beichen, China (P507).</td>
<td>Cobalt/nickel separation, rare earth separation</td>
</tr>
<tr>
<td></td>
<td>Alkyl phosphinic acids</td>
<td>Dialkyl phosphinic acids and sulphur analogues</td>
<td>Cytec Inc. (Cyanex 272, 302 and 301); Daihachi Chemical Industry Co Ltd (PIA-8)</td>
<td>Cobalt/nickel separation, zinc and iron extraction, rare earth separation</td>
</tr>
<tr>
<td></td>
<td>Aryl sulphonic acids</td>
<td>Dinonyl naphthalene sulphonic acid</td>
<td>King Industries Inc. (Synex 1051)</td>
<td>Magnesium extraction</td>
</tr>
<tr>
<td>Acid chelating extractants</td>
<td>Alpha alkaryl hydroxyoximes, beta alkaryl hydroxyoximes</td>
<td></td>
<td>Cognis Inc. (LIX reagents), Cytec Inc. (Acorga reagents)</td>
<td>Copper extraction, nickel extraction</td>
</tr>
<tr>
<td></td>
<td>Beta diketones</td>
<td>LIX 54</td>
<td>Cognis Inc.</td>
<td>Copper extraction from ammoniacal solution</td>
</tr>
<tr>
<td></td>
<td>Hydroxamic acids</td>
<td>LIX 1104</td>
<td>Cognis Inc.</td>
<td>Proposed for nuclear fuel reprocessing, iron extraction and As, Sb, and Bi extraction from copper tank house electrolytes</td>
</tr>
<tr>
<td>Basic extractants</td>
<td>Primary amines</td>
<td>Prime JMT, Prime 81R</td>
<td>Rohm &amp; Haas.</td>
<td>No known commercial use</td>
</tr>
<tr>
<td></td>
<td>Secondary amines</td>
<td>LA-1, LA-25</td>
<td>Rohm &amp; Haas.</td>
<td>Uranium extraction, proposed for vanadium and tungsten extraction</td>
</tr>
</tbody>
</table>
than desire. The attainment of the 3.5 pH range requires prior calcination. Calcrete is evaluated at both pH ranges. A pre-reduction stage with hydrogen sulphide for reduction of the ferric iron to ferrous iron prior to neutralisation with calcrete is incorporated. This serves to both release a portion of the acid associated with the iron for neutralisation by the calcrete and removes elemental sulphur formed during the ferric reduction. The Murrin ore leach solution proves amenable to sulphide precipitation of the nickel and cobalt under moderate conditions, by virtue of the high concentrations of magnesium. A major benefit of precipitation of the metals as sulphides, rather than as hydroxides or carbonates, is the selectivity of the precipitation, with excellent rejection of the major impurities. The refining of sulphides for obtaining high purity products of cobalt and nickel consists of oxidative pressure leaching, solution purification and separation of the cobalt from the nickel by solvent extraction. After pressure leaching, the discharge slurry is sent to a pH adjustment stage where the iron, aluminium and other impurities are precipitated by ammonia with aeration. Remaining zinc and copper are removed by precipitation with hydrogen sulphide. The remaining zinc is separated by Cyanex 272 and stripped sulphuric acid solution from loaded organic phase. Cobalt is subsequently separated in a second stage solvent extraction using

<table>
<thead>
<tr>
<th>Tertiary amines</th>
<th>Various Alamines, in particular Alamine 336</th>
<th>Cognis Inc.</th>
<th>Uranium extraction, cobalt extraction from chloride media, tungsten extraction, vanadium extraction, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary amines</td>
<td>Aliquat 336</td>
<td>Cognis Inc.</td>
<td>Vanadium extraction, other possible uses for chromium, tungsten, uranium, etc.</td>
</tr>
<tr>
<td>Mono N-substituted amide</td>
<td>-</td>
<td>-</td>
<td>Iridium separation from rhodium</td>
</tr>
<tr>
<td>Trialkyl guanidine</td>
<td>LIX 79</td>
<td>Cognis Inc.</td>
<td>Gold extraction from cyanide solution</td>
</tr>
<tr>
<td>Solvating extractants and chelating non-ionic extractants</td>
<td>Phosphoric, phosphonic and phosphinic acid esters and thio analogues</td>
<td>TBP, DBBP, TOPO, Cyanex 921, Cyanex 923, Cyanex 471X</td>
<td>Union Carbide, Albright &amp; Wilson, Daihachi Chemical Industry Co Ltd, Cytec Inc.</td>
</tr>
<tr>
<td></td>
<td>Various alcohols, ketones, esters, ethers, etc.</td>
<td>MIBK etc</td>
<td>Various</td>
</tr>
<tr>
<td></td>
<td>Alkyl and aryl sulphoxides</td>
<td>-</td>
<td>Various</td>
</tr>
<tr>
<td></td>
<td>Alkyl and aryl sulphides</td>
<td>di-n-octyl and di-n-hexyl sulphides</td>
<td>Daihachi Chemical Industry Co Ltd (SFI-6), others</td>
</tr>
<tr>
<td></td>
<td>Palladium extraction in PGM refining</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S. Kursunoglu ve M. Kaya / Bilimsel Madencilik Dergisi, 2019, 58(2), 131-144
Cyanex 272 at different pH range compared to zinc solvent extraction stage. pH is arranged with ammonium hydroxide. The nickel is recovered as metal powder by hydrogen reduction. Ammonium sulphate is recovered from the barren solution. Figure 2 shows proposed flow sheet for Murrin Murrin Nickel /Cobalt Project (Flett, 2004; Flett, 2005; Motteram et al., 1996).

2.3. Bulong Nickel Project

Bulon plant processes a nickel laterite ore 30 km east of Kalgoorlie, Western Australia. The nickel laterite resource at Bulon consists of 150 Mt with a minable reserve of 6.9 Mt at 1.57% Ni and 0.12% Co. This refinery uses a direct solvent extraction process to accumulate nickel cathode from dilute leach solution without any precipitation stage for an intermediate nickel product. DSX process is selected for extraction of nickel and cobalt from PLS due to the production of high quality nickel and cobalt end product at a low capital and operating cost. The leach plant consists of ore preparation unit, pressure acid leaching unit, slurry neutralisation, CCD circuit and solution neutralisation to get a mildly acidic sulphate PLS containing low levels of iron, aluminium and chromium. After solution neutralisation, PLS is directed to cobalt solvent extraction (CoSX) circuit to extract cobalt, zinc, iron, copper and manganese from nickel using organic extractant Cyanex 272. Loaded organic phase is stripped sulphuric acid. Loaded strip liquor is precipitated to remove manganese and magnesium from cobalt using sulphide precipitation method. Nickel, iron (III), zinc and copper are removed as co-precipitates. CoSX raffinate is sent to the nickel solvent extraction (NiSX) circuit. The extraction of nickel from calcium and magnesium is fulfilled using Versatic™ 10 as extractant. After organic stripping, loaded strip liquor is accumulated on cathode by EW. The CoSX circuit is critical to the success of the Bulong process. Target Ni:Co in the nickel cathode is 700+ as well as Co: Ni >700. Separation of manganese is an additional requirement since residual manganese is transferred to the nickel electrolyte where the oxidation leads to precipitation and degradation of organic substances. More than 90% of zinc, manganese and cobalt was extracted at pH about 6 from PLS using Cyanex 272 diluent Shellsol 2046 whereas about %15 percent of magnesium is co-extracted. Iron and chromium are removed in the stage of neutralisation. An ideal Bulong PLS contains negligible chromium and <0.5 mg/L Fe in PLS. The use of limestone and lime for neutralisation process, PLS is saturated with calcium. This results in the precipitation of gypsum on the most surfaces that contact with PLS, causing mechanical problems. The precipitation
of gypsum is greater in NiSX than CoSX circuit. The addition of antiscalent mitigates the formation of gypsum. Figure 3 shows proposed flow sheet for Bulong Nickel /Cobalt Project (Flett, 2004; Flett, 2005; Donegan, 2006).

![Flow Sheet Diagram](image)

Figure 3. Bulong nickel /cobalt project proposed flow sheet

2.4. Goro Nickel/Cobalt Project

New Caledonian laterites represents about 20% of the world’s laterite nickel resources. In 1991, Inco Ltd. acquired various mining concessions in the south of New Caledonia. Between 1993 and 1998, the Goro process was developed and extensively tested at Inco’s facilities in Canada. The solvent extraction was exhibited on a plot plant scale in Port Colborne, Ontario. The process selection work was conducted to find out a suitable process for Goro limonite and saprolite ore types. Due to high moisture content of the ore, fuels requirements, lack of the infrastructure near the project site and sensitive environmental issue, pyro-metallurgical method is unattractive for this project. Pressure acid leaching process is the most appropriate method to obtain higher nickel and cobalt recoveries from lateritic nickel ores. Since the relatively low saprolite to limonite ratio and the relatively low magnesium content of the saprolite in the Goro ore body, a mixed ore is effectively processed directly through the pressure acid leaching. The acidic pressure leach solution is separated from the leach residue by CCD circuit. The solution is treated with sulphur dioxide to reduce Cr (IV) to Cr (III) in the partial neutralisation stage. Limestone is used to neutralize the free acid and precipitate impurities such as Al, Cr, Si, Cu and Fe. The remaining copper is removed by ion exchange chelating resin. The extraction of nickel and cobalt is selectively extracted and concentrated into the hydrochloric acid strip solution. In the solvent extraction works, Cyanex 301 is used due to the simultaneous extraction of nickel and cobalt from leach solution. Zinc is extracted together with nickel and cobalt from the solution. Zinc is removed from the strip solution by ion exchange resin. The extraction of cobalt from nickel is achieved in the secondary solvent extraction stage, using a tertiary octyl amine. The cobalt-free nickel containing hydrochloric acid solution is subjected to high temperature pyro-hydrolysis in order to obtain a high purity nickel oxide product.

The metal selectivity of Cyanex 301 follows the selectivity of metal precipitation with H₂S. Cyanex 301 is a liquid organic sulphide, containing a similar function to H₂S in selectively recovering Ni and Co from laterite acid leach solution. Cyanex 301 strongly extracts Ni and Co at pH<2. Copper and zinc are co-extracted with nickel and cobalt. Copper is not stripped from the loaded organic phase so it needs to be removed before solvent extraction. Ferric iron (Fe⁴⁺) is extracted while ferrous iron (Fe⁺²) is extracted only higher pH values. None of the major impurities such as Mg, Mn and Ca is co-extracted with Cyanex 301. The main advantage of Cyanex 301 over other extractants is that it does not require expensive base addition to control the pH during extraction. Low pH operation favours the phase separation rate and decreases the soluble losses of the extractant. Cyanex 301 does not extract Mn in the operating pH range. This results in a major simplification of the recovery circuits for the Goro project. Nickel is stripped from loaded organic phase using 6N hydrochloric acid, whereas cobalt is stripped at a lower acidic condition, indicating the potential to extract and separate the two metals in a single step. However, a sufficient selectivity is not achieved from the combined strip liquor. The major disadvantages of the Cyanex 301 is that
small amount of ferric iron present in the aqueous feed solution results in significant oxidation of the extractant. Figure 4 shows proposed flow sheet for Goro Nickel/Cobalt Project (Mihaylov et al., 2000; Flett, 2004; Flett, 2005).

Figure 4. Goro nickel/cobalt project proposed sheet

2.5. Ravensthorpe Nickel Project

Ravensthorpe Nickel Operations Pty Ltd (RNO) is a joint venture formed between Comet Resources (50%) and QNI Ltd. to develop the Ravensthorpe nickel laterite resources. The project is located at Ravensthorpe, WA, about 150 km west of Esperance, and 570 km south east of Perth. The Ravensthorpe nickel plant consists of pressure acid leaching, residue re-leach, primary neutralisation, CCD washing, secondary neutralisation, mixed hydroxide precipitation, manganese removal and hydroxide precipitate washing and filtration. Pressure acid leaching is conducted a temperature of 250°C. The nickel, cobalt, magnesium, copper, zinc and manganese recoveries are higher than those of the other elements. 93% Ni, 94% Co, 93% Mg, 85% Zn and 85% Mn are extracted from the laterite ore. Acid consumption is determined as 480 kg/t ore. The residue releach is intended to recovery nickel and cobalt values from process recycle slurries. MgSO₄ is precipitating in the autoclave (incorporating Ni and Co into the matrix), and this mixed salt is re-dissolved under atmospheric conditions. The atmospheric leach increases the average PAL nickel recovery by 2.1% and is completed within 30 minutes. The PAL and re-leached solution is induced Jarosite precipitation step with limestone and then subjected to primary neutralisation step aiming for a discharge pH of 3.5. After counter current decantation, solid and liquid are separated and solution is directed to secondary neutralisation step to precipitate any remaining impurities from solution. Filtered solution from secondary neutralisation is processed to mixed hydroxide precipitation stage for recovery of nickel and cobalt values to a hydroxide intermediate. Metals are precipitated using magnesium oxide. Lime precipitation is rejected because it can result in gypsum contamination on the product. A target discharge pH is 8.2 aiming for a nickel recovery greater than 99%. Residual manganese in solution is precipitated in manganese removal stage. Complete manganese precipitation is achieved at pH 9 using limestone. The remaining nickel and cobalt in the solution also precipitate along with some magnesium. Figure 5 shows proposed flow sheet for Ravensthorpe Nickel/Cobalt Project (Miller et al., 2001; Miller et al., 2005).

Figure 5. Ravensthorpe Nickel/Cobalt Project proposed flow sheet
CONCLUSIONS

The solvent extraction of nickel and cobalt from laterite leach solutions and recent development of hydrometallurgical nickel/cobalt project were presented. It was shown that nickel and cobalt are mainly extracted from lateritic nickel ores using MHP, MSP and DSX processes. These routes have been commercialised in the industrial scale for nickel and cobalt extractions. Each process consists of different operational stages such as neutralisation, secondary neutralisation, precipitation, re-leaching stages, solvent extraction and electrowinning. SSX process has been recently used to extract nickel and cobalt from the ores but has not been applied for the industrial operations. It is believed that SSX is used in the industrial applications in the recent future. It was seen that the selection of appropriate extraction method is highly dependent on the mineralogical content of laterite ore, capital investment expenditure and operational investment expenditure. Therefore, hydro-metallurgists should carefully investigate an appropriate hydrometallurgical process before the application of extraction method.

REFERENCES


NOMENCLATURE

SX: Solvent extraction
DSX: Direct solvent extraction
SSX: Synergistic solvent extraction
MSP: Mixed sulphide precipitation
MHP: Mixed hydroxide precipitation
HPAL: High pressure acid leaching
EPAL: Enhanced pressure acid leaching
PLS: Pregnant leach solution
D2EHPA: Di (2-ethylxyl) phosphoric acid
PC 88A: 2-ethylhexylphosphonic acid, 2-ethylhexyl ester
Cyanex 272: Dialkyl phosphinic acid
Cyanex 301: Bis (2, 4, 4-trimethylpentyl) (Dithiophosphinic acid)
Cyanex 302: Bis(2, 4, 4-trimethylpentyl) (Monothiophosphinic acid)
Versatic 10: Neodecanoic acid
DNNSA: Di-nonylnaphthelene sulphonic acid
Exxon: Neodecanoic acid
LIX 63: Aliphatic hydroxoyximine
4PC: N-decyl-4-pyridinecarboxylate ester
TBP: Tri-n-butyl phosphate
LIX® 1104: Hydroxamic acid
LIX® 1104SM: Hydroxamic acid
CCD: Counter current decantation
EW: Electrowinning
LIX 84I: Oxime extractant
CoSX: Cobalt solvent extraction
NISX: Nickel solvent extraction
PAL: Pressure acid leaching