

Cobalt-Nickel Separation in Hydrometallurgy: a Review*

DOUGLAS S. FLETT

St. Barbara Consultancy Services, 17 Foster Close, Stevenage, Herts, SG1 4SA (UK)

E-mail: doug.flett@lineone.net

Abstract

The separation of cobalt from nickel in aqueous solution has always been a problem for hydrometallurgists. Their adjacent positions in the transition metal series in the periodic table result in aqueous chemical behaviour that is too similar for development of easy separation routes. Traditionally cobalt and nickel were separated by processes based on selective oxidation and/or precipitation of cobalt from either sulphate or chloride solution and such processes are still in use today. However, the process of solvent extraction provides the high degree of separation and yields demanded by industry nowadays.

While alkylamines are the extractants of choice for separation of cobalt from nickel from chloride liquors, for weakly acidic sulphate liquors the alkyl phosphorous acids have found significant commercial application at various locations around the world. Because of the high nickel to cobalt ratio encountered in liquors produced in sulphate-based high nickel matte leach processes or those produced in the acid pressure leaching of nickel laterites, very high separation factors (>1000) are required. That is why the dialkyl phosphinic acid CYANEX 272 has become the reagent of choice for such duties.

This paper reviews the chemistry of cobalt-nickel separation from aqueous solutions and comments on the implications of this chemistry in hydrometallurgical applications. Description of selected applications is given and discussed.

INTRODUCTION

The separation of cobalt from nickel in aqueous solution has always been a problem in hydrometallurgy. Their adjacent positions in the transition metal series in the periodic table results in aqueous chemical behaviour that is too similar for development of easy separation routes. However differences in chemical behaviour do exist. For example, although both cobalt and nickel preferentially exist as divalent hexahydrated ions in dilute aqueous solution, the rate of water exchange on the cobalt ion is very much higher than for nickel. Thus complex ion formation often proceeds much more readily with divalent cobalt than with nickel. On the other hand, the trivalent cobalt ion is much less labile and forms in preference to nickel even though the redox potentials for the $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ couples are nearly identical. Cobalt also in the divalent state exhibits

a marked tendency to form a tetrahedral configuration under more concentrated electrolyte conditions rather than the hexagonal configuration of the six-coordinated species. These general differences help to provide the basis for the various separation processes currently used or proposed for cobalt-nickel separation in hydrometallurgy.

Traditionally cobalt and nickel were separated by processes based on selective oxidation and/or precipitation of cobalt from either sulphate or chloride solution and such processes are still in use today. Indeed, new, improved oxidants are available. However, it is certainly to the process of solvent extraction that one looks nowadays to provide the high degree of separation and yields demanded by today's industry and there can be no doubt of the impact that solvent extraction has had and indeed is increasingly having in commercial operations both existing and under development. Thus, alkylamines are the extractants of choice for separation of cobalt from nickel from chloride liquors such as arise in the Eramet process

*Materials from the 2nd International Conference «Metallurgy of Nonferrous and Rare Metals», Krasnoyarsk, September 9–12, 2003.

in France and in the Chlorine Leach Process as operated by Falconbridge in Norway [1].

For weakly acidic sulphate liquors the alkyl phosphorous acids have found significant commercial application at various locations around the world. The first plant to use this class of reagent was at the Rustenburg Base Metal Refinery of Anglo Platinum Ltd at Rustenburg in South Africa [2, 3] which uses DEHPA for separation and recovery of cobalt. Because of the high nickel to cobalt ratio encountered in liquors such as those produced in sulphate-based high nickel matte leach processes or in the liquors produced in the pressure acid leaching of nickel laterites, very high separation factors (>1000) are required. Only one commercial reagent offers such separation factors and that is why CYANEX 272 has become the reagent of choice for such duties [4].

Much less progress, on the other hand, has been made on the reverse problem of the recovery and removal of nickel from cobalt liquors although solvent extraction and ion exchange now can compete with traditional precipitative processes.

This paper reviews the chemistry of cobalt-nickel separation from aqueous solutions and comments on the implications of this chemistry in hydrometallurgical applications. Description of selected applications is given and discussed.

PRECIPITATIVE SEPARATION

Separation of cobalt and nickel by precipitative processes has been and still is carried out commercially by a number of processes. Thus sulphide precipitation has been used commercially, for example in the original flow-sheet at Queensland Nickel in Australia [5], in order to completely remove cobalt from the nickel process liquor. A slightly different version based on Sherritt Gordon technology was practised at the Marinduque Nickel refinery in the Philippines [5].

Sulphide precipitation can also be used to precipitate nickel from cobalt-rich liquors. This De Merre process [5] was used by Metallurgie Hoboken Overpelt (now Umicore) in Belgium. Reagents such as metallic iron or cobalt, plus

elemental sulphur or iron or cobalt sulphides, *etc.*, were used at pH values between 1–5 at temperatures above 80 °C.

Cobalt and nickel can also be separated by oxidative precipitation. Although the Eh-pH diagrams are very similar [5], nickel is much more difficult to oxidise and cobalt can be oxidised quite selectively in the presence of relatively large amounts of nickel. Strong oxidants are needed in practice, such as chlorine, ammonium persulphate, Caro's acid or ozone, as the redox potential for the cobalt oxidation reaction is +1.75.

Air under pressure can also be used: this formed the basis for the so-called cobaltic ammine process for cobalt-nickel separation, (see ref. [1, 23]).

The use of chlorine for cobalt removal from nickel solutions is practised by INCO [5] and Falconbridge in Canada [5] and by the Jinchuan Group Ltd in China. Careful control of pH is needed to optimise the process, but inevitably a compromise is necessary between cobalt yield and nickel contamination.

The use of peroxygen compounds for cobalt separation was first reported at the beginning of the century. Thus ammonium persulphate was used by AMAX at Port Nickel in Louisiana [5] to replace the well-known Outokumpu process using electrolytically generated nickelic hydroxide.

The use of electrolytically generated nickelic hydroxide for cobalt removal from an impure nickel electrolyte was developed in Finland by Outokumpu Oy [5]. The Ni(OH)₃ is produced by electrolytic oxidation of a black Ni(OH)₂ slurry in cells with iron rods as cathodes and nickel plates as anodes. The Ni(OH)₃ slurry is then mixed with the impure nickel electrolyte in two stages to precipitate Co(OH)₃. This precipitate contains more nickel than cobalt and can be redissolved using H₂SO₄ and SO₂ and further processed to produce pure cobalt. This process is still used at some locations round the world, for example at the Rustenburg Base Metal Refinery in South Africa.

The use of Caro's acid, H₂SO₅, has also been of interest for cobalt-nickel separation. Caro's acid is prepared by direct addition of strong sulphuric acid to hydrogen peroxide. Recent work on Caro's acid [6] has been con-

cerned with cobalt/nickel separation from liquors produced in hydrometallurgical studies on recycling NiCd batteries.

The use of ozone for cobalt oxidation and removal has also been advocated for cobalt-nickel separation and recent work in Japan has been reported [7], although no commercial applications are known. The rate of reaction can be slow, however the long induction period for cobalt precipitation can be significantly shortened by addition of precipitate seed. Cobalt/nickel ratios in the product are said to be as high as 1000 : 1 with careful operation [8]. The best separation is reported as being achieved between pH 2.5 and 4.0.

A comparison of the separation of cobalt from nickel with Caro's acid and ozone has been reported recently by Dunn *et al.* [9]. A pilot campaign employing both oxidants with a Ni : Co ratio of approximately 100 : 1 in the feed was carried out. The residual cobalt content achieved in a single contact with ozone under steady state conditions (~1 ppm) was very similar to that achieved with Caro's acid (10–15 ppm) in the continuously operating pilot plant. Longer retention times with a single contactor were required for Caro's acid (7 h) compared with approximately 1.25 h for ozone.

Corefco, the nickel and cobalt refining arm of the Metals Combined Enterprise, operates the nickel refinery in Fort Saskatchewan, Alberta, Canada which was constructed by Sheritt Gordon Mines in 1954. Redevelopment of the operating processes has led to a new process flowsheet and a new cobalt-nickel separation process. The ammonia pressure leach however was retained. Thus the feed to cobalt-nickel separation is a solution containing cobaltic and nickelous hexammine. About 70 % of the cobalt is precipitated from this solution by sparging in anhydrous ammonia to saturate the solution with ammonia while simultaneously cooling the solution to below 35 °C results in precipitation of $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 2\text{Ni}(\text{NH}_3)_6\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, a crystalline complex salt of Co(III) hexammine sulphate, Ni(II) hexammine sulphate and ammonium sulphate.

After filtration this salt is repulped with water to selectively redissolve nickel hexam-

mine sulphate and produce a crystalline Co(III) hexammine sulphate analysing 15 % Co with a Co : Ni ratio in the range 50 : 1 to 100 : 1. A single stage of recrystallisation of the cobalt salt in ammonium sulphate eliminates the residual nickel and upgrades the cobalt hexammine salt to a Co : Ni ratio of 2000 : 1. In the process copper, zinc, cadmium and essentially all other significant metal impurities, except chromium and iron, are eliminated to very low levels [10].

SEPARATION BY RESIN ION EXCHANGE

Ion exchange separation of cobalt and nickel is most readily accomplished from chloride solution where advantage can be taken of the tendency for cobalt to form complex chloro anions, *i. e.* CoCl^{3-} , CoCl^{4-} , which nickel does not. These complexes are quite weak, however, and relatively high concentrations of chloride ion are needed to produce the CoCl^{4-} species, which is tetrahedral. Other ions forming chloro-complexes will interfere, in particular ferric iron, copper, zinc, *etc.* No commercial use is made of such an ion exchange process and solvent extraction is preferred.

Although no great degree of selectivity between Ni^{2+} and Co^{2+} is achievable by ordinary cation exchange resins, chelating ion exchangers can offer separation opportunities. In particular, the chelating resins originally produced by the Dow Chemical Company known as XFS4195, XFS4196 and XFS43084 can remove nickel selectively from cobalt [11–14]. The resins are based on a macroporous polystyrene divinylbenzene matrix, on which weakly basic chelating functional groups based on picolylamine (2-aminomethyl pyridine) have been attached. The XFS resin shows significant selectivity for nickel over cobalt. Commercial application of the Dow resin XFS 4195 took place at INCO's Port Colborne cobalt refinery for nickel removal from the cobalt electrolyte [5]. Traces of copper present in the electrolyte are also removed with the nickel. The resin is also used commercially in Zambia at the cobalt plants at Chambishi and Nkana [15].

SEPARATION BY SOLVENT EXTRACTION

The separation of cobalt and nickel by solvent extraction has been studied quite intensively over the last 25 years or so. A useful review of the extractants available for cobalt-nickel separation from laterite leach liquors has been given by Ritcey [16] and the chemistry of cobalt-nickel separation, including solvent extraction, has been discussed by Flett [5]. At present many commercial plants are operating, most of which use the dialkyl phosphinic acid extractant, CYANEX 272 (Cytec Industries Inc.). With one exception, these plants remove cobalt selectively from nickel, in contrast to the resin ion exchange developments discussed above. Solvent extraction, unlike the precipitation processes briefly described earlier, does offer the opportunity of complete separation with high yields and purity of the separated metals. The two main methods for solvent extraction of cobalt and nickel are solvent extraction by anion exchangers and solvent extraction by acidic chelating extractants.

For cobalt-nickel separation by anion exchange the same situation exists as for resin anion exchangers with the most important ligand in the aqueous phase being chloride. The extracted anionic species has been shown to be CoCl_4^{4-} . This chemistry is used commercially in solvent extraction plants at Falconbridge Nikkelverk in Norway, by Eramet in France and was used by Sumitomo at Niihama in Japan [17]. Excellent separation factors in excess of 4000 are achieved by this means.

For cation exchangers only the alkyl phosphoric, phosphonic and phosphinic acids show selectivity for cobalt over nickel. All the rest, *i. e.* carboxylic acids, β -diketones, 8-hydroxyquinolines and hydroxyoximes, show marginal selectivity for Ni(II) over Co(II).

Separation of cobalt from nickel in weakly acid sulphate solutions had traditionally been difficult until it was realised [18, 19] that, with alkyl phosphorous acids, the separation factor was a complex function of temperature, cobalt concentration, diluent, modifier and acid type. The separation factor increases in the series phosphoric < phosphonic < phosphinic acids. In summary, separation factors for alkyl

phosphoric acids are in the tens, for alkyl phosphonics the hundreds while for alkyl phosphinics they are in the thousands. 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 with a consequent increase in distribution coefficient. No such behaviour is shown by nickel which remains in the hydrated/solvated octahedral form throughout. 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 selectivity series also undergoes changes within the series phosphoric, phosphonic and phosphinic acids as shown below:

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

The relative position of calcium in these series is worth noting: for DEHPA and PC88A it is extracted before cobalt but for CYANEX 272 cobalt is preferred over calcium and magnesium. This is a significant advantage. Unfortunately none of these extractants can extract cobalt selectively from ferric iron. However, unlike DEHPA which requires 6 M HCl to strip any co-extracted iron, CYANEX 272 can be readily stripped with relatively dilute (150 g/l) H_2SO_4 . Cobalt can be selectively stripped from any co-extracted iron or zinc at a pH of 2.5.

The first cobalt SX plant from sulphate solution was at Rustenburg Refiners in South Africa. This plant operates on a cobalt cake produced by precipitation of cobalt from the main nickel electrolyte with nickelic hydroxide (the Outokumpu process). Dissolution of this cake gives a solution containing 2 : 1 to 4 : 1 Co : Ni which was easily treated by solvent extraction with DEHPA at 50 °C to achieve a cobalt recovery of >95 % at a cobalt to nickel ratio of >500 : 1 [2]. The flowsheet is shown in Fig. 1. For less favourable Co : Ni ratios such as would arise from leaching of nickel ores, be they laterites or sulphides, DEHPA would not be an

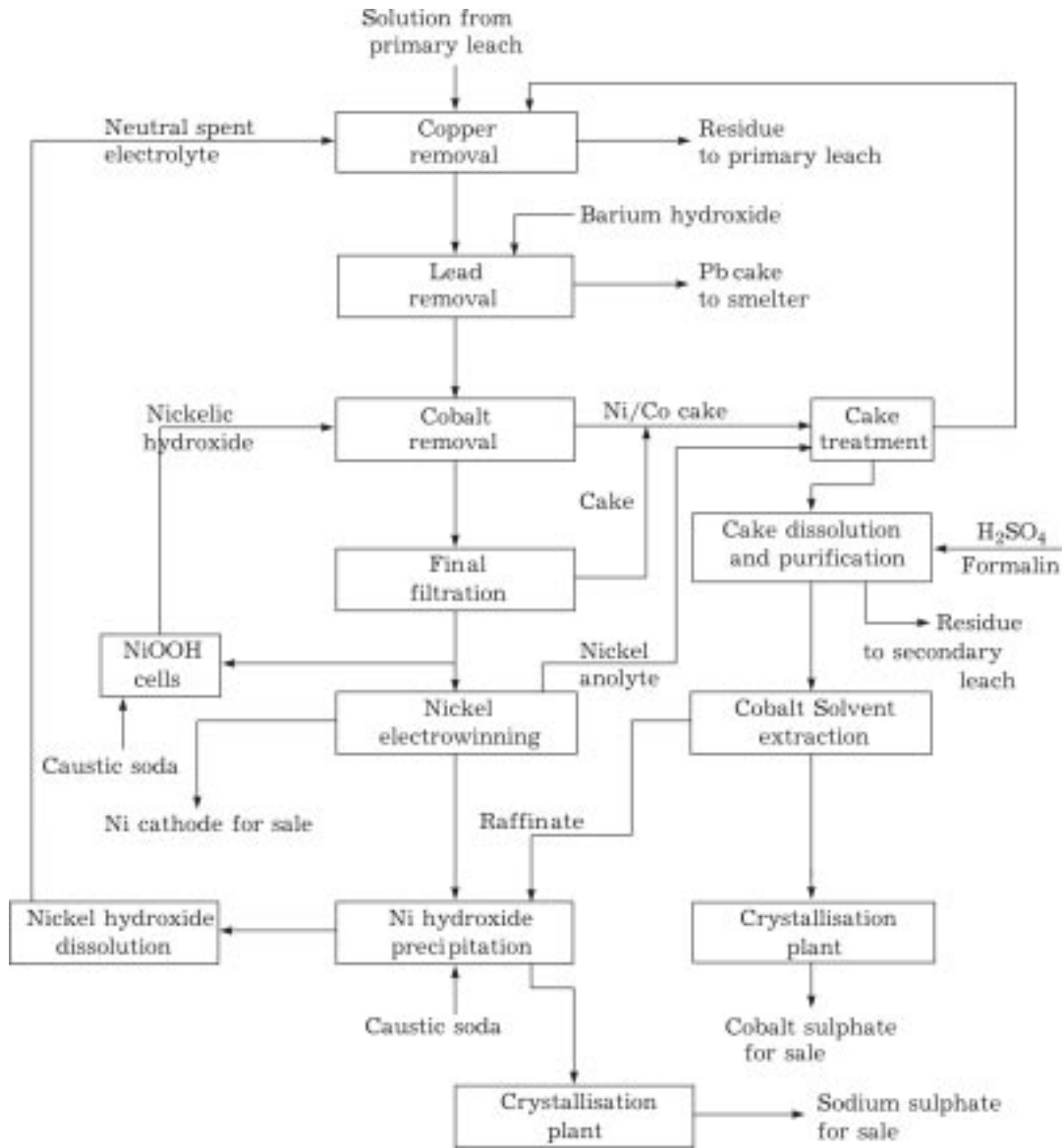


Fig. 1. Flowsheet for nickel and cobalt circuits at Rustenburg Base Metal Refinery.

adequate extractant. The effect of separation factor is well exemplified for disparate Co/Ni ratios in extraction isotherms shown in Fig 2. It should be noted that, when the Rustenburg plant was installed, CYANEX 272 was not available.

Nippon Mining used PC88A (2-ethyl hexyl ester of phosphonic acid) for Co removal and recovery from the Co/Ni solution produced by leaching the sulphide cake from Queensland Nickel [20]. High removal of Co was necessary to minimise degradation of the hydroxyoxime extractant used later in the flowsheet caused by oxidative extraction of Co(II). PC88A or Ionquest 801 are also used in India for Co/Ni separation

in some small plants as described by Koppiker [21].

The development in the 1980s of the di(2,4,4-trimethylpentyl)phosphinic acid, CYANEX 272, by American Cyanamid, now Cytec Industries Inc., opened the way for direct solvent extraction of cobalt from liquors containing very disparate Co/Ni ratios. There are thought to be at least 13 plants operating commercially using CYANEX 272. Approximately 50 % of the Western World's cobalt is produced *via* a CYANEX 272 plant.

The CYANEX 272 cobalt solvent extraction plant at Harjavalta, now owned by OMG, treats a feed from leaching of the mattes produced

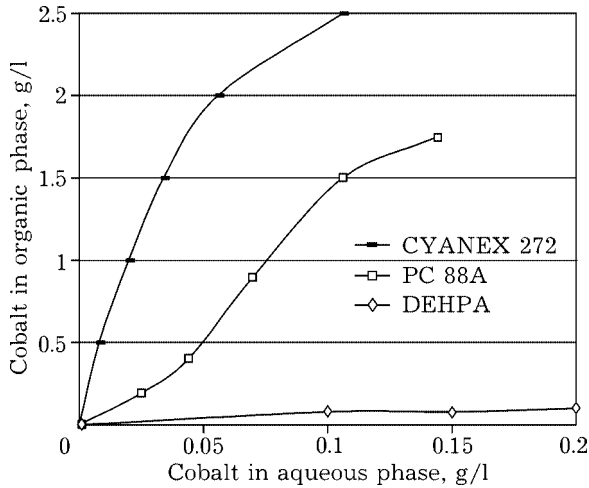


Fig. 2. Extraction of cobalt from a nickel matte leach liquor using different alkyl phosphorous acids. Organic phase: 10 v/o alkyl phosphorous acid in Escaid 110, plus 5 v/o TBP, 85 % conversion to Na form. Feed: Co, 0.22 g/l; Ni, 89.6 g/l.

in the DON smelting process [22] 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 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. Co-extracted zinc and iron are not significantly stripped with the cobalt and these metal ions are removed in a single stage with 200 g/l H_2SO_4 . The mixer-settlers used are the Outokumpu developed Vertical Smooth Flow (VSF) mixer-settlers [23]. 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. Organic phase: 10 v/o alkyl phosphorus acid in Escaid 110, plus 5 v/o TBP, 85 % conversion to Na form. Feed: Co, 0.22 g/l; Ni, 89.6 g/l.

CYANEX 272 has also been adopted as the reagent of choice for various laterite acid pressure leach projects in Australia. Thus the Murrin Murrin project (Fig. 3) [24–26] uses solvent extraction with CYANEX 272 for Co/Ni separation from a mixed sulphide pressure leach liquor.

The Bulong project (Fig. 4) uses solvent extraction directly on the leach liquor after puri-

fication. 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. The nickel in the raffinate is then extracted and separated from magnesium with a carboxylic acid, Versatic 10 [26–28]. Results of continuous miniplant trials [28] 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.

New thio-based extractants, bisdithiophosphoramides [29], were developed by Zeneca in the UK. Originally developed for zinc extraction from sulphate media under the development title of DS5869, modifications to the molecule provided a further development reagent designated DS6001 specifically for cobalt/nickel separation. This reagent could separate both cobalt and nickel from manganese and magnesium. CYANEX 301 and 302 also separate cobalt from manganese and magnesium and this attribute together with its strong pH functionality has led to the selection of Cyanex 301 as the reagent of choice for INCO's

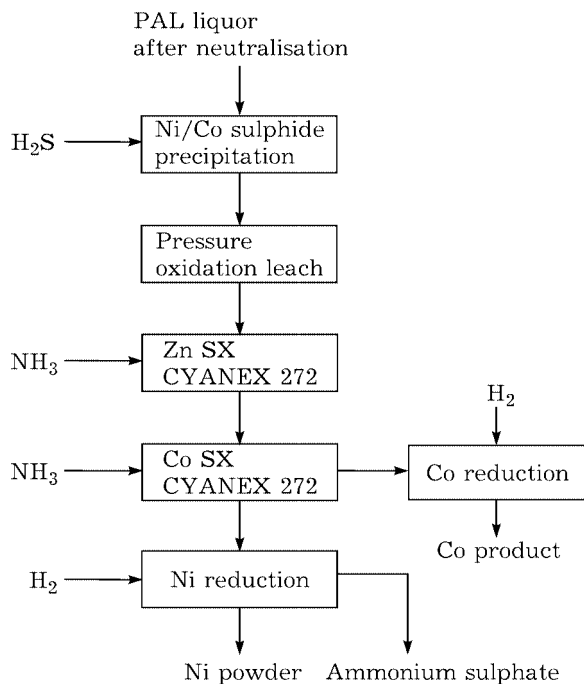


Fig. 3. Murrin Murrin purification flowsheet.

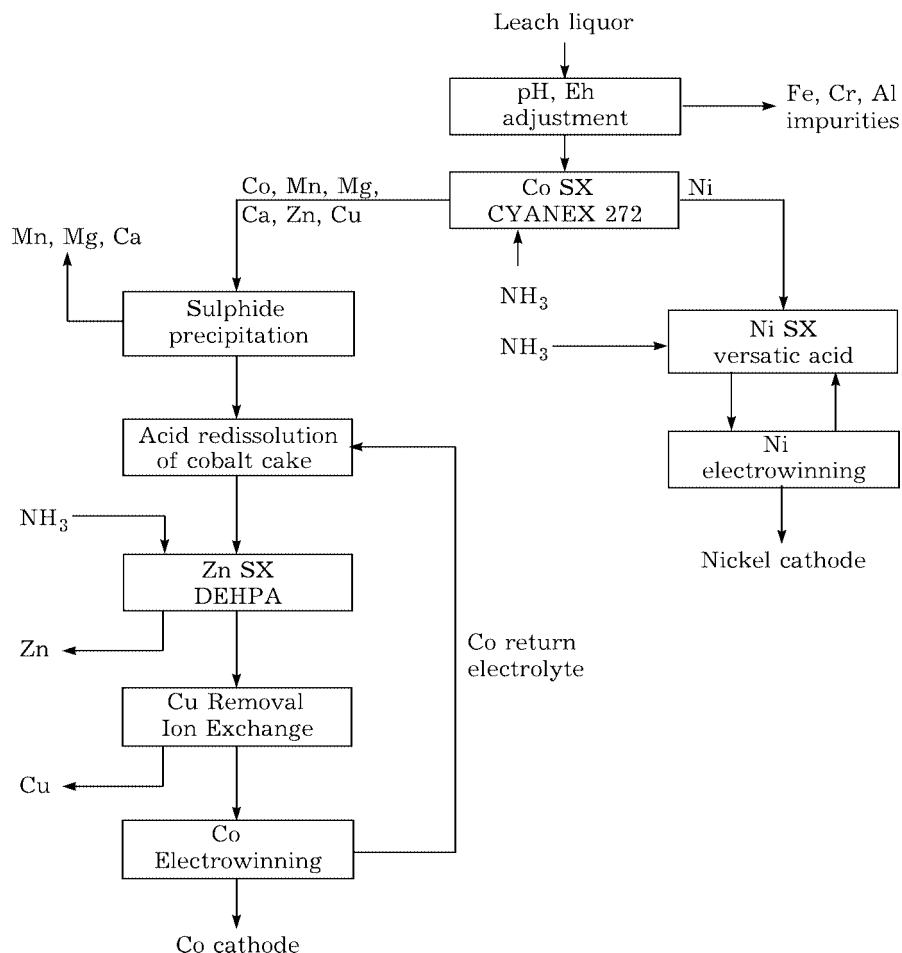


Fig. 4. Bulong nickel/cobalt purification flowsheet.

Goro project in New Caledonia [30, 31]. DS6001 also extracted both cobalt and nickel at much lower pH values than either CYANEX 272 and 302. However, while Zeneca reported good separation of both cobalt and nickel from manganese [29], this was not found in work reported by Lakefield [32] which shows a long tail on the manganese extraction curve below the pH at which nickel ceases to be extracted. The cause of this discrepancy is not known. This Zeneca reagent has been withdrawn.

The stability of the organic phase in cobalt extraction became an issue in the Rustenburg Refiners cobalt solvent extraction plant when it became clear that oxidative degradation of the diluent to a carboxylic acid was taking place causing a significant reduction in separation factor and increasingly poor phase break. The problem was shown to be due to cobalt catalysed oxidative degradation of the diluent. A study of this problem [33] 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. Phenolic antioxidants such as BHT were shown to be effective in conferring diluent stability. 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. 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.* [34]. 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 com-

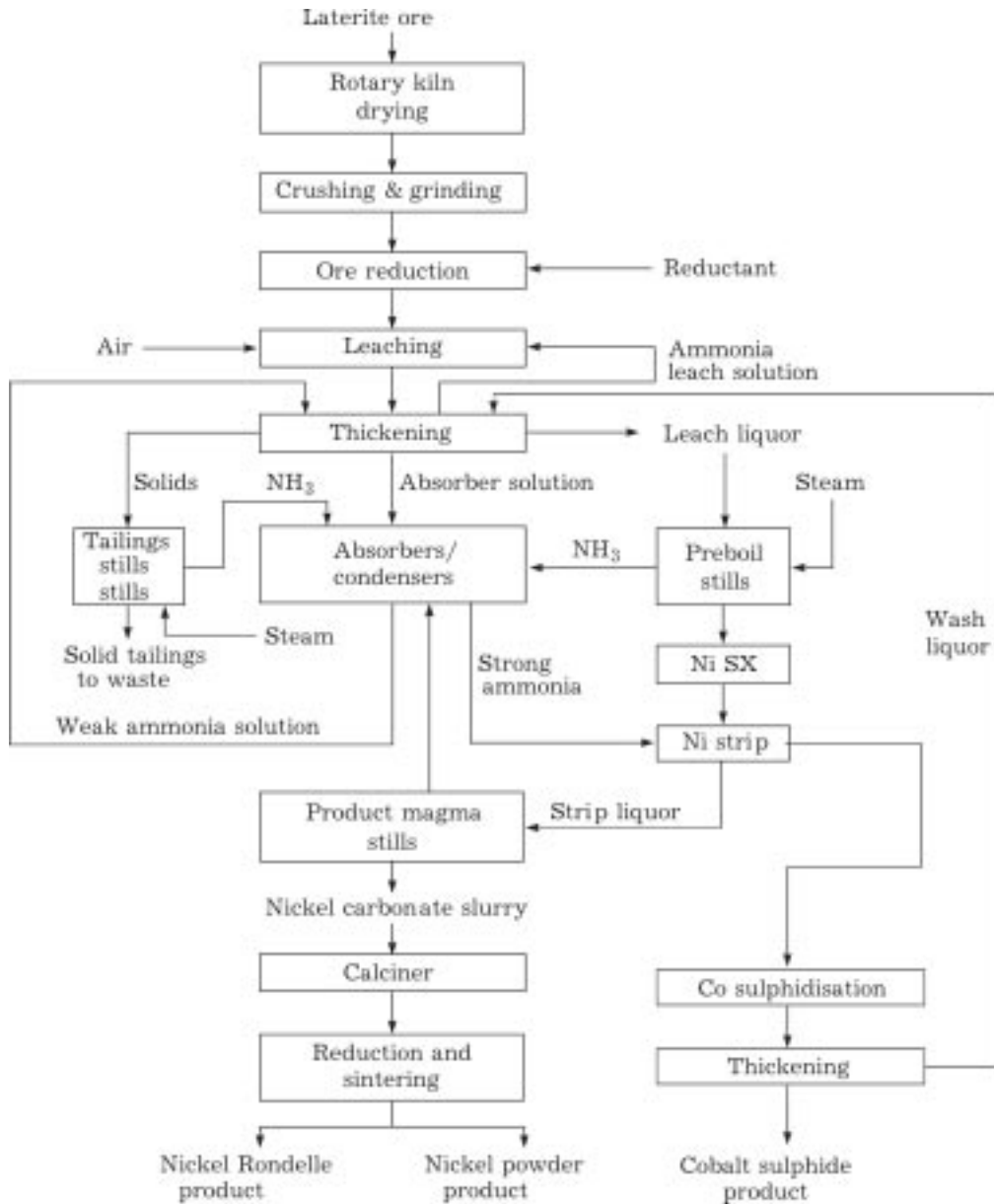


Fig. 5. Flow sheet of the QNI Yabulu Plant.

mercial plants appears standard practice now at levels of 0.5–1.0 g/l [35].

The selective removal of nickel from cobalt has long been of interest. While, as noted above, all extractants other than the phosphorus acids and the dithiophosphoramides extract nickel in preference to cobalt, the separation factors are not large. Thus other systems have been sought. As long ago as 1983 Grinstead and Tsang [36] showed that a mixture of an N-alkylated bispicolylamine and dinonyl naphthalene sulphonic acid could extract both nickel and cobalt selectively from ferric iron and that

nickel could be selectively separated from cobalt. No commercialisation of this system has taken place not least because there were problems with poor phase disengagement.

From ammoniacal solutions however, provided cobalt is in the Co(III) state, nickel can be successfully separated from cobalt with hydroxyoximes as Co(III) is not extracted by these reagents. This has been successfully commercialised by Queensland Nickel at their Yabulu refinery in Queensland, Australia (Fig. 5). Reagent screening showed that the best reagent mixture was a modified LIX 84 in Escaid 110.

The main leach liquor is treated directly by solvent extraction after a preboil to reduce ammonia levels. Small amounts of Co(II) are oxidatively extracted which cannot be stripped conventionally. Nickel stripping was with 280 g/l NH_3 to give a nickel concentration in the strip of 80 g/l and <20 mg/l cobalt. Nickel carbonate is produced from the strip liquor which is worked up to nickel oxide or, if the calciner is operated under reducing conditions, a product containing >97 % nickel metal. Cobalt oxidation is accompanied by degradation of the hydroxyoxime to a ketone, but this can be reversed by re-oximation with an aqueous ammoniacal solution of hydroxylamine sulphate [37].

This approach was also used at the original Cawse plant in Western Australia although the nickel here was acid stripped and nickel recovered by electrowinning. This refinery was closed recently after takeover by OMG. The plant now produces mixed Co/Ni hydroxides for shipment to Harjavalta.

Separation of nickel from cobalt is also possible with mixtures of carboxylic acids or alkyl phosphorous acids with pyridine carboxylic esters [37, 38]. Good separation of Ni from Co is achieved with the former mixture, less good with the latter which also has a major drawback in the very strong extraction of ferric iron which would require elimination before nickel solvent extraction.

SEPARATION BY PRESSURE HYDROGEN REDUCTION

Separation of nickel and cobalt is possible by direct hydrogen reduction of nickel + cobalt loaded DEHPA solutions [39]. Just as it is possible to recover nickel selectively from aqueous solutions by direct hydrogen reduction in the presence of cobalt, so nickel can be selectively reduced in the presence of cobalt from a metal-loaded DEHPA phase in an autoclave at 140 °C and an initial pressure of 120 atm. It is reported that a solution containing 24 g/l Ni and 1.2 g/l Co could be reduced to produce a nickel powder containing less than 0.15 % Co (the limit of the analytical method used) and a final organic phase containing 3.5 g/l Ni and 1.2 g/l Co. However it is clear that the nickel to

cobalt ratio effect comes into play here just as in the aqueous phase work, although tests with organic phases loaded with cobalt only show no significant reaction under experimental conditions. Nickel reduction, on the other hand, was rapid and complete in 30 min. This interesting approach has not been developed beyond the laboratory.

Nickel powder is also precipitated selectively by reduction of aqueous solutions containing nickel and cobalt amines in concentrated ammonium sulphate solution at around 240 °C with hydrogen gas at a total pressure of up to 3103 kPa. When the concentration of nickel in solution is lowered to around that of cobalt, the reaction is stopped and the solution discharged from the autoclave leaving nickel powder inside [1]. This process, originally developed by the Chemical Construction Corporation of America and further developed by Sherritt Gordon in Canada is used commercially, for example, at Fort Saskatchewan in Canada, by Impala Platinum at Springs in South Africa and at Murrin Murrin in Western Australia albeit here after Co/Ni separation by solvent extraction. Currently however, in the new Corefco plant at Fort Saskatchewan the nickel reduction is carried out on a solution after Ni/Co separation by selective precipitation of Co(III) hexammine [10].

DISCUSSION AND CONCLUSIONS

Because of the inability of precipitation processes to produce high quality cobalt products directly it is small wonder that solvent extraction has attracted so much attention over the years, offering, as it does, a one step approach to achieving a very high degree of separation of cobalt from nickel with high yields of both metals with low levels of contamination of each metal in the respective cobalt and nickel streams. The first breakthrough in this respect was the chloride-based processes operated by Falconbridge and Eramet.

Application of solvent extraction for cobalt-nickel separation from weakly acidic sulphate solutions really did not take off until the development of CYANEX 272. This reagent has transformed the Co/Ni separation process in

weakly acidic sulphate solutions, particularly for high Ni : Co ratio liquors. However there is no standard set of operating conditions as the objectives set for such solvent extraction plants varies from plant to plant. For example, at Bulong, it is necessary to ensure minimum cobalt in the nickel liquor going forward to Versatic acid extraction and subsequently electrowinning, whereas, at Murrin Murrin some cobalt in the nickel going forward to pressure hydrogen reduction is tolerable because of the degree of selectivity found for nickel in this reduction step. Rather it is the requirement for minimal nickel in the cobalt liquor proceeding to cobalt pressure hydrogen reduction that is the main requirement.

On the other hand, separation of nickel selectively from cobalt remains elusive except for the chelating resin ion exchange process for removal of small amounts of nickel from relatively rich cobalt streams as at Inco's Port Colborne operations in Canada, at the cobalt refineries at Nkana and Chambishi in Zambia and at the QNI SX plant in Australia. Little research effort appears to be on-going in this area currently and there appears little incentive for such work. Adoption of solvent extraction to provide the interface between the purified cobalt liquors arising in the cobalt refineries in Zambia and the Democratic Republic of Congo and cobalt electrowinning, as envisaged by Burks [40], should avoid the need to use this expensive resin ion exchange process and developments here are keenly awaited.

Molecular recognition technology (MRT) has been promoted as being of great potential for selective recovery of cobalt and extensive trials have been carried out using a skid-mounted unit in Australia [41] and on the Zambian Copper Belt, for example. While it is believed that technically the trials were successful, the economics were unfavourable, not least because of the very high replacement rate requirement for the very expensive MRT material.

Thus it is concluded that it is unlikely that any radical, new methods for the separation of cobalt from nickel are likely to emerge in the immediate future. The two thio analogues of CYANEX 272, namely CYANEX 301 (the dithio analogue) and CYANEX 302 (the monothio analogue) do have the ability to separate

cobalt from manganese as well as the alkaline earth elements which is certainly of interest in the treatment of the leach liquors arising from the pressure acid leach process for nickel laterites. However CYANEX 302, which does separate cobalt from nickel as well as, if not better than, CYANEX 272, irreversibly decomposes to CYANEX 272 and elemental sulphur in the presence of even minor amounts of ferric iron. CYANEX 301, on the other hand, decomposes in two stages, the first of which is reversible. That this reagent has been chosen for Inco's Goro project in New Caledonia, stems not from its ability to separate Co from Ni but rather from its ability to bulk extract both cobalt and nickel selectively from Mn, Ca and Mg from the acid leach liquor produced in the pressure leach process after removal of iron. Both reagents also extract copper in a redox process which also causes degradation of these reagents and so copper must be eliminated prior to cobalt solvent extraction. This will be done by use of a chelating ion exchange resin in the Goro project [31]. Such decompositions and the oxidation of cobalt on extraction with di(2-ethyl hexyl)dithiophosphoric acid (DTPA) have been studied by V. I. Kuz'min *et al.* [42, 43] who have shown that the irreversible decomposition of DTPA occurs by its direct water hydrolysis and decomposition of the disulphide which is formed as a result of the reversible redox reaction with cations of transition metals such as Cu, Co and Fe. The results of this work are of direct relevance to the decomposition issue of CYANEX 301.

While it has been successfully demonstrated that the decomposition of CYANEX 301 can be contained and, indeed, reversed [31], the same cannot be said for CYANEX 302. What would be useful here would be the development of some means of retarding the rate of decomposition of CYANEX 302 in order to render it acceptable in terms of solvent loss in operating conditions. Unfortunately no such development work appears to be on-going at this time.

REFERENCES

- 1 A. R. Burkin, in A. R. Burkin (Ed.), *Critical Reports in Applied Chemistry*, vol. 17, John Wiley & Sons, 1987, p. 98.

- 2 D. De J. Clemente, B. I. Dewar and J. Hill, Paper presented at CIM 10th Annual Hydrometallurgical Meeting, Edmonton, Alberta, Canada, 1980.
- 3 Z. Hofirek and P. J. Nofal, *Hydrometallurgy*, 39 (1995) 91.
- 4 W. A. Rickelton and D. Nucciarone, in W. C. Cooper and I. Mihaylov (Eds.), Nickel-Cobalt'97, vol. 1: Hydrometallurgy and Refining of Nickel and Cobalt, The Metallurgical Society of CIM, 1997, p. 275.
- 5 D. S. Flett, in A. R. Burkin (Ed.), Critical Reports in Applied Chemistry, vol. 17, John Wiley & Sons, 1987, p. 76 and references therein.
- 6 P. J. Wyborn and C. F. McDonagh, Minerals, Metals and the Environment II, IMM, London, 1996, p. 421.
- 7 T. Nishimura and Y. Umetsu, *Hydrometallurgy*, 30 (1992) 483.
- 8 J. R. Boldt and P. Queneau, The Winning of Nickel, Methuen, London, 1967, p. 372.
- 9 G. M. Dunn, H. W. Schubert and H. E. Holliday, in W. C. Cooper and I. Mihaylov (Eds.), Nickel-Cobalt'97, vol. 1: Hydrometallurgy and Refining of Nickel and Cobalt, The Metallurgical Society of CIM, 1997, p. 195.
- 10 D. G. E. Kerfoot and P. D. Cordingley, in W. C. Cooper and I. Mihaylov (Eds.), *Ibid.*, p. 355.
- 11 K. C. Jones and R. M. Wheaton, US Pat. 3 998 924, Dec. 21, 1976.
- 12 R. R. Grinstead and W. A. Nasutavicus, US Pat. 4 031 038, June 21, 1977.
- 13 R. R. Grinstead and W. A. Nasutavicus, US Pat. 4 098 867, July 4, 1978.
- 14 R. R. Grinstead and A. L. Tsang, in: Int. Solvent Extraction Conf., Denver, Colorado, 1983, American Inst. of Chem. Engrs., New York, 1983, p. 230.
- 15 A. S. Rao, R. Mingango, J. Nkhoma and H. P. Singh, in R. G. Reddy and R. N. Weizenbach (Eds.), The Paul Queneau Int. Symp. Extractive Metallurgy of Copper, Nickel and Cobalt, vol. 1: Fundamental Aspects, The Minerals, Metals & Materials Soc., 1993, p. 853.
- 16 G. M. Ritcey, in: Nickel'96, The Australasian Institute of Mining and Metallurgy, 1996, p. 251.
- 17 M. Anthony and D. S. Flett, *Minerals Industry Intern.*, January (1997) 26.
- 18 D. S. Flett and D. W. West, in: Complex Metallurgy'78, Institution of Mining and Metallurgy, London, 1978, p. 49.
- 19 J. S. Preston, *Hydrometallurgy*, 9 (1982) 115.
- 20 M. Ando, M. Takahashi and T. Ogata, in: Hydrometallurgy, Research, Development and Plant Practice, Symposium, Atlanta, AIME, New York, 1983, p. 463.
- 21 K. S. Koppiker, *Cobalt News*, 2 (2001) 9.
- 22 I. V. Kojo, T. Mäkinen and P. Hanniala, in C. Diaz, I. Holubec and C. G. Tan (Eds.), Nickel-Cobalt'97, vol. III: Pyrometallurgical Operations, the Environment and Vessel Integrity in Nonferrous Smelting and Converting, The Metallurgical Soc. CIM, 1997, p. 25.
- 23 B. Nyman, A. Aaltonen, S.-E. Hultholm and K. Karpale, *Hydrometallurgy*, 29 (1992) 461.
- 24 G. Motteram, M. Ryan, R. Berezowsky and R. Raudsepp, Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, Alta Metallurgical Services, Australia, 1996.
- 25 G. Motteram, M. Ryan and R. Weizenbach, in W. C. Cooper and I. Mihaylov (Eds.), Nickel-Cobalt'97, vol. 1: Hydrometallurgy and Refining of Nickel and Cobalt, The Metallurgical Society of CIM, 1997, p. 391.
- 26 K. C. Sole and P. Cole, *Ion Exchange and Solvent Extraction*, 15 (2001) 143.
- 27 G. M. Ritcey, N. L. Hayward and T. Salinovich, Australian provisional patent, PN0441, 9 January, 1995.
- 28 K. Soldenhoff, N. Hayward and D. Wilkins, in B. Mishra (Ed.), EPD Congress 1998, The Minerals, Metals & Materials Soc., 1998, p. 153.
- 29 J. R. Lawson, and M. A. Cox, in W. C. Cooper and I. Mihaylov (Eds.), Nickel-Cobalt'97, vol. 1: Hydrometallurgy and Refining of Nickel and Cobalt, The Metallurgical Society of CIM, 1997, p. 319.
- 30 I. O. Mihaylov, E. Krause, S. W. Laundry and C. V. Luong, US Pat. 5 378 262, Jan. 3, 1995.
- 31 I. Mihaylov, E. Krause, D. F. Colton *et al.*, *CIM Bull.*, 93 (2000) 124.
- 32 C. J. Ferron, R. Molnar and R. G. Williamson, in W. C. Cooper and I. Mihaylov (Eds.), Nickel-Cobalt'97, vol. 1: Hydrometallurgy and Refining of Nickel and Cobalt, The Metallurgical Society of CIM, 1997, p. 427.
- 33 D. S. Flett and D. W. West, Proc. Int. Solvent Extraction Conf. ISEC'86, Preprints, vol. II, 1986, p. 3.
- 34 W. A. Rickelton, A. J. Robertson and J. H. Hillhouse, *Solvent Extraction and Ion Exchange*, 9 (1991) 73.
- 35 S. F. Burks, in Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, Alta Metallurgical Services, Australia, 1996.
- 36 I. G. Skepper and J. E. Fittock, in D. C. Shallcross, R. Paimin and L. M. Prvcic (Eds.), Value Adding through Solvent Extraction, Proc. ISEC'96, vol. 1, The University of Melbourne, 1996, p. 777.
- 37 J. S. Preston and A. C. du Preez, *Solvent Extraction and Ion Exchange*, 13 (1995) 465.
- 38 J. S. Preston and A. C. du Preez, *J. Chem. Technol. Biotechnol.*, 66 (1996) 86.
- 39 A. R. Burkin and J. E. A. Burgess, *Het Ingeniersblad*, 41 (1972) 459.
- 40 S. F. Burks, in Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, Alta Metallurgical Services, Australia, 1996.
- 41 S. R. Izatt, R. L. Bruening, N. E. Izatt *et al.*, in: Alta 2000 SX/IX-1, Conf. Tech. Proc., Day 1, Session 4, Alta Metallurgical Services, Blackburn South, Victoria, Australia, 2000.
- 42 V. I. Kuz'min, T. A. Klimkina and O. A. Logutenko, *Russian J. Inorg. Chemistry*, 43 (1998) 798.
- 43 V. I. Kuz'min, O. A. Logutenko and V. N. Kuz'mina, *Ibid.*, 44 (1998) 1155.