

Solvent extraction in hydrometallurgy: the role of organophosphorus extractants

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Abstract

Solvent extraction (SX) has come to be one of the most important separation processes in hydrometallurgy. Phosphorus-based extractants have proved to be of particular importance, especially for the separation of cobalt from nickel. However it was not until the dialkyl phosphinic acid reagent, CYANEX 272, and its dithio analogue CYANEX 301, became available that liquors containing very low Co:Ni ratios of at least 1:40 to even >1:100 could be treated. This has opened the way to the direct application of SX for the separation of Co from Ni in liquors derived from the leaching of nickel mattes from the smelting of nickel sulphide ores and from the pressure acid leaching of nickel laterite ores. This paper describes the development of the range of Cytec extractants and, in particular, discusses the development of their application for the separation of cobalt from nickel. Examples of actual industrial operating plants will also be given and individual flowsheets discussed.

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1. Introduction

Solvent, or liquid–liquid, extraction has come to be one of the most important separation processes in hydrometallurgy. It is now used somewhere around the world in the hydrometallurgical processing of Cu, Ni, Co, Zn, U, Mo, W, V, Zr, Hf, Nb, Ta, rare earths, Ga, Ge, the platinum group metals (PGMs), B, reprocessing of nuclear fuels, purification of wet process phosphoric acid, nitric acid recovery, etc. Solvent extraction (SX) in hydrometallurgy began in 1942 in the Manhattan project where ether was used as the extracting solvent for the recovery and purification of uranium from nitric acid solution. Ether was however soon replaced with tributyl phosphate (TBP) as the solvent for the extraction of uranyl nitrate. The SX process was then applied to the recovery of uranium from sulphuric acid liquors produced in the leaching of uranium ores in the 1950s using extractants such as alkyl amines and di(2-ethylhexyl) phosphoric acid (DEHPA). Thus the utility

of extractants based on phosphorus-containing compounds was established early on in SX history.

The process of SX was by this time also being applied to the separation and recovery of more exotic metals such as Zr/Hf and Nb/Ta. However it was not until the development of the hydroxyoxime extractants by what was then General Mills Inc. in the 1960s and their application in the recovery of copper from the sulphuric acid solutions produced in copper oxide ore heap leaching that the major breakthrough came in the application of the SX process in large scale hydrometallurgical processing of base and transition metals.

2. Reagent classification

Nowadays a very large number of extractants are available for use in hydrometallurgy with more than 40 reagents on offer, of which at least a dozen are in everyday use. A listing of commercial and development

reagents is given in Table 1, together with their manufacturers and uses.

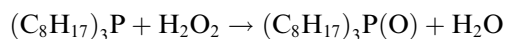
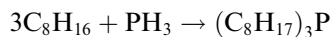
Note that the Daihachi reagents DP-8R, DP10-R and TR-63 are DEHPA, bis-isodecyl phosphoric acid and bis-isostearyl phosphoric acid, respectively. CYANEX 272 is bis(2,4,4 trimethylpentyl) phosphinic acid and CYANEX 302 and 301 are respectively the mono and dithio analogues of CYANEX 272. PIA-8 is di(2-ethyl-hexyl) phosphinic acid. SFI-6 is dihexyl sulphide.

In recent years there has been some significant changes in suppliers and availability of supply. Thus Hoechst, now Clariant, no longer supply their Hostarex range of reagents so they are not included in Table 1. Bayer nowadays only offers Baysolvex D2EHPA pure and Baysolvex TBP as shown in the table. Also the range of Acorga hydroxyoxime reagents which used to be supplied by Avecia are now supplied by Cytec. These reagents, as they are not based on phosphorus, will not be discussed in this paper. Tianjin Beichen is the largest producer in China of P507, a phosphonic acid similar to PC88A or Ionquest 801.

3. The CYANEX range of extractants

The starting point for the CYANEX range of extractants is phosphine, PH_3 . Cytec Canada Inc. has been producing phosphine since 1970 by the conversion of phosphorus via the acid process.

The ability to produce phosphine commercially opened up the way for the production of a whole range of derivatives either by the acid catalysed addition of phosphine to an aldehyde or by free radical addition to an olefin as has been discussed by Rickelton [1]. Thus phosphine oxides can be produced by the following reactions:



Formation of mono and dialkyl phosphine oxides, i.e. $(\text{C}_n\text{H}_{2n+1})_2\text{POH}$, is favoured by using sterically hindered olefins such as 2,4,4-trimethyl-1-pentene and/or operating the reaction at higher pressure (4 MPa).

The thio-analogue can be made easily by reaction of the trialkyl phosphine with elemental sulphur instead of hydrogen peroxide.

The phosphinic acids are made by using mono-dialkyl phosphine derivative mixtures and treating this with hydrogen peroxide. From the resulting product the mono acid is removed by caustic scrubbing and the major impurity in the dialkyl phosphinic acid is the corresponding trialkyl phosphine oxide.

The thio analogues of the phosphinic acids can be made by treating the dialkyl phosphine derivatives with elemental sulphur and NaOH to form the sodium salts

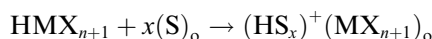
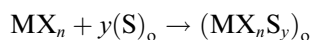
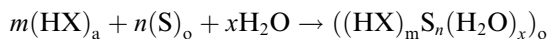
which can then be converted to the acids by treatment with mineral acid.

The range of CYANEX SX reagents are given in Table 2 together with their uses, actual and potential.

The large commercial use of phosphine derivatives in SX is concerned with uranium extraction and recovery, the separation of cobalt from nickel and the recovery of acetic acid from waste liquors. The uses and potential uses of the CYANEX range of reagents is discussed for each extractant.

3.1. The trialkyl phosphine oxides and sulphide

The trialkyl phosphine oxides and sulphide are solvating extractants. Trialkyl phosphine oxides can extract both acids and metal complexes while trialkyl phosphine sulphides can extract metal complexes. Thus their extraction chemistry is as shown, first for acids and secondly for metal complexes.



where M is an n -valent cation, X is a monovalent anion, S is the trialkyl phosphine oxide or sulphide and the subscripts 'o' and 'a' denote the organic and aqueous phases, respectively.

Because of the increasingly polar nature of the phosphoryl group the solubility of neutral organophosphorus compounds in water decreases in the following order:

Phosphine
oxides > Phosphinates > Phosphonates > Phosphates

The order of basicity is the same as above. Thus the trialkyl phosphine oxides are the most basic of this class of solvating extractants.

To date the most important applications of CYANEX 921, otherwise known as trioctyl phosphine oxide or TOPO, and CYANEX 923 have been in the recovery of acetic acid from effluents and in the recovery of uranium from wet process phosphoric acid and for the treatment of rare earths arising in phosphoric acid liquors produced in the Odda process for the treatment of apatite rock. While the recovery of acetic acid is somewhat outwith the scope of this paper, this application can be exemplified by the plant at Lenzing in Austria where 30 v/o of CYANEX 921 in undecane is used to recover not only acetic acid but also furfural from the aqueous effluents from the plant. Distillation of the organic phase yields an azeotrope of water, acetic acid and furfural which is further distilled to yield pure glacial acetic acid and furfural which are sold. Thus the cost of effluent treatment has been converted into a business opportunity by the use of this Cytec reagent. The

Table 1
Solvent extraction reagents

Class of extractant	Type	Examples	Manufacturers	Commercial uses
Acid extractants	Carboxylic acids	Naphthenic acids, Versatic acids	Shell Chemical Co.	Copper/nickel separation, nickel extraction, yttrium recovery
	Alkyl phosphoric acids	Dialkyl phosphoric acids and sulphur analogues	Daihachi Chemical Industry Co Ltd (DP-8R, DP-10R, TR-83, MSP-8); Bayer AG (BaySolvex D2EHPA pure); Albright & Wilson Americas (DEHPA).	Uranium extraction, rare earth extraction, cobalt/nickel separation, zinc extraction, etc.
	Alkylphosphonic acids	2-ethylhexyl phosphonic acid 2-ethylhexyl ester and sulphur analogues	Daihachi Chemical Industry Co Ltd (PC-88A); Albright & Wilson Americas (Ionquest 801), Tianjin Beichen, China (P507).	Cobalt/nickel separation, rare earth separation
	Alkyl phosphinic acids	Dialkyl phosphinic acids and sulphur analogues	Cytec Inc. (CYANEX 272, 302 and 301); Daihachi Chemical Industry Co Ltd (PIA-8)	Cobalt/nickel separation, zinc and iron extraction, rare earth separation
	Aryl sulphonic acids	Dinonyl naphthalene sulphonic acid	King Industries Inc. (Synex 1051)	Magnesium extraction
Acid chelating extractants	Hydroxyoximes	Alpha alkaryl hydroxyoximes, beta alkaryl hydroxyoximes	Cognis Inc. (LIX reagents); Cytec Inc. (Acorga reagents)	Copper extraction, nickel extraction
	Beta diketones	LIX 54	Cognis Inc.	Copper extraction from ammoniacal solution
	Hydroxamic acids	LIX 1104	Cognis Inc.	Proposed for nuclear fuel reprocessing, iron extraction and As, Sb and Bi extraction from copper tankhouse electrolytes
Basic extractants	Primary amines	Primene JMT, Primene 81R	Rohm & Haas.	No known commercial use
	Secondary amines	LA-1, LA-2.	Rohm & Haas.	Uranium extraction, proposed for vanadium and tungsten extraction
	Tertiary amines	Various Alamines, in particular Alamine 336.	Cognis Inc.	Uranium extraction, cobalt extraction from chloride media, tungsten extraction, vanadium extraction, etc.
	Quaternary amines	Aliquat 336,	Cognis Inc.	Vanadium extraction, other possible uses for chromium, tungsten, uranium, etc.
	Mono N-substituted amide Trialkyl guanidine	LIX 79	Cognis Inc.	Iridium separation from rhodium Gold extraction from cyanide solution
Solvating extractants and chelating non-ionic extractants	Phosphoric, phosphonic and phosphinic acid esters and thio analogues	TBP, DBBP, TOPO, CYANEX 921, CYANEX 923, CYANEX 471X.	Union Carbide, Albright & Wilson, Daihachi Chemical Industry Co Ltd, Cytec Inc.	Refining of U ₃ O ₈ , nuclear fuel reprocessing, Fe extraction, Zr/Hf separation, Nb/Ta separation, rare earth separation, gold extraction
	Various alcohols, ketones, esters, ethers, etc.	MIBK etc	Various.	Nb/Ta separation, Zr/Hf separation
	Alkyl and aryl sulphoxides	?	?	?
	Alkyl and aryl sulphides	di-n-octyl and di-n-hexyl sulphides	Daihachi Chemical Industry Co Ltd (SFI-6), others.	Palladium extraction in PGM refining

Table 2
CYANEX solvent extraction reagents

CYANEX extractant	Chemical formula	Specific gravity	Solubility in water (mg/l)	Uses (actual and potential)
272	(C ₈ H ₁₇) ₂ P(O)OH	0.92	16	Separation of Co from Ni, rare earth separation, zinc extraction
301	(C ₈ H ₁₇) ₂ P(S)SH	0.95	7	Selectively extracts many heavy metals from alkali and alkaline earth metals and manganese
302	(C ₈ H ₁₇) ₂ P(S)OH	0.93	3	Similar to CYANEX 272 in performance except that extraction takes place at lower pH and Co is separated from Mn
921	(C ₈ H ₁₇) ₃ PO	0.88	<5	Recovery of uranium from wet-process phosphoric acid, recovery of acetic acid from aqueous effluents
923	R ₃ PO	0.88	<10	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
471X	(C ₄ H ₉) ₃ PS	0.91	3	Selectively recovers silver, separates Pd from Pt, extracts mercury and gold

advantages of CYANEX 921 in this application over CYANEX 923 lie in low solubility losses, high stability during distillation at elevated temperatures and high extraction coefficients for acetic acid in comparison to other solvating reagents. As a consequence, plant operating and capital costs are minimised. On the other hand, if CYANEX 923 was used in place of CYANEX 921 advantage would lie in the ability of the former to use a concentrated and low freezing point solvent resulting in higher acetic acid recoveries and thus leading to lower staging requirements.

The application of TOPO in the recovery of low concentrations of uranium (100–200 mg/l) which occurs naturally in wet process phosphoric acid liquors stemmed from R&D carried out at Oak Ridge National Laboratory, Tennessee, in the mid to late 1960s [2]. The process as developed relied on the synergistic mixture of DEHPA and TOPO. The uranium feed liquor was first oxidised with H₂O₂ to ensure that the uranium was in the six valent state. The uranium was then extracted with a solvent phase composed of 0.5 M DEHPA and 0.125 M TOPO in an aliphatic hydrocarbon diluent. Uranium was then reductively stripped with acid containing ferrous iron as the reductant. The stripped uranium was re-oxidised and re-extracted with 0.3 M DEHPA and 0.075 M TOPO. After washing with acid and water, the uranium was stripped with ammonium carbonate to give ammonium uranyl tricarbonate which was then calcined to yellow cake, U₃O₈.

The major plants using this technology were located in Florida although there was a plant operated by Prayon in Belgium. These plants are now all closed.

CYANEX 923 is also useful for the extraction of rare earths from nitrate solutions. A systematic study of this process has been carried out by Chu et al. [3]. The possibility of separation of the light rare earths and yttrium from heavy rare earths was demonstrated.

The commercial application of CYANEX 923 for the bulk extraction of rare earths from phosphoric acid liquors arising in Norsk Hydro's Odda process has been described by Al-Shawi et al. [4]. In this process apatite

rock is first digested with nitric acid and insolubles removed. Cooling the leach liquor crystallises out calcium nitrate tetrahydrate. Neutralisation with ammonia precipitates the rare earths contained in the leach liquor as their respective phosphates. Re-dissolution of the phosphate precipitate in nitric acid provides the feed for the SX circuit after pH adjust and removal of insolubles. CYANEX 923, 50 v/o in Exxol D80, is used in the first SX step to bulk extract the rare earths and separate them from calcium and phosphate ions. The raffinate is passed to the fertiliser process. The loaded organic phase containing both nitric acid and rare earths is washed with water to remove the nitric acid and the wash liquor used to wash the precipitate from the pH adjust step. The rare earths are now stripped with nitric acid and subjected to a second SX step using TBP as the extractant to separate the rare earths from the ammonium ion and other impurities. Washing with water and finally stripping with water produces the final rare earth product solution. The CYANEX 923 circuit had one extraction stage mixer-settler, 4 washing and 4 stripping stages. Although technically highly successful the plant is now closed for commercial reasons.

CYANEX 923 has also been studied as a replacement solvent for the methyl isobutyl ketone (MIBK) normally used in the separation of Nb/Ta by SX [5] at Umicore's plant in Belgium. While technically CYANEX 923 performed very well indeed compared to MIBK, the CYANEX 923 circuit required substantially greater flowrates of the organic and aqueous strip solutions which would thus have a detrimental effect on capital cost. A complete comparison through continuous countercurrent testwork was not done as the company decided to stop treatment of Nb/Ta scrap so the final judgement on the substitution of MIBK with CYANEX 923 remains open.

The removal of As, Sb and Bi with several extractants including CYANEX 923 has been studied by Cox et al. [6]. Work was carried out using LIX 1104, CYANEX 923 and SBX 50 (an Avecia reagent now no longer available), either singly or in admixture, particularly

CYANEX 923/SBX 50 mixtures, to determine comparative performances of these reagents both in extraction and stripping of As, Sb and Bi. H₂SO₄ co-extraction data were also reported. From the results of this study it was concluded that CYANEX 923 was easily the best reagent for the removal of all three impurities. However more work was necessary to develop a system which could be considered for commercial operation.

CYANEX 923 has also been proposed for mineral acid recovery. Although not applied commercially as yet, the potential of this reagent for this purpose has been discussed by Rickelton [7] who describes the use of CYANEX 923 to selectively extract sulphuric acid from an acidic copper refinery electrolyte bleed stream to the point where the raffinate from this process is of a composition, 15 g/l H₂SO₄, suitable for metal recovery (e.g. nickel) using commercially available extractants.

One potential disadvantage of the process is the dilution of sulphuric acid which occurs whence the acid is extracted from a feed containing 175 g/l H₂SO₄ to provide a strip solution containing 120–130 g/l acid. This may or may not be a drawback depending on the route chosen to recycle the acid.

Further data for sulphuric acid and hydrochloric acid are contained in a Cytec brochure [8].

Work carried out by Tecnicas Reunidas on the recovery of nitric acid and HF from spent stainless steel pickling baths has been presented at a European Commission TRAWMAR meeting in Rhodes in 1998. In this work [9] several methods of recovery of these acids were examined and SX with CYANEX 923 was found to be superior to other methods. This report however does not contain stripping results [10] which showed that, while nitric acid stripped with water to the concentration in the feed, HF stripping was very poor, which would make such a process for recovery of the two acids together impracticable. However recovery of nitric acid on its own is clearly a practical proposition as the acid can be recovered at approximately the same concentration as in the feed.

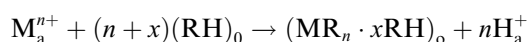
The thio analogue of tributyl phosphine oxide is CYANEX 471X. This extractant is in commercial use for silver recovery although no details of this application are available. It is, however, known that silver can be extracted from sulphate or nitrate solutions by sulphur-containing extractants. Thus information developed by Cytec on the selective extraction of silver from nitrate solution with CYANEX 471X is available in the literature [11]. Abe and Flett [12] studied the extraction of silver from chloride solutions with CYANEX 471X and found that it could be selectively extracted from cupric copper but not from cuprous copper. Thus this extractant could be very useful in the removal of silver from leach liquors in chloride hydrometallurgy provided that copper is in the cupric state. The deportment of zinc in chloride solution with this reagent is unknown but re-

moval of zinc before recovery of copper would solve any possible problems of zinc co-extraction.

The extraction of palladium with CYANEX 471X has much improved kinetics compared with the dialkyl sulphides used commercially thus offering the opportunity for countercurrent separation and recovery of palladium from platinum compared with the batch process required for the dialkyl sulphides. Unfortunately low solubility of the Pd-CYANEX 471X complex has so far hindered the commercial use of this extractant for this duty.

3.2. The dialkyl phosphinic acid CYANEX 272 and its thio analogues

Acids extract metal ions by a cation exchange mechanism viz.:



where Mⁿ⁺ is an *n*-valent metal cation, RH is the organic acid and the subscripts 'a' and 'o' represent the organic and aqueous phases, respectively. Cytec's dialkyl phosphinic acid, CYANEX 272 and its thio analogues CYANEX 301 and 302 therefore extract metal ions by the extraction mechanism given above.

The best known of all Cytec's CYANEX range of reagents is CYANEX 272. This reagent, bis(2,4,4-trimethylpentyl)phosphinic acid, developed specifically for the separation of cobalt from nickel by SX from weakly acidic sulphate liquors, became available in the early 1980s and an excellent description of its utility in this application has been published [13].

The separation and recovery of cobalt from nickel in sulphate solutions has long been a problem for hydrometallurgists. For such a separation a cation exchanger is required as neither metal forms sulphato complexes and thus cannot be extracted by anion exchangers or solvating extractants. This may be compared with chloride solutions wherein cobalt forms anionic chloro complexes which are extractable by anion extractants. Nickel does not form such complexes and this forms the basis of the SX separations operated commercially by Falconbridge Nikkelwerk in Norway, Eramet in France and Sumitomo in Japan [14].

Separation of cobalt from nickel in weakly acid sulphate solutions had traditionally been difficult. Commercially available extractants such as carboxylic acids, hydroxyoximes and β-diketones all show marginal selectivity for Ni(II) over Co(II). This problem remained unsolved until it was realised [15,16] that, with alkyl phosphorous acids, the separation factor for cobalt over nickel was a complex function of temperature, cobalt concentration, diluent, modifier and acid type. Indeed the separation factor increases in the series phosphoric < phosphonic < phosphinic acids. In summary, separation factors for alkyl phosphoric acids are in the tens,

Table 3

A comparison of separation factors for acid alkyl phosphorous extractants

Extractant	Co/Ni separation factor
DEHPA	14
PC88A	280
CYANEX 272	7000

Conditions: 0.1 M extractant in Shell MSB 210, metal ion concentration = 2×10^{-2} M, temperature: 25 °C; pH 4 and a phase volume ratio (A/O) = 1.

for alkyl phosphonics the hundreds while for alkyl phosphinics they are in the thousands as shown in Table 3.

This remarkable variation in separation factor is due to a change in the nature of the cobalt complex in the organic phase, whereby with increasing temperature and cobalt concentration, the pink hydrated/solvated octahedral complex changes into the blue anhydrous/unsolvated tetrahedral polymeric species. No such behaviour is shown by nickel which remains in the hydrated/solvated octahedral form throughout. Thus the distribution coefficient for cobalt increases as the degree of conversion to the tetrahedral form increases thus increasing the separation factor of cobalt from nickel. Specific separation factor values will also depend on the degree of steric hindrance caused by the degree and location of branching of the alkyl chains in the extractant molecule. The extraction pH is determined by the acid strength. This is demonstrated by comparing CYANEX 272 with 2,4,4-trimethylpentylphenyl phosphinic acid which shows a clear reduction in the pH of 50% extraction of all metal ions compared to CYANEX 272 [17]. It also shows a change in the selectivity series with regard to calcium which now extracts with Mn and Cu which thus makes this reagent less attractive for cobalt extraction. On the other hand, iron can be separated very cleanly from zinc with this reagent which may make it attractive for iron extraction from acidic sulphate solutions.

Apart from the high Co/Ni selectivity, another key factor which distinguishes CYANEX 272 from its competitors is its ability to extract Co selectively from Ca thus eliminating the possibility of the formation of gypsum cruds on stripping cobalt from the organic phase with sulphuric acid. A comparison of the selectivity series for the extractants listed in Table 3 show this viz.:

DEHPA	$\text{Fe}^{3+} > \text{Zn} > \text{Ca} > \text{Cu} > \text{Mg} > \text{Co} > \text{Ni}$
PC88A	$\text{Fe}^{3+} > \text{Zn} > \text{Cu} > \text{Ca} > \text{Co} > \text{Mg} > \text{Ni}$
CYANEX 272	$\text{Fe}^{3+} > \text{Zn} > \text{Cu} > \text{Co} > \text{Mg} > \text{Ca} > \text{Ni}$

Unfortunately none of these extractants can extract cobalt selectively from ferric iron. However, unlike DEHPA which requires 6 N HCl to strip any coextracted iron, CYANEX 272 can be readily stripped with

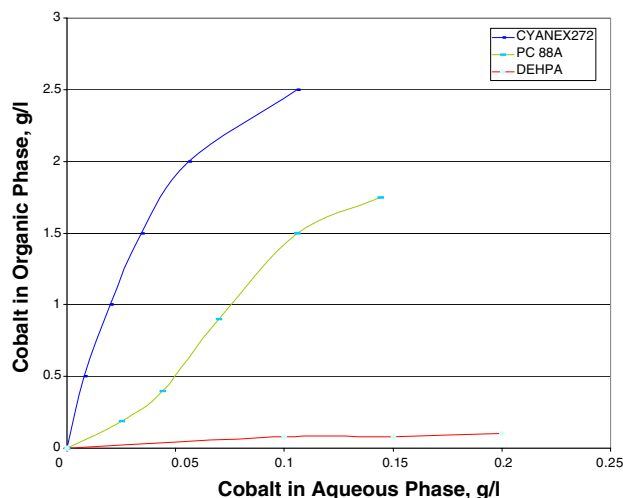


Fig. 1. Extraction of cobalt from a nickel matte leach liquor using different alkyl phosphorous acids. Organic phase: 10 v/o alkyl phosphorous acid in Escald 110, plus 5 v/o TBP, 85% conversion to Na form. Feed: Co, 0.22 g/l; Ni, 89.6 g/l.

relatively dilute (150 g/l) H_2SO_4 . Cobalt can be selectively stripped from CYANEX 272 from any coextracted iron or zinc at a pH of 2.5. With regard to ferric iron it is interesting to note that Rickelton [18] has reported that addition of CYANEX 923 to DEHPA will allow stripping of iron with 100 g/l H_2SO_4 . No doubt the small amount of trialkyl phosphine oxides present in CYANEX 272 also assist iron stripping.

Extraction and stripping kinetics for CYANEX 272 are similar to those of the other organophosphorous acids. Thus, in general, a 3 minute residence time for both extraction and stripping is considered adequate.

Operating plants treat a wide variety of solutions derived from such sources as high grade nickel mattes and nickel laterite ores. This results in a large variation in the Co:Ni ratio in the feed liquors ranging from 20 to 30 g/l each Co and Ni to 0.5–2.0 g/l Co and 90–110 g/l Ni. Only CYANEX 272 can treat Ni:Co ratios as high as >100:1 as shown in Fig. 1.

Thus the development of CYANEX 272 opened the way for direct SX of cobalt from liquors containing very disparate ratios of cobalt and nickel.

The stability of the organic phase in cobalt extraction is an issue. This was first experienced at the Rustenburg Refiners cobalt SX plant in South Africa which uses DEHPA as the extractant where over time the separation factor for cobalt over nickel decreased and the phase separation became increasingly poor. Examination of the problem showed that carboxylic acids were present in the organic phase thus causing a significant reduction in separation factor and increasingly poor phase break. The ability of cobalt to act as an oxidising agent is well known so it was clear that the problem was due to cobalt catalysed oxidative degradation of the diluent. A study of this problem [19] using Solvesso 150 as

the model diluent showed that in the cobalt/DEHPA system the rate of oxidation increased with increasing diluent aromaticity, temperature and cobalt solvent loading. The octahedral form of the cobalt complex was considered to be the active species in this catalysis converting the diluent to the corresponding carboxylic acid and the presence of a carboxylic acid certainly would reverse the cobalt/nickel selectivity. Phenolic antioxidants such as BHT were shown to be effective in conferring diluent stability, but it was concluded to be essential to monitor and maintain antioxidant concentration for long term satisfactory plant performance. Other extractants were studied, namely PC88A and CYANEX 272. Diluent oxidation with PC88A was found to be faster than with DEHPA but significantly slower with CYANEX 272. Thus solvents containing CYANEX 272 are significantly more resistant to oxidation than solvents containing DEHPA or PC88A. Manganese was found to oxidise Solvesso 150 just as fast as cobalt in the DEHPA system. A further study of cobalt catalysed diluent oxidation in the CYANEX 272 system has been carried out by Rickelton et al. [20]. In this work tetradecane was used as the model diluent. The mechanism of oxidative degradation was suggested to be from the alkane to the hydroperoxide to the alcohol to the aldehyde and finally to the carboxylic acid. Adoption of BHT as the antioxidant for addition in the CYANEX 272 commercial plants appears standard practice now at levels of 0.5–1.0 g/l [21].

Following market introduction in 1982, there are now some 13 plants located in Western Europe, South America, Canada, Africa, China and Australia using CYANEX 272 for cobalt separation and recovery from nickel. Currently CYANEX 272 is used to produce approximately 50% of the cobalt in the Western world. Unfortunately operating companies have tended to regard the use of CYANEX 272 as confidential for competitive reasons and it is only recently that operating details of some of the newer plants have been published. Outokumpu Oy has published details of its CYANEX 272 cobalt SX plant at Harjavalta [22], now owned by OMG. The plant treats a feed from leaching of the mattes produced in the DON process [23] containing 130 g/l nickel, 0.8–1.0 g/l cobalt with very minor amounts of zinc, copper, lead, manganese, magnesium, calcium and iron. Cobalt is extracted in four countercurrent stages, the loaded organic is scrubbed with dilute sulphuric acid in five stages and cobalt is stripped with sulphuric acid in four stages to produce a raffinate containing 130 g/l Ni, 0.01 g/l Co and a cobalt strip liquor containing 110 g/l Co, 0.02 g/l Ni, together with coextracted copper, lead, manganese and some calcium. Coextracted zinc and iron are not significantly stripped with the cobalt and these metal ions are removed in a single stage with 200 g/l H₂SO₄. This selective stripping of cobalt can only be used when the zinc content is low,

say <1 g/l. The mixer-settlers used are the Outokumpu developed vertical smooth flow (VSF) mixer-settlers. The continuous countercurrent operation is controlled using the Outokumpu Courier X-ray system for on-line analysis of cobalt and nickel in both aqueous and organic phases. On-line pH measurements can also be used.

CYANEX 272 has also been specified as the reagent of choice for INCO's Voiseys Bay project. The process [24] for the treatment of the Voiseys Bay nickel sulphide concentrate consists of an atmospheric chlorine leach of the nickel–cobalt concentrate followed by a pressure oxygen leach. After separation of the leach liquor from the leach residue, the impure nickel solution is purified to remove Cu, Co, Zn and Pb impurities and nickel metal cathode produced by electrowinning in a chloride electrolyte. The presence of chloride ions, while significantly increasing the rate of base metal dissolution also inhibits the oxidation of the sulphide sulphur beyond the elemental sulphur stage. Thus the bulk of the sulphide sulphur exits the process as elemental sulphur in the leach residue. The precipitation of iron with lime will serve to control excess sulphate through gypsum precipitation. The sulphuric acid-containing nickel anolyte stream is recycled to both the atmospheric acid chlorine leach step and the oxygen pressure leach step. The combined oxygen/chlorine gas stream produced at the anode in the nickel electrowinning step is also recycled to the atmospheric acid chlorine leaching step. The process flowsheet is shown in outline in Fig. 2.

CYANEX 272 has also been specified as the reagent of choice for two laterite PAL projects in Australia. Thus the Bulong project flowsheet, Fig. 3, uses SX directly on the leach liquor after purification. Thus any iron aluminium and chromium present in the leach liquor are removed hydrolytically in a two step precipitation to yield a liquor at pH 4.2–4.5.

Cobalt together with the manganese and zinc present in the liquor is then extracted with CYANEX 272. Interestingly enough the nickel in the raffinate is extracted and separated from magnesium with a carboxylic acid, Versatic 10 [25–27]. Results of continuous miniplant trials [27] showed that extraction with CYANEX 272 can achieve 97.5% cobalt recovery and >99% removal of Mn and Zn with very good separation of Co and Ni with Co:Ni ratios in the strip of >1000:1. Zinc stripping was shown to be inhibited by the presence of chloride ion present in the strip liquor made up from borehole water. The Bulong plant is currently closed.

While DEHPA was used for zinc removal from cobalt at Bulong, where zinc SX is followed by cobalt SX with CYANEX 272 it is better to use CYANEX 272 for selective removal of zinc from cobalt to avoid the possibility of cross contamination of reagents and that has been adopted at the Murrin Murrin plant in Western Australia. In the Murrin Murrin project flowsheet [25,28,29], Fig. 4, sulphide precipitation is used

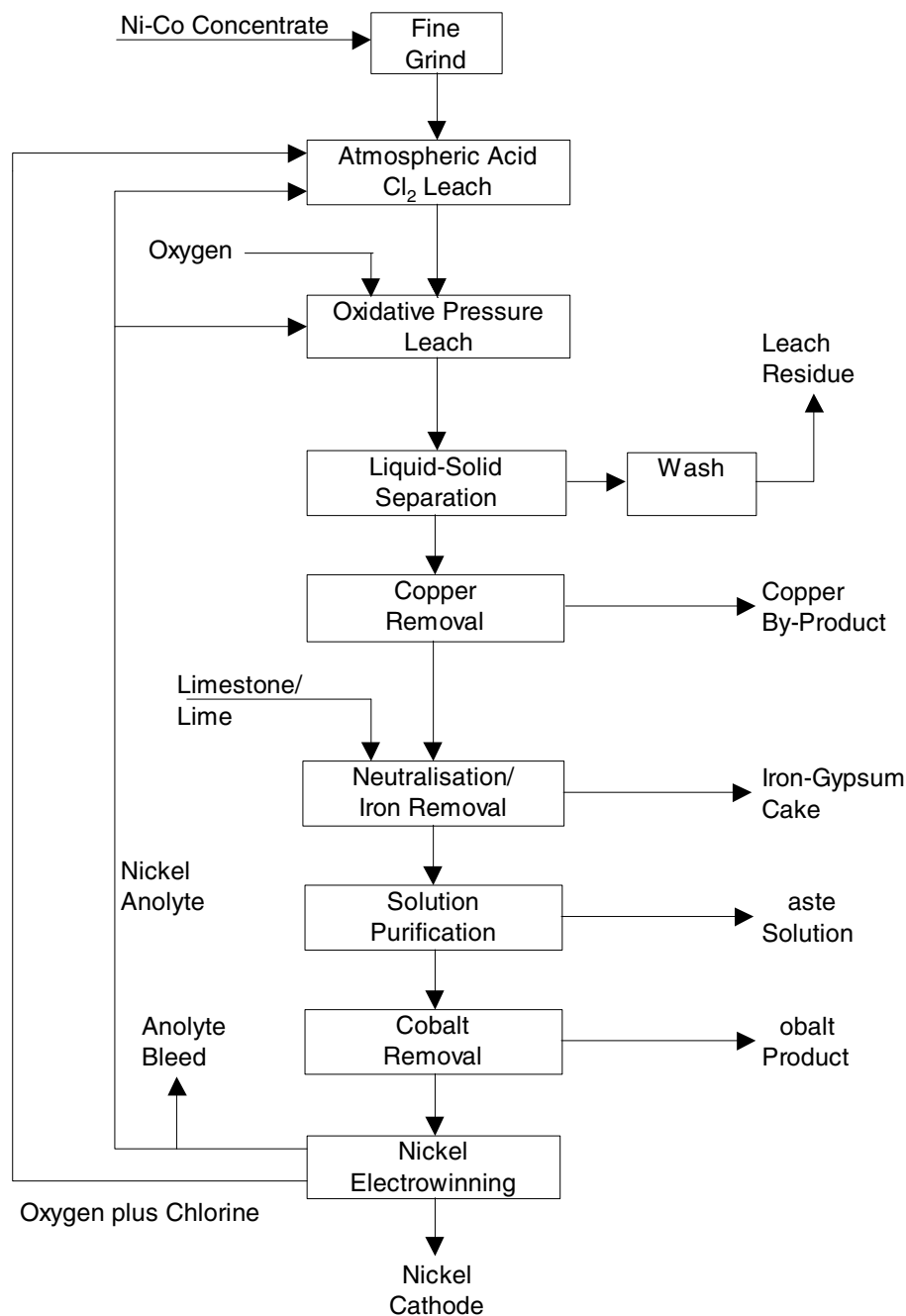


Fig. 2. Outline refinery flowsheet for INCO's Voiseys Bay project.

to recover nickel and cobalt from the leach liquor after neutralisation with calcite thus effectively separating the Co and Ni from Mn and Mg. Sulphide precipitation at 90 °C provides good rejection of manganese. The sulphides are pressure leached and cobalt separated from nickel by SX with CYANEX 272. Co and Ni are then recovered from the strip liquor and raffinate by pressure hydrogen reduction.

It is interesting to compare the operating philosophies for Bulong and Murrin Murrin. At Bulong, because nickel was recovered by electrowinning, the Co extraction circuit is basically an impurity removal step

in order to provide as pure a nickel stream as possible to the nickel SX circuit, then the CYANEX 272 plant is run to maximise the amount of cobalt recovered. At Murrin Murrin however, as a small amount of cobalt in the nickel feed to pressure hydrogen reduction will not affect the quality of nickel powder produced but a small amount of nickel in the cobalt strip will affect the quality of cobalt produced by pressure hydrogen reduction, then the CYANEX 272 circuit is run to minimise the amount of nickel reporting to the cobalt strip.

The use of CYANEX 272 for zinc removal has also been adopted by QNI at the Yabulu plant in Queens-

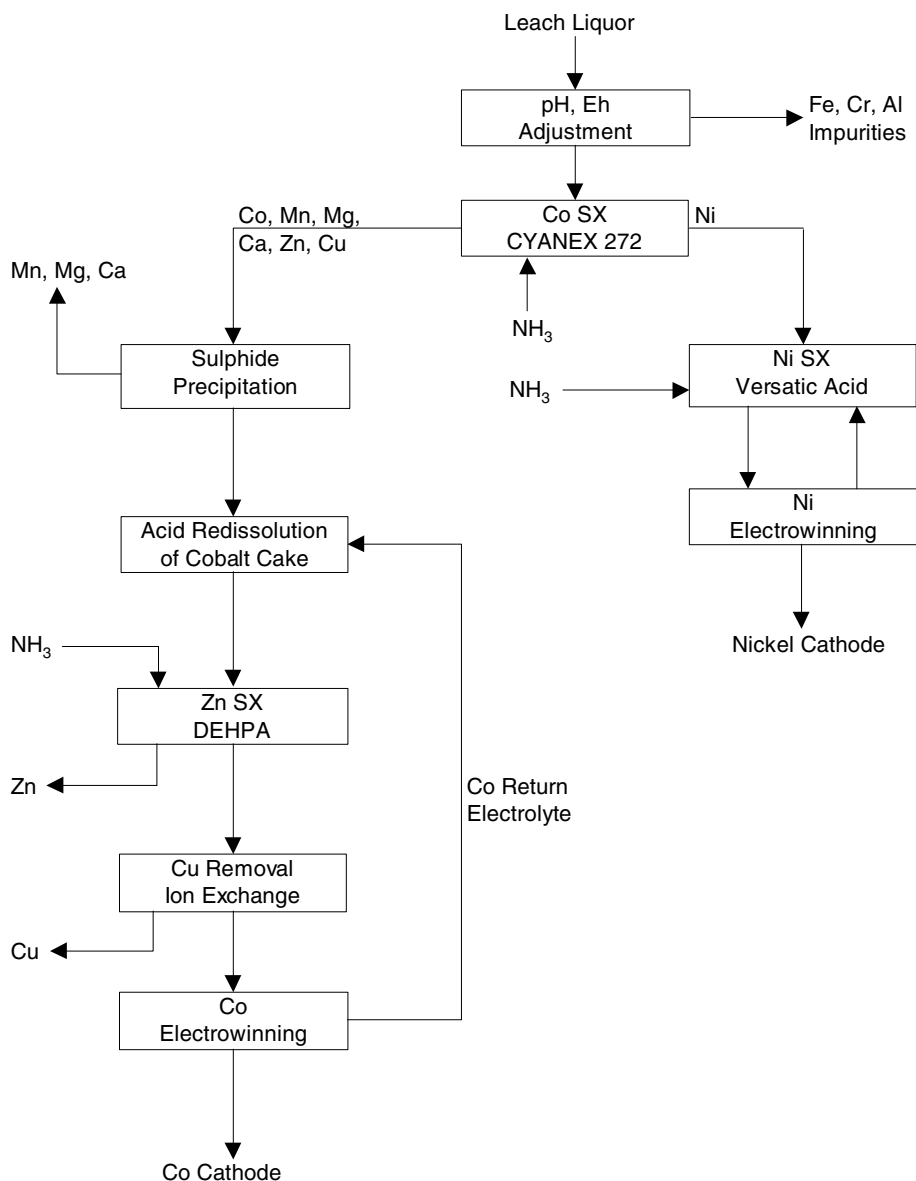


Fig. 3. Bulong nickel/cobalt purification flowsheet.

land, Australia [30]. Here, nickel laterite feed is treated by reduction roasting in the Caron process followed by an ammoniacal ammonium carbonate leach of the roaster calcine. Cobalt is oxidised to Co^{3+} and nickel is then selectively extracted with a hydroxyoxime extractant which does not extract Co^{3+} . The cobalt is precipitated as a sulphide which is then oxidatively pressure leached. The leach liquor which contains 50–60 g/l Co also contains some zinc, a little ferric iron and some residual nickel. The zinc and iron is removed by SX with CYANEX 272, cobalt and nickel bulk extracted with DEHPA and stripped with ammoniacal ammonium carbonate, cobalt oxidised and nickel removed with the same hydroxyoxime used in the main nickel extraction circuit. The nickel-free cobalt raffinate is then treated by resin ion exchange to re-

move Ca and Mg and cobalt is finally precipitated as the carbonate.

CYANEX 272 has also been selected for cobalt recovery in the absence of nickel in Morocco [31]. Here, Reminex treat arsenical cobalt concentrates from the Bou-Azzer mine by roasting to recover the arsenic, leaching of the roaster calcine with sulphuric acid, precipitation of $\text{FeAsO}_4 \cdot 3\text{H}_2\text{O}$ followed by SX of cobalt and recovery of cobalt by electrowinning. This then suggests that CYANEX 272 SX should be considered as a replacement for the processes based on cobalt hydroxide precipitation and re-dissolution as practised in Zambia and the DRC. Adoption of SX would improve cobalt overall percentage recovery and permit the use of stronger cobalt electrolytes, thus also improving current efficiency and cathode purity and morphology. Use of

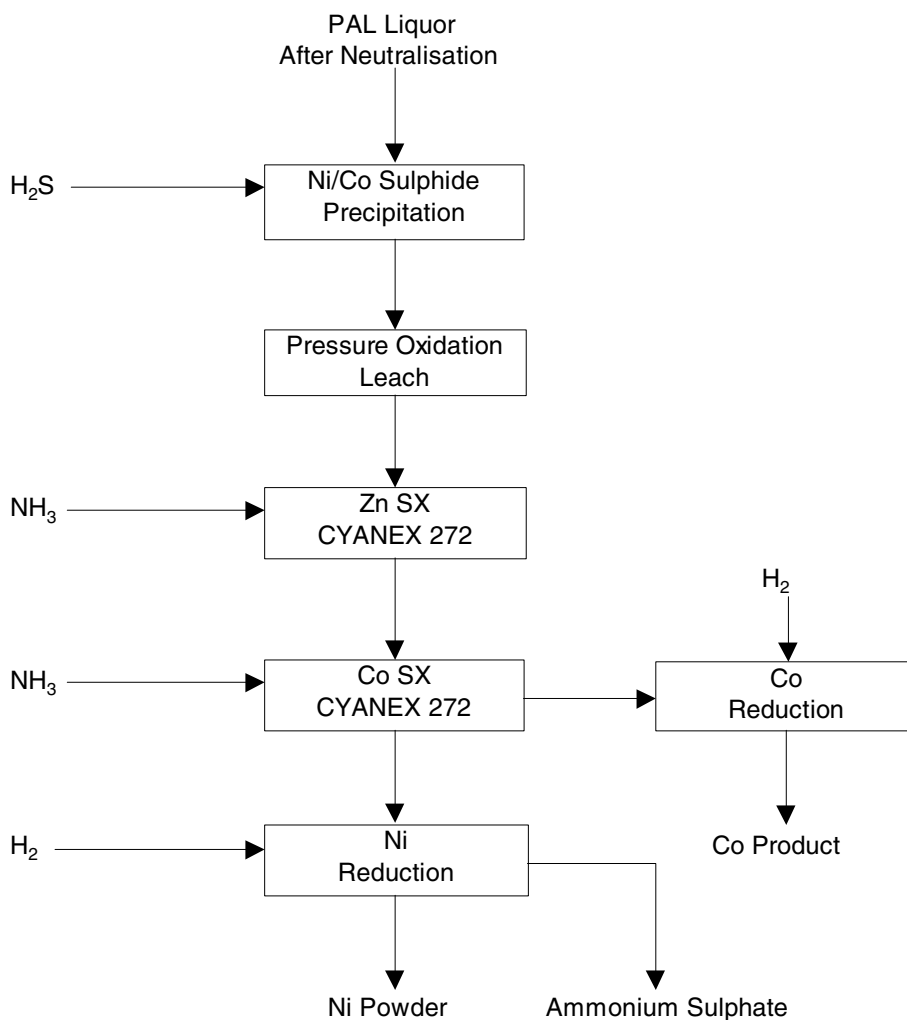


Fig. 4. Murrin Murrin purification flowsheet.

other reagents such as the phosphonic acids, while certainly permitting good cobalt extraction and recovery may result in gypsum precipitation in the strip circuit as the separation of cobalt from calcium is now no longer possible. Magnesium co-extraction could also become a problem.

Alkyl phosphorous acids are used widely for rare earth extraction and separation, particularly DEHPA and PC88A, Ionquest 807 and P507. CYANEX 272 has not been used commercially although in some cases this reagent exhibits higher selectivity than its phosphoric and phosphonic acid counterparts. CYANEX 272 unfortunately has significantly lower loading capacities and distribution coefficients for rare earths than the alkyl phosphoric or phosphonic acids. However it has been found [32] that synergistic mixtures of phosphonic acids and CYANEX 272 give much improved distribution factors, loadings and separation factors for the heavy rare earths and improved stripping performances compared to the acids on their own. Thus, where as much as 6 M HCl is required for the stripping of heavy rare

earths, 100% stripping is achieved with the CYANEX 272 alkyl phosphonic acids mixture with only 4 M HCl thus reducing neutralisation costs and minimising chloride contamination of the final product. However stripping with HNO_3 gave at best only 80% recovery. This has been shown to be due to re-extraction of rare earth nitrate complexes by the trialkyl phosphine oxide impurity present in CYANEX 272 [33]. On the other hand, the presence of the trialkyl phosphine oxides enhances HCl stripping. This mixed reagent is in commercial use in China for separation of heavy rare earths.

Cyanex 301, the dithio analogue of CYANEX 272, has been selected as the extractant for bulk extraction of nickel and cobalt in INCO's Goro project in New Caledonia [34]. Originally developed as a zinc extractant, it was found to be too strong an extractant for zinc requiring strong sulphuric acid to effectively strip the zinc. Although this extractant does not possess a large separation factor for Co over Ni, it does extract both Co and Ni at much lower pH values than CYANEX 272. Thus bulk extraction of both nickel and cobalt

and their separation from Mn, Ca and Mg could be carried out without the need for a high degree of neutralisation of the PAL leach liquor. However, as might be expected with thio acids, CYANEX 301 is not stable and decomposes in a two stage process wherein the first stage, which is reversible, involves the formation of the disulphide. The second stage, which is irreversible, involves the decomposition of the disulphide to elemental

sulphur and CYANEX 272. The reversible first degradation step can be reversed by treatment with zinc powder and sulphuric acid to generate nascent hydrogen [35]. The plant will treat both limonite and saprolite ore. The Goro process flowsheet is shown in Fig. 5. In this process CYANEX 301 is used for bulk SX of nickel plus cobalt after partial neutralisation with saprolite. The loaded organic phase is stripped with HCl to allow final

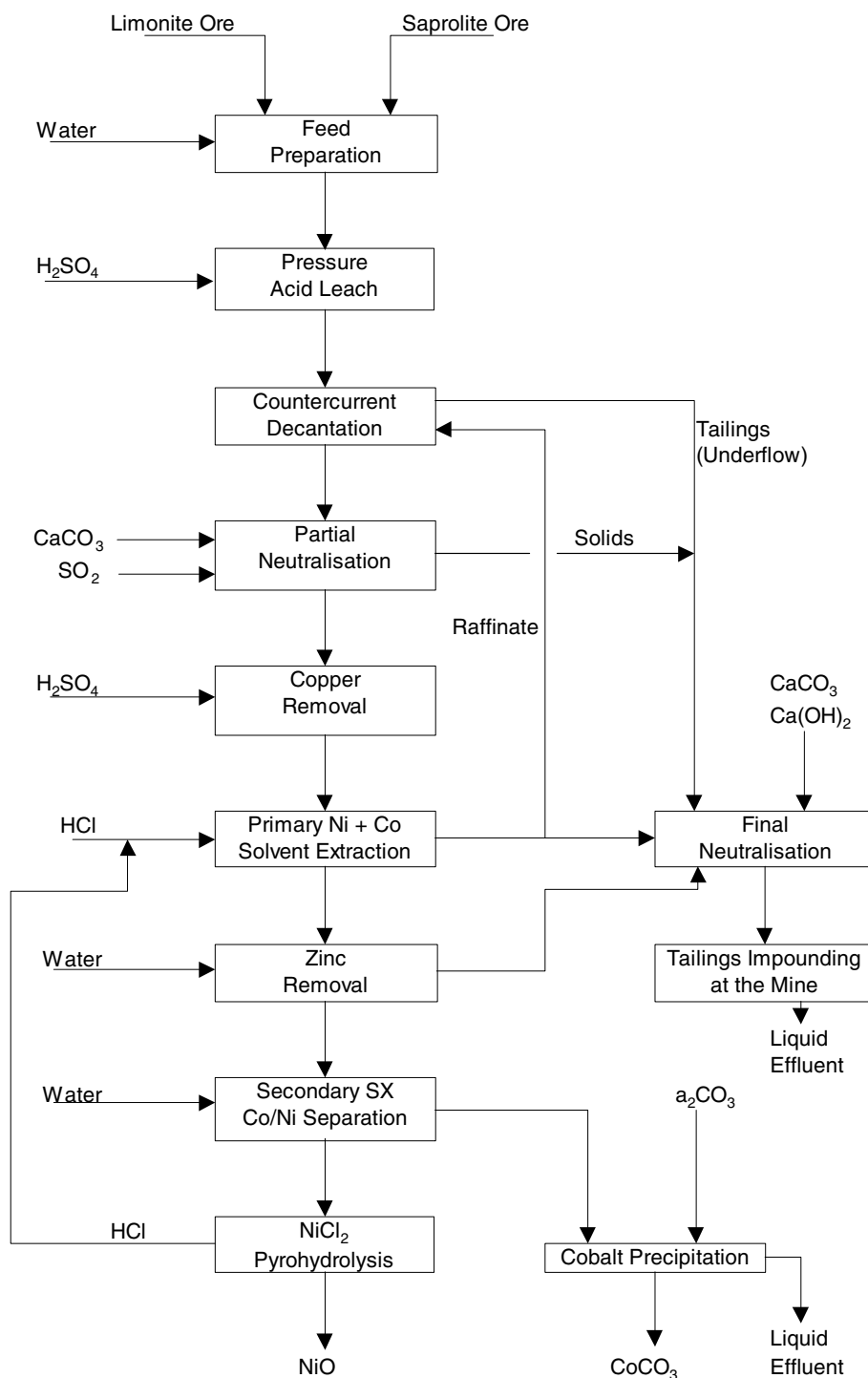


Fig. 5. Outline flowsheet of the Goro process.

Co/Ni separation to be carried out with an alkyl amine. As this is a dithiophosphinic acid, iron and copper must be eliminated before the SX step to avoid degradation of the CYANEX 301 by these metal ions. Iron is removed by the partial neutralisation step while copper is removed by using a chelating ion exchange resin. Although the resin is not specified in the quoted reference it is believed to be an iminodiacetic acid resin such as Lewatit TP 207 from Bayer or S930 from Purolite. An aminophosphonic acid resin such as Purolite's S950 could also be used. Zinc is also removed by resin ion exchange before Co/Ni separation using a strong base anion exchange resin. Interestingly enough it was found during the operation of the pilot plant that much less degradation of CYANEX 301 took place than was predicted.

CYANEX 302 has not so far found true commercialisation. However it was used, albeit briefly, for cobalt separation and recovery from lithium in the process originally developed by Pacific Rare Metals Industries in the Philippines for reprocessing lithium-ion battery scrap [36]. The process as originally operated had two SX circuits, the first, using an extractant combination of 10% CYANEX 272 and 1% of an unspecified hydroxyoxime reagent, removed impurities from the cobalt–lithium leach liquor. Then a 20% solution of CYANEX 302 in a Shellsol diluent separated cobalt from lithium. This plant is now owned by Umicore and no longer uses CYANEX 302 or the hydroxyoxime. This is not too surprising as CYANEX 302 is known to degrade like CYANEX 301 but in one irreversible step to elemental sulphur and CYANEX 272. Hydroxyoximes also degrade in the presence of acids and the presence of CYANEX 272 promotes such degradation.

4. Conclusions

The range of Cytec's CYANEX extractants and their applications in hydrometallurgy has been fairly fully described above. From this it is clear that currently the major applications for the trialkyl phosphine oxides is in environmental applications for the recovery of organic acids rather in hydrometallurgy and the commercial application of CYANEX 921 at Lenzing in Austria demonstrates this conclusion nicely. However in the past these oxides have been used quite extensively for uranium recovery from wet process phosphoric acid and it is only the oversupply of uranium that has caused this application to cease. The use of CYANEX 923 for rare earth extraction from nitrate solutions has been well demonstrated commercially. Again supply issues has caused this activity to cease. However it is possible that the application of this extractant for this purpose may well reappear in the future. The ability of CYANEX 923 to extract mineral acids is a most interesting capabil-

ity and it is possible that such an application may well take place in future, thus providing added flexibility to hydrometallurgical flowsheets where strong acid treatment is required, thus avoiding expensive neutralisation although co-extraction of metals as anionic complexes may occur.

CYANEX 923 has also been considered as the extractant for removal of sulphuric acid from copper electrowinning tankhouse electrolyte bleeds as opposed to electrorefinery spent electrolytes and its performance compared with tris(2-ethylhexyl)amine [37,38]. It is believed that implementation of such a process was being contemplated at Mount Gordon in Australia but it is not known if such a project was implemented nor what the choice of extractant might have been.

Without a doubt CYANEX 272 is the reagent of choice for the separation and recovery of cobalt from nickel. The reasons for this are very clear namely that it is the only reagent that can effectively separate Co from Ni at low Co:Ni ratios of >1:40, and it is the only reagent amongst the organophosphorous acids that will extract Co selectively from both calcium and magnesium. Because it is the weakest acid amongst the organophosphorous acids, it is the easiest to strip and the acidity of the strip liquor is ideal for cobalt electrowinning. Also ferric iron does not poison this reagent as it does for DEHPA and indeed good iron/zinc separation from cobalt is possible with CYANEX 272 and this has been exploited at the QNI plant at Yabulu in Australia. The ability to achieve good zinc/cobalt separation with CYANEX 272 is also exploited commercially at Murrin Murrin in Australia thus avoiding the need to use a different extractant and the risk of cross contamination. Indeed it would be advantageous for the two cobalt plants in Zambia [39] to adopt CYANEX 272 in place of DEHPA which would avoid the problem of gypsum precipitation in the sulphuric acid strip and the occasional ferric iron poisoning incident. Thus CYANEX 272 has superior properties to the organophosphoric and organophosphonic acids.

There are currently many new nickel sulphide and laterite projects under study. Several of them will consider SX separation and recovery of cobalt and nickel using CYANEX 272. Thus projects such as Ambatovy in Madagascar (a joint venture between Dynatec of Canada and Phelps Dodge of USA), Weda Bay in Halamahera, Indonesia and Syerston in New South Wales, Australia all provide potential applications for CYANEX 272 and there are other, less well developed projects which also offer opportunities for application of CYANEX 272.

Currently the use of CYANEX 301 in INCO's Goro project is unique. It remains to be seen if other applications can be found for this most interesting extractant. Unfortunately, unless some way of stabilising CYANEX 302 can be found, the one step, irreversible decom-

position of this extractant is likely to militate against its commercial use in the immediate future.

With regard to new reagents, the willingness to prepare novel dialkyl phosphinic acids is clearly shown by reference 17. Further new, novel reagents will be eagerly anticipated.

In conclusion therefore it is clear that Cytec's CYANEX range of extractants have found very important applications in hydrometallurgy. This situation is not likely to change in future and indeed it is more than likely that the percentage of the Western World's cobalt that is treated by CYANEX 272 will continue to increase as it is clearly the reagent of choice for the separation and recovery of cobalt from nickel particularly when the ratio of nickel to cobalt is high which is always the case when the hydrometallurgical treatment of nickel sulphide and nickel laterite ores in sulphate media is contemplated.

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