Solvent extraction as an enabling technology in the nickel industry

by G. Bacon* and I. Mihaylov*

Synopsis

The past decade has witnessed unprecedented growth in the development and implementation of solvent extraction technology in the extractive metallurgy of nickel and cobalt. Solvent extraction is proving to be a powerful tool, opening new opportunities for simpler, more cost efficient and environmentally sound metal refining processes. These advances, however, could not have been possible without the cooperative efforts between the nickel industry and the people and organizations involved with reagents, materials and equipment development and supply as well as solvent extraction research, aided by the accumulated knowledge and practical experience from the copper and uranium solvent extraction operations. This paper provides an overview of these developments and some of the challenges ahead.

Introduction

Historically, the main source for primary nickel production has been the nickel-iron-copper sulphide ores (typically 1–3% Ni). The ability to upgrade these ores to a sulphide concentrate is essential as it ensures that the subsequent processing involves low volume high-grade nickel material. However, with a few notable exceptions, the known sulphide ore resources are located deep underground and their mining costs are high. As the more economical of these resources are gradually exhausted, the complexity of mining and processing inevitably increases.

The sulphide ores represent only about 30% of the world’s land-based nickel resources. The remaining ~70% are represented by the nickeliferous lateritic ores (typically 1–2% Ni), which are also a major source for cobalt. The laterites are located close to surface and can be mined at significantly lower costs. Unfortunately, they are not readily amenable to upgrading thus resulting in higher processing costs than for the sulphides. For this reason, the use of these resources has been largely limited to the high-Ni saprolitic fraction leaving, as generally uneconomical, the much more abundant limonitic fraction.

Two hydrometallurgical technologies have played a key role in the development of commercially viable nickel recovery processes for these resources. One has been the pressure acid leaching of laterites using horizontal agitated autoclaves. Sustantial advances in autoclave design and engineering were made over the past 10–12 years as part of the successful introduction of pressure leaching technology for treating refractory gold ores as well as zinc and nickel sulphide concentrates. Although the autoclaves used in these processes typically operate below 220°C, the accumulation of engineering know-how and operating experience spurred renewed interest in applying the technology to laterites.

The other hydrometallurgical technology has been the solvent extraction (SX) of base metals. Its acceptance by the nickel industry has been primarily influenced by the following factors:

➤ development and commercial availability of new solvent extraction reagents
➤ demonstrated success in copper refining over a wide range of throughputs, and
➤ developments in solvent extraction equipment design and engineering.

Other factors, common to all base metals producers, such as declining ore grades and increasing ore complexity, decreasing (in real terms) prices and pressure to meet increasingly stringent environmental regulations, require continuous improvement, development and implementation of innovative techniques to address these issues.

Solvent extraction has a significant potential as a metal refining hydrometallurgical process—its operation is continuous, easily automated and requires little supervision. Unlike alternative separation/concentration techniques, no solids handling is routinely required (except for

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* Inco Technical Services Limited, Mississauga, Canada.
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occasional crud and in some rare cases scale handling). These features contribute to low operating costs and high online availability of the typical solvent extraction circuit.

The first relatively large-scale SX application in hydrometallurgy—for uranium refining—dates back to the years around World War II. Solvent extraction is also well established in the refining of precious metals and rare earths. However, because in this case the amount of material to be processed is relatively small, the refining circuits are generally smaller in size, requiring less capital to build and to modify as needed in the future.

On the other hand, the business of base metals mining and refining is very capital intensive. For example, the capital cost of a nickel laterite plant is generally in the range of US$8–12 per pound of Ni annual production. With few exceptions, the plants producing base metals as their primary product are by necessity large to maximize the economy-of-scale benefits and be economically viable. Hence, the acceptance of solvent extraction as a new technology in base metals refining is a fairly complex task. It requires not only a credible demonstration of the particular process at all levels of testing/piloting and in good integration with the upstream and downstream operations, but also a careful evaluation of the available engineering designs to support the technology and all potential risks associated with its implementation. It is, thus, not surprising that it usually takes years before the industry would embrace an otherwise technically and economically viable SX process. At the same time, the continuing pressure to develop more efficient and environmentally sensitive refining technologies inevitably dictates that the whole range of available process tools, and combinations thereof, are carefully evaluated in the quest to determine the optimum one for the specific feed material and the specific circumstances of the base metal producer.

One relevant example has been the development of the technology for the copper H2SO4 leach-solvent extraction-electrowinning (L/SX/EW) operations. This particular experience had a substantial effect on the large-scale solvent extraction application in the nickel industry and it is from that point of view that some of the major advances are reviewed below.

Coming of age in copper solvent extraction

The classical route for Cu recovery from sulphide ores involves concentration, smelting and electrorefining. It is well suited when the ore also contains appreciable amounts of precious metals. The route becomes uneconomical for low grade sulphides (and with minimal precious metals content) and for oxide ores. The preferred way to extract Cu from these types of ores is by mild H2SO4 leach producing a dilute (~0.5–4.0 g/l Cu) CuSO4 solutions with a pH of ~1.4–2.0. The solution would then be treated to precipitate and concentrate the copper in one form or another—for example, by cementation using metallic iron or by precipitation using H2S. The concentrate would then be processed through smelting and electrorefining.

Solvent extraction provided a winning alternative to these routes. Building upon the class of known Cu-selective hydroxoyamine reagents used in analytical chemistry methods, the first commercial Cu extractants were developed in the mid-1960s. These extractants (LIX®63, and particularly LIX®64 and LIX®665N) were able to selectively transfer copper from the dilute acidic leach solution with minimal Fe co-extraction (the main impurity) into a concentrated CuSO4 solution (typically ~50 g/l Cu and 150–180 g/l H2SO4) from which copper could be electrowon. The acidic raffinate after extraction is used for leaching while the highly acidic lean copper electrolyte electrowinning is used for copper stripping from the loaded organic. In this elegant refining scheme, by separation and concentration, the SX process provides the link between leaching and electrowinning to produce high purity electrolytic copper.

The use of solvent extraction resulted in significantly reduced operating costs (by some estimates, about 50% lower than for the cementation with Fe route). One of the newest Cu L/SX/EW plants, Codelco’s Radomiro Tomic, is said to have cash production costs of about US$0.38/lb of Cu. This lowering of costs allowed to include as copper resources feed materials previously considered uneconomical. Today, there are roughly about 50 such plants with a total production capacity of close to 2 million tonnes of Cu per year. The individual SX circuit capacity of these plants ranges from ~200 to ~3,000 m3/h of pregnant leach solution (PLS), proving that the technology can deliver a reliable and consistent performance over a wide range of throughputs. It is also quite telling that about 50% of these plants were commissioned during the past 10 years and another ~27% during the 1980s. This pattern of exponential growth is a testament to the success of the SX technology for this copper recovery route.

Perhaps the most important factor for the success of the solvent extraction in this case has been the development of solvent extractants and fine-tuning of their performance to meet the range of optimal process conditions both for the leaching and electrowinning side, as dictated by the individual plant’s copper sources conditions. That meant having a copper-selective extractant, with fast extraction and stripping kinetics, able to maintain high Cu extractions over pHs of as low as 1.2–1.4 while allowing at the same time to be readily stripped using lean copper electrolyte (typically ~30–35 g/l Cu and ~200 g/l H2SO4) to produce feed to electrowinning. One particular advantage of this Cu SX system is that no base addition is necessary during the extraction, resulting in base reagent cost saving and a simplified circuit operation since no pH control is necessary.

The constituents of the proprietary extractants, available from Aveca (formerly Zeneca) and Cognis (formerly Henkel), are nonyl (C9) and dodecyl (C12) hydroxyphenyl ketoximes and aldodoxes (Table 1). The ketoximes are weaker extractants than the aldodoxes but are more readily stripped at lower free H2SO4 levels. Thus, the majority of the copper SX plants use specific formulations to balance the extraction and stripping properties required. These formulations include ketoxime/aldodoxe mixtures (such as LIX®® 984 and LIX®® 973 from Cognis) or an aldodoxe with the addition of various modifiers, such as nonylphenol (e.g., Acorga® P5100 from Aveca), tridecanol (e.g., LI®® 622), or proprietary esters (e.g., Acorga® M5640). The past few years have also seen a gradual trend of phasing out the C12 in favour of the C9 aldodoxes.
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Table I

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The Cu/Fe selectivity, phase-separation and crude formation, and to a certain degree the extractant stability, also affect the choice for a particular formulation of the SX plant organic. Crud formation has been and continues to be one of the biggest problems in the operation of these circuits; detailed studies on crud formation have identified a number of contributing factors (e.g., colloidal silica, surfactants, solids, certain and organic additives, etc.).

Improvements in mixer-settler design have also helped to minimize crud formation and phase entrainment (organic loss to raffinate and to copper electrolyte and transfer of leach solution with the loaded organic to copper stripping) and to maximize settler throughputs. Entrainment of leach solution with the loaded organic is particularly critical in those cases when the leach solution has high levels of Fe, Mn and Cl; in such circumstances, installation of a dedicated wash stage for the loaded organic is often required.

In addition to the standard box-type agitated mixer with gravity settler design, proprietary mixer-settlers are also in use. Krebs mixer-settlers were introduced in late 1980s at Phelps Dodge’s Morenci and at WMC’s Olympic Dam. By employing a conical pumper and superimposed launder for gentle mixing achieved with a helical Spirok impeller. This results in minimized overmixing and air entrapment leading to lower phase entrainment and crud formation.

Other developments include the implementation of methods for organic removal from raffinate and strip solution (e.g., coalescers, multimedia filters, Jameson cell) and for the clay treatment of the organic to remove organic-soluble contaminants (e.g., surfactants) which negatively affects plant performance (e.g., worsened phase separation, poorer extraction kinetics, etc.).

All SX plants represent a fire-hazard risk. This fact alone has historically been a major stumbling block for the adoption of otherwise technically and economically sound SX processes. The development and introduction of higher flash point diluents helped in reducing the fire hazards. The demonstrated effectiveness of fire prevention and fire fighting measures over time have increased the confidence in the ability of the technology to mitigate this risk. However, recent incidents (December 1999 and October 2001) at WMC Olympic Dam’s Cu SX plant have shown that a lot more is needed in the areas of equipment design, layout and plant operating practices. Notwithstanding the success of the L/SX/EW process, it should be noted that the development of a similar chloride route has not been successful. Suitable copper extractants were developed (e.g., Acorga® CLX-50 for the Cuprex process), but difficulties in electrowinning high purity copper from chloride solutions are a major impediment. This example shows that as with any other tool, solvent extraction is not, and cannot be, a fit-for-all hydrometallurgical process.

The Cu L/SX/EW plant operations clearly showed that the solvent extraction technology does work over a wide range of scales. This engineering and operating experience, together with the already accumulated knowledge from existing nickel-cobalt solvent extraction operations, was particularly important for the acceptance of the technology for the large-scale commercial hydrometallurgical processes for laterites, in development over several past years.

**Solvent extraction in nickel/cobalt refining**

From solvent extraction’s perspective, there are three principal types of solutions important in commercial Ni/Co refining, reflecting the range of lixiviants used to solubilize Ni/Co values.

- **Chloride solutions**—resulting from Cl and/or HCl leaching of nickel matte, intermediates or secondary nickel sources (e.g., Falconbridge’s Kristiansand, SLN’s Le Havre, SMM’s Niihama, and Metallurgie Hoboken refineries).
- **Ammoniacal** (ammonia-ammonium carbonate) solutions—resulting from leaching of reduction roasted laterites as part of the Caron process (e.g., QNI’s Yabulu refinery, Tocantins in Brazil and Punta Gorda in Cuba) and of nickel-cobalt hydroxide precipitate (as practised by Cawse).
- **Sulphate solutions**—resulting from O2 pressure leaching and/or H2SO4 leaching of sulphide concentrates and precipitates, matte and lateritic ores.

**Chloride solutions**

In strong chloride solutions, the separation task is helped by the fact that cobalt forms anionic chloro-complexes (e.g.,
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CoCl₂ and CoC₂O₄) while Ni does not. Hence, an anion-exchange extractant such as a tertiary alkyl amine in its salt form ([R₃NH]Cl) is able to selectively extract Co away from the Ni-containing concentrated chloride (typically ≥ 5 N Cl⁻) solution. Other metals, often present as impurities, such as Fe, Cu and Zn, also form strong chloro-complexes and can be selectively removed from the nickel solution as well. Impurities, such as Pb and Mn can also be extracted from the nickel solution, if required. Nickel is electrowon from the purified NiCl₂ solution and the generated Cl₂ is used in the upstream leaching operation. The cobalt is readily stripped from the loaded amine organic with any low in chlorides solution (such as water) producing a CoCl₂ solution with ≥60 g/l Co. This solution is typically low in acid and after additional purification, if required, becomes the starting point for producing a variety of Co products, such as Co metal (electrowinning), metal powders, salts, etc.

Not surprisingly, the first commercial SX applications in the Ni industry were based on this chemistry. Major developments in this area from late 1960s to mid-1970s resulted in the adoption of the selective Co extraction with tertiary amines such as tri-isooctyl amine (tioOA) or tri-n-octyl amine (TnOA) from concentrated Ni/Co chloride solutions at several refineries at about the same time in early to mid-1970s, with most of the operations continuing to this day.

Because Ni is not chemically co-extracted, the Co/Ni ratios in the Co product can be very high, from at least ~3,000 to as high as 8,000–10,000. The main problem in reaching and maintaining these ratios has been the transfer of entrained Ni solution with the Co-loaded organic to stripping. For example, the Ni/Co feed to Co SX at Kristiansand contains about 220 g/l Ni (and ~11 g/l Co) and it would not take much physical entrainment of that solution into the loaded organic to substantially raise the nickel level in the cobalt strip product.

Various measures are in place to reduce the aqueous entrainment with the loaded organic. They include the use of one or more scrub stages in which the cobalt-loaded organic is contacted with an aqueous solution to remove entrained nickel; in most cases, this solution is a small portion of the cobalt strip product solution (subsequently reverted to extraction) in order to chemically displace less extractable metals, such as Mn, from the organic. Other measures include special design mixer-settlers to minimize entrainment or additional mechanically forced phase-separators (e.g., centrifugal separators).

Despite the very convenient Ni/Co separation chemistry, there are two particular process and engineering challenges. The first one is having to operate with highly corrosive Cl⁻ solutions. Since the start-up of these refineries about a quarter century ago, the development of various acid-resistant composite materials and the accumulation of considerable expertise in materials selection have made the task of designing and building SX circuits for this type of solutions somewhat easier, yet it is still a challenge. The second one is the necessity to use all-aromatic diluents for the amine organic. There are several reasons for that, the primary one being the need to keep the viscosity of the Co-loaded organic low and thus minimize the entrainment of Ni solution. The problem with these diluents is that they have lower flash points than the aliphatic diluents with low (e.g., ~20 vol%) or no aromatic content, are more volatile and more corrosive.

One such diluent initially used by some of these refineries was xylene, which has a flash point of only ~26°C and thus represents a major fire hazard. While it is not clear whether the choice of diluent was a factor in the May 1972 major fire at the new Ni/Co refinery at Kristiansand, this event did raise serious and long-lasting concerns about SX as a reliable hydrometallurgical process in the minds of many. On the positive side, there were subsequently significant developments in the areas of SX plant layout, piping design and construction, materials and instrumentation selection as well as fire fighting measures at Kristiansand and elsewhere to minimize the risk of this happening again.

Today's aromatic diluent formulations used by some of these refineries, such as Exxon's Aromatic® 100 and Shell's ShellSol® A100 have higher flash-points of ~42–47°C and are thus safer alternatives. Using diluents with even higher flash-points, such as Exxon's Aromatic® 150 and Shell's ShellSol® A150 (flash point of ~63–64°C), would be preferable whenever possible.

Ammoniacal solutions

In the early 1970s, a small Cu and Ni SX plant was commissioned and operated for some time by the SEC Corporation in El Paso, Texas. The plant treated a 70–90 g/l Cu, 30–40 g/l Ni liquor after the crystallization of CuSO₄ from Cu electrolytes of a close-by Phelps Dodge refinery. Following Cu extraction with LIX® 64N (LIX® 65N containing ~1 vol% LIX® 63; see Table I), Ni was then extracted at pH 9–10, with LIX® 64N and using ammonia for pH control. The Ni-loaded organic was washed (pH~3–5) to remove entrained ammonia and then stripped with dilute H₂SO₄ at pH~2 producing NiSO₄ electrolyte for Ni electrowinning. Although a very small scale (about 2 t of Cu and 0.5 t of Ni per day), this plant operation was significant in that it focused the attention of a major extractor on opportunities to use Cu extractants in Ni refining.

In 1975 Nippon Mining's Hitachi refinery began using LIX® 64N for Ni extraction in about the same way. Following sequential Zn and Co removal in separate SX steps, Ni was extracted from a sulphate solution (~30 g/l Ni) at pH 9–10 using ammonia for pH control; Ni was recovered to final product by electrowinning and spent electrolyte was used to strip the Ni from the organic. This operation (producing about 3,300 t of Ni and 1,300 t of Co per year in early 1980s) provided invaluable information and a working resolution for the problem of hydroxyoxime degradation. Further to the known almost irreversible Co extraction as Co(II) and accumulation in the hydroxyoxime organic as CO (III) it was discovered that LIX® 64N was losing its oxime group (C=NOH) by conversion to ketone (C=O) through Co-catalysed oxidation, hence losing its extractive capacity. Fortunately, it was found that the ketone could be re-oximated with high yields to the original oxime through contact with hydroxylamine salts in alkaline solutions. This regeneration process was further developed into a workable technology with the involvement of the extractants' manufacturer. Without the re-oximation process, the commercial application of the ammoniacal SX process for Ni would not have been possible.
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The QNI’s Yabulu refinery uses the high cost and energy intensive Caron process, developed in the 1920s; at Yabulu, it involved ore drying and grinding, followed by reduction roast and ammonia-ammonium carbonate leaching of the reduced ore. Co removal by precipitation with H₂S as mixed Ni/Co sulphide (Ni:Co~2) and shipment for refining elsewhere, Ni recovery by precipitation as NiCO₃ with subsequent calcination to NiO and partial reduction to 85–90% Ni in the final NiO product. By mid-1980s, the local (Greenvale) laterite feed was being exhausted and the plant had to switch to processing New Caledonian and Indonesian laterites with higher Co content. The change to imported laterite feed meant increased transportation costs; the higher Co content would have required a substantial expansion of the existing Ni/Co sulphide plant with increased costs for drying the sulphide and shipping it for refining overseas while reducing the proportion of the nickel available for on-site NiO production. The net result would have been substantially higher operating costs, undermining the viability of the entire operation.

In the modified Yabulu refinery operation, the NH₃/[Ni(H₂)₂]CO₂ leach liquor, containing ~10 g/l Ni, ~0.5 g/l Co, 80–90 g/l NH₃ and ~60 g/l CO₂, is first pre-boiled to reduce the free ammonia from ~80 g/l to ~40 g/l (Ni extraction decreases with increasing ammonia concentration) and then the liquor is aerated to oxidize Co(II) to Co(III) to prevent co-extraction in the subsequent Ni ammoniacal SX (ASX) process. Nickel is extracted with LIX®87QN, an extractant formulation prepared by Cognis for QNI containing (ASX) process. Nickel is extracted with LIX® 84 from the extractant requires contact with high-strength ammonia-ammonium carbonate solution (~280 g/l NH₃ and ~230 g/l CO₂) and produces strip liquor with ~80 g/l Ni. From this liquor, Ni is recovered to basic nickel carbonate and nickel oxide as before. The cobalt from the raffinate is removed by H₂S as sulphide, but the produced quantity is ~3 times less due to substantially lower nickel content (28% Ni and 14% Co before ASX, 2% Ni and 42% Co thereafter).

The development and implementation in late 1980s of the ASX process at Yabulu, in cooperation with the extractant supplier (Cognis), was crucial to the refinery’s continuing operation. It also provided the additional confidence in the SX technology to proceed with the introduction in the late 1990s of a Co refining process, involving several SX steps, for on-site production of cobalt oxide hydroxide which also had the benefit of keeping all of the primary nickel for refining on site. The ASX process also enabled the refinery to expand the range of laterite feed materials it can process. At the present time, feasibility studies are in progress to expand the refinery (from the ASX process onwards) to almost double capacity to treat the mixed Ni/Co hydroxide from the Ravensthorpe pressure acid leach laterite project.

The ASX process does suffer from several disadvantages, although none are too critical: slow extraction and even slower (>5 min per stage required) stripping, a need to reductively strip accumulating cobalt from the organic and to operate the re-oximation process, relatively slow phase-separation. In addition, the small amounts of copper in the feed to extraction would accumulate in the organic due to high pH conditions in both extraction and stripping; copper removal would require separate H₂SO₄ stripping. Transfer of ammonium with the organic between Ni extraction and stripping at Yabulu is inconsequential, as the solutions at both ends of the SX process are ammoniacal, but it is an issue in other refining schemes.

A similar SX process was adopted for the Cawse project. In this most technically successful operation (start-up early 1999) of all three Western Australian pressure acid leach laterite projects to date, an intermediate Ni/Co hydroxide precipitate is re-leached in NH₄/NH₃-CO₂ solution and then nickel is selectively extracted with LIX® 84 from the resulting solution (~12–15 g/l Ni and ~2–3 g/l Co). Unlike at Yabulu, the nickel-loaded organic is first scrubbed/washed to remove loaded ammonium, producing (NH₄)₂SO₄ solution. This scrub/wash operation is also essential in minimizing the co-extraction of zinc, present in small quantities in the feed to extraction. The scrubbed/washed nickel-loaded organic is then stripped with H₂SO₄ from the spent nickel electrolyte from electrowinning. Copper and cobalt removal from the organic as well as re-oximation is required.

With a nameplate capacity of only 9,000 t of Ni and 1,600 t of Co (in cobalt sulphide) per year Cawse is a relatively small operation but serves as a proving case for the technologies involved, including the solvent extraction.

**Sulphate solutions**

As a common solution matrix in Ni/Co hydrometallurgy, the Ni/Co SX from sulphate solutions have received considerable attention in the areas of extractants and applications development. The Ni/Co commercial SX processes to date involve the use of five extractants (Table II).

Three of these extractants are used for selective Co extraction from Ni/Co solutions. In chronological order of development to market, they are the di-2 ethylhexyl phosphoric acid, known as D2EHPA, the 2-ethylhexyl...
phosphonic acid mono 2-ethylhexyl ester available as PC-88A (Daihachi Chemical Industries) and Ionquest® 801 (Albright and Wilson), and the bis (2,4,4-trimethylpentyl) phosphinic acid, available from Cytec Canada Inc. as Cyanex®272.

The first SX process for Co separation from Ni was developed using D2EHPA in mid-1960s. The process developed for Eldorado Nuclear refinery in Canada was actually for ammoniacal leach solutions and prior to extraction the leach solution was aerated to oxidize Co(II) to Co(III). D2EHPA extracted Co as Co(III) pentamine in some preference to Ni; in the hydroxyoxime processes (QNI, Cawse), Co(II) is oxidized to Co(III) prior to SX so that it will not be extracted. Due to D2EHPA’s relatively low Co/Ni selectivity, many extraction stages are required. This was perhaps a reason to choose sieve-plate pulsed column in the piloting. The loaded organic was scrubbed with high-cobalt solutions. The D2EHPA process was further developed in the early 1970s at CANMET in Ottawa for sulphate leach solutions. The organic was pre-loaded with ammonia or sodium to avoid adding base for pH control (pH 5–6) during Co(II) extraction. The cobalt was stripped with H2SO4 to produce electrolyte suitable for electrowinning.

At about the same time, a similar D2EHPA process was developed in the UK (Warren Springs laboratory) and later adopted at the Rustenburg base metals refinery, still in operation today. Cobalt is separated from the primary Ni feed to EW by precipitation of Co(OH)3 with electrolytically produced Ni(OH)2. A reductive re-leaf of the solids produces a Ni/Co sulphate solution, which is fed, after removal of impurities such as Fe, Cu, and Pb, to the Co D2EHPA SX circuit. The organic is pre-loaded with Na prior to extraction. A large number of extraction and scrubbing stages are needed to achieve the required Co/Ni ratio in the Co strip solution.

The development of the D2EHPA process was a major advance in Ni/Co refining from sulphate solutions which also focused the attention of extractant developers on the organophosphate chemistry. Some of the disadvantages of using D2EHPA are the very strong Fe extraction, requiring a reductive or HCl stripping, low degree of Co/Ni selectivity, and preferential Ca, Mg and Mn extraction ahead of cobalt and nickel. In the Rustenburg operation, NaOH is used for iron removal thus the feed to Co SX contains only traces of Ca and Mg—both are co-extracted and occasional gypsum removal from the Co strip stages is necessary.

The D2EHPA separation process was introduced at Nippon Mining’s Hitachi refinery in 1975. Several years later Daihachi introduced the organophosphonic acid extractant PC-88A. In many respects it was similar to D2EHPA. However, it was a poorer Ni extractant (same Ni extraction required a higher pH) and was thus more selective for cobalt over nickel. The testwork at Nippon Mining confirmed at least an order of magnitude better Co/Ni separation with PC-88A. On that basis, the new extractant was adopted at the refinery, despite being more expensive than D2EHPA. The rest of the SX operation remained essentially the same. The use of the PC-88A for cobalt continues to this day in at least one major Ni/Co refinery.

In 1980 Cyanamid (now Cytec) Canada Inc. developed at their Welland, Ontario, plant a new extractant, Cyanex® CNX, which showed significant promise as a selective reagent for Co over Ni. Inco’s research laboratory in Mississauga, Ontario, was apparently the first facility outside Cyanamid to test the new reagent. It was not ‘perfect’ (for example, it was in solid rather than in liquid form) but the internal Inco results were very encouraging and had a positive effect on the continuing efforts at Cyanamid. In early 1982, an improved version, Cyanex® 272, became available (‘27’ signified Co, ‘2’—the ‘second generation’ reagent).

Keeping with the trend from D2EHPA and PC-88A/Ionquest® 801, Cyanex® 272 is an even poorer Ni extractant, while still extracting Co at about the same pH (i.e., pH 5–6), resulting in a substantially higher Co/Ni separation factor. With Cyanex® 272 it is much easier (less extraction and scrub stages) to achieve the required high Co/Ni ratios in the cobalt strip product, on par with what is achieved in the chloride system.

Due to its superior Co/Ni selectivity, Cyanex® 272 was relatively quickly adopted in Ni/Co refineries: the first plant to use this reagent was started in 1985 and by 1990 there were three more plants, including two major Co refineries in Europe. By 1995, the number of plants had doubled, with the latest addition being the newly upgraded and expanded Outokumpu’s Harjavalta Ni/Co refinery, now part of the OM Group, Inc.

At Harjavalta, the Co SX process with Cyanex® 272 replaced Outokumpu’s older process of Co removal from the NiSO4 electrolyte by precipitation as Co(OH)3 with Ni(OH)2. Hence, the Ni:Co ratio in the feed to Co SX is >100 (typical feed (g/l): 130 Ni, 0.8–1.0 Co). Selective Co extraction from a solution with such a high Ni:Co ratio would not have been feasible with D2EHPA or PC-88A/Ionquest® 801. The Rustenburg base metals refinery uses that same Outokumpu process and its Co D2EHPA circuit is on the redissolved Co(OH)3 stream (Ni:Co ratio of only ~0.3); the Nippon Mining Co PC-88A circuit used to process Ni/Co feed with Ni:Co ratio of ~2–3 only.

The development of Cyanex® 272 in Canada expanded the range of possible SX applications in Ni/Co refining and enabled the replacement of more costly and/or environmentally and operator unfriendly technologies. According to Cytec’s estimates, by the end of 1995, about 50% of the world Co production involved a Cyanex® 272 Co refining step. At the present time the total number of refineries (including Murrin-Murrin and Bulong) using the reagent has grown to about 10–12. Perhaps, the biggest disadvantage of Cyanex® 272 is its relatively high cost, hence its users are careful to limit entrainment and soluble losses to outgoing aqueous streams.

The fourth extractant used for Ni/Co refining in sulphate solutions is the Versatic® 10 carboxylic acid. Similarly to D2EHPA, it has been around for a long time, it is not particularly selective and its price is one of its most attractive features. Unlike D2EHPA Versatic® 10 is selective for Ni and Co over Ca and Mg. Unlike all three organophosphorus reagents, Versatic® 10 is selective for Ni over Co; the selectivity is minimal, however, and cannot be used in reality. There have been considerable efforts to increase the extractant’s affinity for Ni by introduction of various modifiers and improve its selectivity for Ni over Co. Although not particularly successful to date, the approach is worth
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pursuing, given the low cost of the extractant. Versatic® 10 is also a weaker, extractant, requiring pH of ~7 for efficient Ni extraction, which exacerbates its biggest problem, namely, the high aqueous solubility (3-5 g/L) and relatively poor phase separation.

For ~20 years SMM’ Niihama refinery used Versatic® 10 to transfer Ni and Co from sulphate into a concentrated chloride solution. Similarly to the Rustenburg refinery operation, the feed to Versatic® 10 SX was the Ni/Co product solution from the reductive re-leach of Co(OH)₂ precipitate after the removal of impurities such as Fe, Mn and Cu. Ammonia was used for pH control and the raffinate was contacted with H₂SO₄ to recover some of the solubilized organic. Nickel and Co were stripped with HCl, producing ~200 g/L Ni/Co strip solution. Cobalt was then selectively extracted with a tertiary amine, both Co and Ni were recovered by electrowinning.

Recent interest in Versatic® 10 results largely from its application at the Bulong laterite plant for Ni SX. This plant (design capacity of ~9,000 t of Ni and ~1,000 t of Co per year) is one of the three new Western Australian laterite projects to use SX directly on the partially neutralized Ni/Co leach solution. At Bulong, there are two SX circuits on the entire volume of the dilute Ni/Co leach solution after partial neutralization with limestone ([g/L]: 3.5 Ni, 0.3 Co, 1.0 Mn, 15 Mg, 0.5 Ca). Cyanex® 272 is first used for Co and ammonia is added for pH control. Cyanex® 272 extracts Mn preferentially to Co while the selectivity for Co over Mg is relatively small at the unfavourable Co:Mg ratio in the feed. Because the feed to extraction is also Ca-saturated some Ca would be extracted in one extraction stage and displaced in another, resulting in likely gypsum formation; aqueous phase dilution due to the water from the ammonia for pH control will help to minimize the formation of gypsum.

The raffinate from the Cyanex® 272 circuit is processed through the Versatic® 10 circuit. Here Ni is separated from the Ca and Mg; any Cu not extracted in the Cyanex® 272 circuit will follow Ni and enter into the electrolyte. Ni metal, ammonia is used for pH control and Ni electrolyte bleed is needed to balance the transfer of co-extracted ammonia to nickel stripping. One main problem at the circuit has been the cross-contamination with Cyanex® 272, resulting in higher Ca extraction and displacement within the extraction stages, leading to gypsum precipitation.

The fifth, and the newest, reagent used for Ni/Co refining is Cyanex® 301. The Ni/Co strip solution (~80–100 g/L Ni) with neutralized leach solution (~4.5 g/L Ni) without the co-extraction of any of the major impurities (Mn, Ca, Mg), without the need for pH control and having to add expensive base reagents. Any traces of Cu in solution after partial neutralization are removed by ion-exchange ahead of SX, to prevent practically irreversible Cu extraction. Due to strong Ni and Co extraction, the strip kinetics is relatively slow and contact with strong acid is required. The use of HCl produces a concentrated Ni/Co strip solution (~80–100 g/L Ni) with about 20 times reduction in volume, significantly reducing the size of the downstream refining circuits. Zinc is completely co-extracted with Ni and Co but is selectively removed by ion-exchange from the chloride solution. Cobalt separation from Ni is done using a tertiary amine extractant. Nickel is recovered by pyrohydrolysis as the desired NiO product, while the HCl is regenerated and recycled back to Cyanex® 301 stripping.

Compared with the other four extractants, Cyanex® 301 has the lowest aqueous solubility which is even lower under the acidic conditions of the raffinate (pH ≤1.5). The phase separation in both extraction and stripping is fast, thus contributing to very low soluble and entrainment losses.

Extensive testing of the Cyanex® 301 process was required as there were no commercial operations using this new reagent. It was carried out at the Inco’s laboratory, mini-plant and pilot plant scale operations in Canada and at the fully integrated pilot plant operation at Goro. In close collaboration with Cytec’s Phosphine Technical Centre, the stability of the extractant was thoroughly investigated. The product of Cyanex® 301 (R₂P(S)S-S(S)PR₂) and several processes to convert it back into R₂P(S)S(SH)₂ were developed. The Cyanex® 301 degradation was caused by metal-catalysed (e.g., Fe) oxidation by air. By operating under an O₂-excluded atmosphere, the degradation rate was demonstrated to be essentially nil. In the Goro pilot plant operations (processing 12 t (dry basis) of ore per day) to date, the Cyanex® 301 circuit has performed very much as expected, and in fact with much less trouble than anticipated.

In many respects, Cyanex® 301 may be regarded as a sulphide, performing a similar function to H₂S in selectively recovering Ni and Co from the laterite acid leach solution as practised at Moa Bay and more recently at Murrin-Murrin. One major difference, and advantage of using Cyanex® 301, is that this selective Ni/Co recovery is achieved without the safety concerns associated with the use of H₂S and without the need for solids handlings and subsequent re-dissolution of the sulphide precipitate. The Cyanex® 301 development by Cytec and the development of the technology for Ni/Co refining by Inco is yet another demonstration of the potential of SX to streamline and improve refining operations in the nickel industry.

**Equipment and materials**

At the present time, all SX operations in Ni/Co refining use mixer-settlers contacting equipment. Proprietary technologies, such as the Krebs mixer-settler and Outokumpu’s Vertical Smooth Flow (VSM) mixer-settler were first developed in mid-1970s to early 1980s and introduced at Ni refineries in France and Finland, respectively. Both technologies are used to this day and are continuously evolving.
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In the past ~5 years, there has been a renewed interest in using columns in Ni/Co/SX circuits. This has been due in part to the considerable efforts of Bateman Projects Engineering in Israel of promoting their pulsed column technology for Ni/Co refining. However, it also reflects nickel industry’s increased confidence in SX technology and the ever-present need for further operational and capital cost savings. Columns have been used for decades as contacting equipment for many processes in the chemical industry, including liquid extraction, but except for a few cases of uranium refining (e.g., in France), there have been no hydrometallurgical applications.

This all changed with the successful introduction of the Bateman disc and doughnut pulsed columns in late 1990s for uranium extraction as WMC’s Olympic Dam operation, which served as a powerful stimulus for a number of metal refineries to consider possible adoption in their operations. Pilot tests were carried out in the past 2-3 years at many Ni/Co refineries; examples include Impala’s base metals refinery and QNI’s Yabulu refinery.

The use of columns instead of mixer-settlers is advantageous in processes where many extraction or stripping stages are required, where extractants are costly, flammable, volatile where processes require special atmosphere and/or well sealed environment, and where processes are particularly sensitive to moving parts and materials of construction. Columns are often easier to operate than mixer-settlers. Columns with axial energy input provide much more uniform size distribution of droplets, thus leading to reduced organic entrainment in outgoing aqueous streams.

Figure 1—The Goro process

[Diagram of the Goro process]
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With significantly reduced organic vapours, acid and other emissions, due to their fully sealed environment, and with their more uniform mixing thus leading to lower organic entrainment in the outgoing aqueous streams, the pulsed columns are a particularly attractive option for minimizing the impact of the solvent extraction operations on the environment.

As part of the testwork and piloting of the Inco-Goro process for laterites, the Bateman pulsed columns technology was also evaluated. The use of pulsed columns for both SX circuits is attractive for a number of reasons, including the ability to seal the equipment, to maintain the required atmosphere and to limit fugitive organic and acid emissions, lack of internal moving parts, reduced fire risks, simpler operation and minimum organic entrainment losses.

The increased interest in columns application in Ni/Co refining has also attracted the attention of other developers/suppliers of columns equipment. One example is Koch-Otto York who have many years of experience in various types of columns technology for the chemical industry.

These increased activities in the area of contacting equipment are expected to result not only in improvements in known technologies but also in novel, more efficient and safer ways of carrying the process of solvent extraction in the hydrometallurgical refineries.

As the scope of solvent extraction systems and range of applications increases, so does the challenge of finding and proving the right materials for the equipment. Despite significant advances in that area, there are still concerns particularly when the materials have to withstand combinations of various corrosive reagents, such as organic extractants, diluents and modifiers, in contact with corrosive acids, gases, etc., sometimes at elevated temperatures. These concerns, of course, are not limited to solvent extraction processes only. In addition, the science of detection and removal of any products of such interactions needs further development to better address these types of issues in refining operations.

Conclusions

The use of solvent extraction for nickel/cobalt refining in the nickel industry have substantially progressed since its earliest applications in the 1970s. The successful development of new extractants and the advances in contacting equipment technology (mixer-settlers and columns) have significantly expanded the scope of technologically and economically sound nickel-cobalt refining options. All these are very much needed as the industry is faced with having to process feed materials of increasing complexity and often decreasing grades while meeting, at the same time, the challenges of stricter limits on the environmental impact of its operations.

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**CSIR:Miningtek and Hatch team up**

CSIR:Miningtek and Hatch Africa have entered into a strategic alliance to provide clients in the resources industry with an enhanced service by linking the strong research and development expertise of CSIR:Miningtek with the global consulting, engineering and project management skills of Hatch.

Both organizations have over 40 years experience in the mining, metals, minerals and mineral exploration industries, and under the agreement will work together on various projects for clients in these industries. Together they will deliver strong knowledge, technology, R&D and commercial application skills, offering clients a depth of services that neither party can offer alone.

‘This alliance offers value to our clients through its strong synergy of thoroughbred capabilities and an unprecedented array of innovative skills and expertise,’ says Bodo Schmitz of Hatch.

The team can provide services which include all stages of mine project development from concept to commissioning and are skilled to perform technical reviews, highlight inefficiencies and recommend actions to reduce operating costs to cover the entire spectrum of the mining value chain,’ says Schmitz.

‘The purpose of this alliance is to work together, where the broader range skills of the two organizations can deliver a strategic advantage to our existing and prospective clients,’ says Pat Willis of CSIR:Miningtek.

Willis says that the synergy that exists between the two organizations means that very little duplication of skills exists but rather the skills and competencies of each organization complement one another.

The alliance can pool skills ranging from, inter alia, all aspects of mine design, simulation, engineering design, project management, technology implementation and environmental impact assessments,’ concludes Willis.

The value of the alliance is to offer a full range of services to clients, from concept to commissioning and operational support.

For further information contact: Hatch Africa, Bodo Schmitz, Tel: +27 (0) 11 239-5302, CSIR:Miningtek, Pat Willis, Tel: +27 (0) 11 358-0110.

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* Issued by: Alison Bull, Alison Bull Communications, Tel: (011) 783-0594, Fax: (011) 784-6916, E-mail: abcomms@iafrica.com
After the great success of ProEXPLO 2001 in April this year, we have formally initiated the organization work for the III International Congress of Prospectors and Explorationists—ProEXPLO 2003 that will be held in Lima between the 22 and 25 April 2003.

The Organizing Committee nominated by the Peruvian Institute of Mining Engineers includes outstanding professional geologists actively involved in exploration activities in Peru and other Latin American countries. Main institutions and companies of the geological and mining business sector are represented in the Organizing Committee and guarantee a significant national and international attendance of the meeting.

ProEXPLO is one of the principal mining and geology forums in Latin America. This is certainly due to its interesting lecture programme and the high quality of the guest speakers. It also constitutes a unique opportunity to learn about new projects and identifying new investment possibilities in Peru and the other countries of the region.

The programme of ProEXPLO 2003 intends to reflect the process of change affecting all aspects of mining and the exploration business. It intends to offer new ideas, concepts, and creative applications of technology that help to promote exploration activities in Peru and in the Latin American region, and to highlight that exploration is crucial for the development of the mining industry: There is no mining without exploration.

According to the Metals Economics Group, worldwide exploration in the year 2000 amounted US$2,600 millions, the lowest expenditure level in the last nine years, and approximately a half of the investment completed in 1997, when worldwide exploration budgets reached a peak of US$5,200 millions. Latin America has received in the last years between 28% and 29% of this amount. In 2000, the investment in the region amounted US$662 million, of which US$139 million were expended in Peru—fifth in the ranking, as compared to US$ 144 million in Chile, US$124 million in Brazil, US$96 million in Mexico and US$ 69 million in Argentina. For comparison it should be noted that US$ 405 million, US$ 348 million and US$ 235 million were invested in Australia, Canada and the United States, respectively. These eight countries, followed by Indonesia and South Africa constituted the top ten destinations for mining exploration dollars.

On the other hand, it should be highlighted that in year 2000, five major companies disappeared through takeovers and mergers, and the 2001 budgets of the merged companies are considerably lower than those of the combined pre-merged entities. It is estimated that the worldwide exploration budget will decrease by 15% in 2001 compared to the previous year. Furthermore, in 2001 there have been an additional six mining company mergers and proposed mergers, and this will result in a further reduction of the investment in mining exploration worldwide.

ProEXPLO 2003 will offer a complete programme of activities in consonance with the changes that the exploration business is and will be facing over the next years. Professionals of international renown will lecture on the following themes:

- Most recent discoveries and exploration projects in the region
- Geological and exploration concepts and models at local and regional scales
- Exploration costs and mining legislations in Latin America
- The role of the geological surveys in promoting exploration
- Role of structural geology in mining exploration and its possibilities to predict the location of new ore deposits
- Renewed application of traditional exploration tools and state-of-the-art technology capable of generating new discoveries
- The mining exploration business, risk, financial sources, valuation of projects, global, regional and local investment tendencies, etc.
- Environmental care and sustainable development.

There will also be pre-congress short courses and guided field trips to significant ore deposits of the region.

On the other hand, the Technical Exhibition, which had a great success in the previous meeting, will also be a high point in ProEXPLO 2003. It will bring together suppliers of equipment and services, and mining and exploration companies. Exhibitors have already realized that offering their products and services in ProEXPLO is a good investment, as it offers invaluable opportunities to interact with their current and future clients.

The Technical Exhibition also includes an extended display of drill cores of the main exploration projects and operating mines.

As in 2001, ProEXPLO will attract a large number of geoscientists, prospectors, exploration managers, mining executives, service companies, government bodies, geological services, and investors of different parts of the world. Peru takes a natural leadership as one of the main destinations for mining exploration investment, and the city of Lima will offer again its variety of cultural and tourist attractions for visitors.

Our web page www.proexplo.com will permanently offer detailed information on the progress of the organization and programme of ProEXPLO 2003, as well as mining exploration news.

* Issued by: Luis Chang Boldtini, First Secretary (Economic Section), Embassy of Peru. Contact: www.proexplo.com