Recent developments in the separation of nickel and cobalt from sulphate solutions by solvent extraction

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SYNOPSIS

The properties of some recently developed solvent-extraction reagents for the separation of cobalt and nickel in sulphate solutions are reported. New commercial extractants based on alkyl phosphonic and alkyl phosphinic acids are described. These reagents show much improved selectivity for cobalt compared with established extractants. Some novel extractants developed at Mintek for the selective recovery of nickel in the presence of cobalt are also described. These reagents, which are based on mixtures of carboxylic acids and non-chelating oximes, are of interest in that no commercial nickel-selective reagents are currently available. Graphs showing metal loading and stripping, and pH-functionality, are presented, together with details of the metal separations achieved in batch counter-current-extraction experiments with the various reagents.

SAMEVATTING

Die eienskappe van sommige reagense wat onlangs ontwikkel is vir vloeistofekstraksie aangewend vir die skeiding van kobalt en nikkel in sulfaatoplossings word hier weergegee. Nuwe kommersiële ekstraheermiddels gebaseer op alkielfosfoonsure en alkielfosfiensure word beskryf. Hierdie reagense toon, in vergelyking met gevestigde ekstra-heermiddels, baie verbeterde selektiwiteit vir kobalt. Sommige nuwe ekstraheermiddels wat by Mintek ontwikkel is vir die selektiewe herwinning van nikkel in die teenwoordigheid van kobalt word ook beskryf. Hierdie reagensie, wat gebaseer is op mengsels van karboksielsure en nie-chelaatvormende oksieme, is van belang aangesien daar geen kommersiële nikkel-selektiewe reagense tans beskikbaar is nie. Metalladings- en metaalstropingskrommes en pH-funksionaliteitskrommes word aangegee tesame met besonderhede van metaalskeidings wat verkry is in lotteen-stroomekstraksie eksperimente met die verskillende reagense.

Introduction

Solvent extraction is now a well-established unit process in the hydrometallurgical recovery of base metals. Until recently, however, there were no suitable reagents for the efficient separation of cobalt and nickel in sulphate media. Although the selective extraction of cobalt has been achieved commercially by use of di(2-ethylhexyl)phosphoric acid[1,2], the process must be carried out at elevated temperature (50 to 70°C) and considerable reflux of the refined cobalt sulphate solution is required to achieve a product of acceptable purity. In contrast, no proprietary reagents are available for the selective extraction of nickel in the presence of cobalt.

This paper describes some recent developments in the separation of cobalt and nickel by solvent extraction from sulphate solutions. The properties of some new organophosphorus acid-based extractants developed in Japan and North America for the selective recovery of cobalt in the presence of nickel are reported. Some novel carboxylic acid-based reagents developed at Mintek for the selective extraction of nickel from cobalt sulphate solutions are also described.

Experimental

Reagents

Samples of commercial extractants were supplied by South African Cyanamid (Pty) Ltd (Cyanex 272) and by B.J. Johnson Associated (Pty) Ltd (Daihachi DP-8R and PC-88A). The naphthenic acid used was a BDH laboratory agent. Di-isopropylsalicylic acid and octanal oxime were prepared by previously described methods[3].

Isodecanal oxime and isotridecanal oxime were manufactured for Mintek by Fine Chemicals Corporation, Cape Town. Xylene (Saarchem, AR grade) was used as the solvent.

Metal Distributions

The metal distributions were determined after the required organic and aqueous phases had been contacted by means of rapid stirring. The pH of the aqueous phase was monitored continuously and was adjusted to the required value by the addition of 10 M sodium hydroxide solution. When only one metal was present, samples of the aqueous phase were analysed by titration against standard EDTA solution and, when cobalt and nickel were both present, by atomic-absorption spectro-photometry. Metal contents of the organic phases were determined by back-extraction into 1M perchloric acid and analysis of the resulting aqueous solutions as described above.

Results and Discussion

Selective Extraction of Cobalt in the Presence of Nickel

The use of di(2-ethylhexyl)phosphoric acid (D2EHPA, $(RO)_2PO.OH$, where $R=C_4H_9CH(C_2H_5)CH_2$) for the separation of cobalt from nickel in sulphate solutions is well known. The process was developed in Canada by Ritcey et al.[1,4], and one modification is currently in use at the base-metals refinery of Matthey Rustenburg Refiners (Pty) Ltd in the Transvaal[2,5]. The extraction of cobalt and nickel as a function of equilibrium pH using D2EHPA (in the form of the Daihachi product DP-8R) at 20 and 50°C is shown in Fig. 1. Although the cobalt–nickel separation is poor at ambient temperature, reasonably efficient separations can be achieved by means of a multistage process at elevated temperature.

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Thus, for example, the Matthey Rustenburg Refiners' plant operates at 50°C and treats a feed with a cobalt-to-nickel ratio of 3:1 using eight extraction stages and four scrubbing stages (in which co-extracted nickel is displaced from the organic phase by contacting with a concentrated cobalt sulphate solution bled from the stripping circuit). The cobalt recovery is 92 to 96 per cent, and the cobalt sulphate product has a cobalt-to-nickel ratio of 700:1.
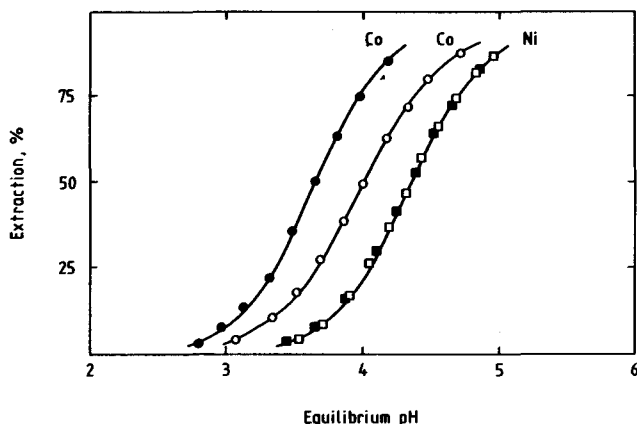

Fig. I—Extraction of cobalt and nickel by 0,45 M D2EHPA in xylene at 20° (unshaded symbols) and 50° C (shaded symbols). Initial aqueous phase: Ammonium sulphate, 40 g/l Cobalt or nickel as sulphate, 3 g/l.

In 1978, the refinery of Nippon Mining Co. at Hitachi, Japan, which had previously employed D2EHPA for the recovery of cobalt, changed to a new extractant, 2-ethylhexyl 2-ethylhexylphosphonic acid (R(RO)-PO.OH, where $R=C_4H_9CH(C_2H_5)CH_2$, which shows improved selectivity for cobalt. This reagent was developed by the Daihachi Chemical Industry Co., and is designated PC-88A. (It is also marketed by Shell International, under the name SME 418.) The marked improvement in cobalt–nickel separation obtainable with PC-88A is evident from the curves of extraction versus pH given in Fig. 2. As with D2EHPA, operation at elevated temperatures increases the separation of the cobalt and nickel extraction curves.

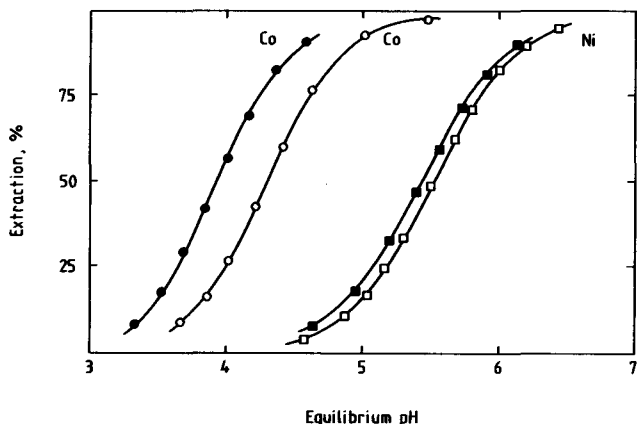More recently, the American Cyanamid Co. developed

Fig. 2—Extraction of cobalt and nickel by 0,45 M PC-88A in xylene at 20° (unshaded symbols) and 50°C (shaded symbols). Initial aqueous phase: Ammonium sulphate 40 g/l Cobalt or nickel as sulphate, 3 g/l.
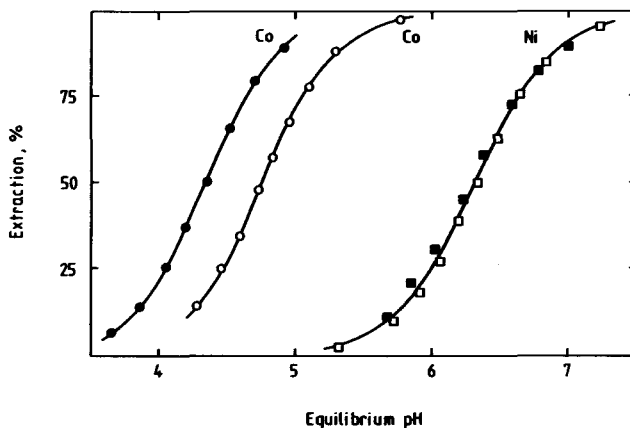

Fig. 3—Extraction of cobalt and nickel by 0,45 M Cyanex 272 in xylene at 20°(unshaded symbols) and 50° C (shaded symbols). Initial aqueous phase: Ammonium sulphate, 40 g/l Cobalt or nickel as sulphate, 3 g/l.

extractants based on dialkyl phosphinic acids ($R_2PO.OH$, where R has not been disclosed). The earliest of these products, a crystalline material designated Cyanex CNX, was found to suffer from the disadvantage of poor solubility of the extractant itself and of its metal complexes in hydrocarbon diluents[6]. However, the more recently available Cyanex 272 is a liquid reagent with much improved solubility. Extraction curves for cobalt and nickel using Cyanex 272 at 20 and 50°C are shown in Fig. 3. Excellent cobalt–nickel separation characteristics are evident, even at ambient temperature.

The extraction results for cobalt and nickel using equimolar (0,45 M) solutions of D2EHPA, PC-88A, and Cyanex 272 in xylene are summarized in Table I in terms of the $pH_{0,5}$ values (the equilibrium pH at which there is a metal extraction of 50 per cent). It can be seen that the $pH_{0,5}$ values increase for both metals in the order phosphoric < phosphonic < phosphinic acids, but that the change through the series is considerably greater for nickel than for cobalt, resulting in an increase in selectivity for cobalt over nickel through the series.

TABLE I
EXTRACTION OF COBALT AND NICKEL BY 0,45 M ORGANOPHOSPHORUS ACIDS IN XYLENE

Initial aqueous phase:
Ammonium sulphate, g/l 40
Cobalt or nickel as sulphate, g/l 2,95

Extractant	$pH_{0,5}$ at 20°C			$pH_{0,5}$ at 50°C		
	Co	Ni	Ni–Co	Co	Ni	Ni–Co
D2EHPA	4,00	4,35	0,35	3,65	4,35	0,70
PC-88A	4,30	5,51	1,21	3,95	5,43	1,48
CYANEX 272	4,76	6,34	1,58	4,36	6,30	1,94

To illustrate the degree of cobalt–nickel separation attainable with the reagents PC-88A and Cyanex 272, batch experiments on countercurrent extraction were carried out at 20°C using aqueous feeds containing cobalt (3 g/l) and nickel (3 g/l) as sulphates in ammonium sulphate (40 g/l) solution. The curves of cobalt extraction for Cyanex 272 (Fig. 4) indicate that the optimum extraction consistent with the low co-extraction of nickel (c.f. Fig. 3) is obtained at an equilibrium pH value

of about 5,25 to 5,5. A McCabe–Thiele construction on the extraction isotherm for a pH value of 5,5 (Fig. 5) revealed that three countercurrent extraction stages at an organic-to-aqueous ratio of 1 :2 would suffice to reduce the cobalt content of the raffinate to 10 p.p.m. or less. Similar considerations for PC-88A showed that the optimum pH value for operation was 5,0, and that three extraction stages would be required to produce a raffinate containing less than 10 p.p.m. of cobalt at an organic-to-aqueous ratio of 1 :2.

Batch countercurrent experiments were carried out under the conditions determined above using a sufficient number of complete cycles to achieve steady-state conditions. The steady-state concentrations of cobalt and nickel in each stage are shown in Tables II and III for PC-88A and Cyanex 272 respectively. Excellent separations of cobalt and nickel were achieved with both reagents. The cobalt product obtained contained 0,11 and 0,18 per cent nickel (Cyanex 272 and PC-88A respectively), and the nickel product contained 0,24 and 0,32
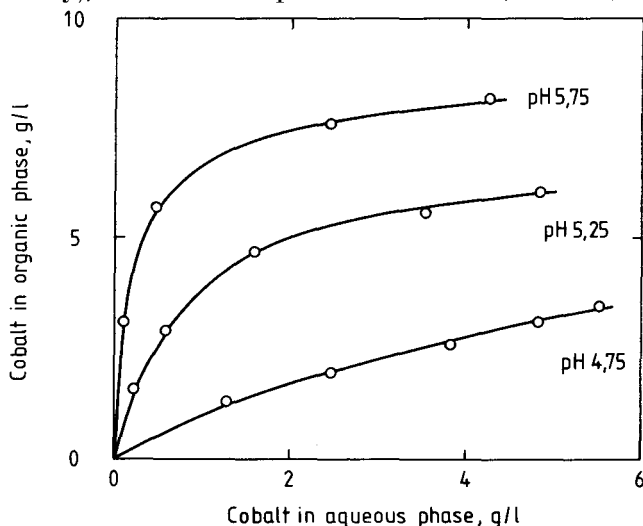

Fig. 4—Metal-loading curves for the extraction of cobalt from ammonium sulphate solution (40 g/l) into 0,45 M Cyanex 272 in xylene at 20°C
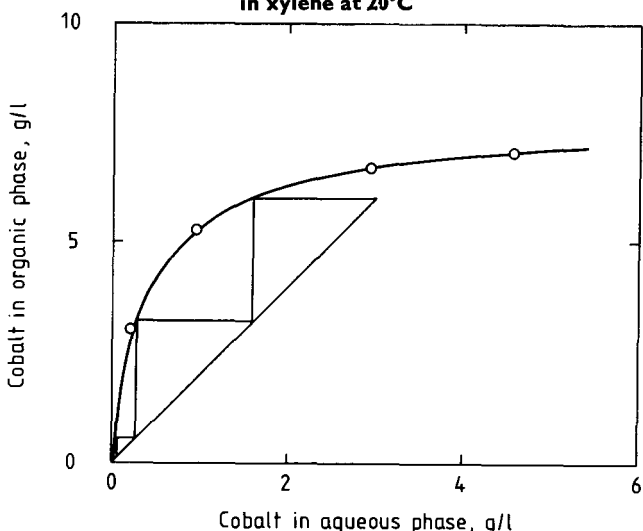

Fig. 5—McCabe–Thiele construction for the extraction of cobalt from ammonium sulphate solution (40 g/l) into 0,45 M Cyanex 272 in xylene at 20°C using an aqueous-to-organic ratio of 2:1 and an equilibrium pH value of 5,5

per cent cobalt (Cyanex 272 and PC-88A respectively). These purities could easily be improved if necessary by the use either of additional extraction stages at a slightly lower pH value or of temperatures a little above ambient.

TABLE II

BATCH COUNTERCURRENT EXTRACTION OF COBALT BY 0,45 M PC-88A IN XYLENE AT 20°C

Initial aqueous phase:
Ammonium sulphate, g/l   40
Cobalt as sulphate, g/l   3,03
Nickel as sulphate, g/l   3,08
Equilibrium pH in each stage 5,0

| Stage | Metal concentrations p.p.m. | | | |
| | Aqueous phase | | Organic phase | |
	Co	Ni	Co	Ni
1	1421	3122	6151*	11*
2	161	3300	2672	136
3	10†	3100†	326	415

*Loaded organic phase
†Raffinate

TABLE III

BATCH COUNTERCURRENT EXTRACTION OF COBALT BY 0,45 M CYANEX 272 IN XYLENE AT 20°C

Initial aqueous phase:
Ammonium sulphate, g/l   40
Cobalt as sulphate, g/l   3,18
Nickel as sulphate, g/l   2,94
Equilibrium pH in each stage 5,5

| Stage | Metal concentrations p.p.m. | | | |
| | Aqueous phase | | Organic phase | |
	Co	Ni	Co	Ni
1	1661	2940	6318*	7*
2	161	2978	2966	37
3	7†	2925†	317	112

*Loaded organic phase
†Raffinate

It is interesting that, when the fresh organic phase entered into contact with the cobalt-lean aqueous phase (stage 3), a considerable amount of nickel was extracted in both systems. However, as the organic phase progressed to the remaining stages, in which the aqueous phases were less depleted in cobalt, the co-extracted nickel was gradually 'crowded out' by the higher cobalt loading of the organic phase. This effect is characteristic of all the systems reported here.

Experiments were conducted on the stripping of cobalt from PC-88A and Cyanex 272 into a solution containing sulphuric acid (44 g/l) and cobalt (53 g/l) as sulphate in simulation of a spent electrolyte (anolyte) from a cobalt electrowinning circuit. The McCabe–Thiele construction (Fig. 6) shows that, for both reagents, an advance electrolyte (catholyte) containing cobalt (80 g/l) could be produced with only two stripping stages at an organic-to-aqueous ratio of 4,5:1. The maximum pH values attainable for these advance electrolytes were found to be 3,4 (PC-88A) and 3,9 (Cyanex 272), indicating that little, if any, adjustment of pH would be required prior to electrowinning.
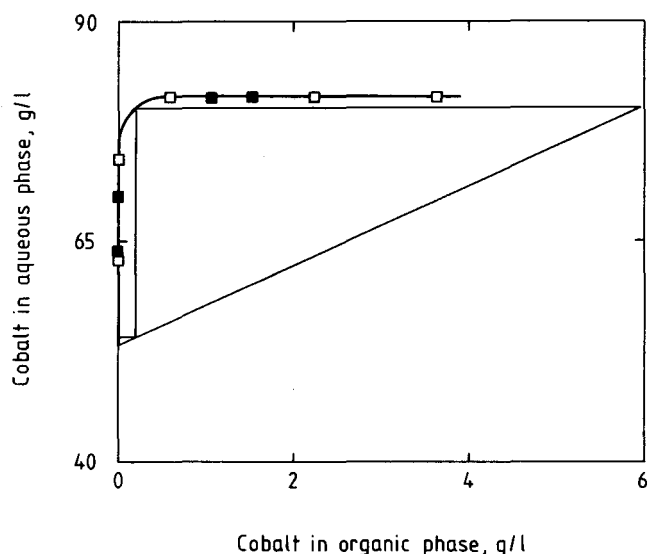
Fig. 6—McCabe–Thiele construction for the stripping of cobalt from 0,45 M PC-88A (unshaded symbols) and 0,45 M Cyanex 272 (shaded symbols) in xylene into a solution of sulphuric acid (44 g/l) and cobalt (50 g/l) as sulphate at 20° C using an organic-to-aqueous ratio of 4,5:1

Selective Extraction of Nickel in the Presence of Cobalt

In a recent investigation of the chemical reactions during the extraction of cobalt and nickel by organo-phosphorus acids[6], it was noted that the incorporation of certain solvents or other additives affected the extraction of cobalt and nickel to different extents. In particular, the addition of oximes of simple aliphatic aldehydes (e.g. octanal oxime, 2-ethylhexanal oxime) brought about pronounced synergistic shifts of the extraction curves to lower pH values, which means that these metals can be extracted under more acidic conditions. Moreover, the synergistic shifts for nickel were found to be considerably larger than those for cobalt so that, for example under conditions where D2EHPA alone (0,5 M in xylene) shows a selectivity for cobalt over nickel of 0,43 pH unit; a selectivity of 0,41 pH unit for nickel over cobalt was observed in the presence of an equimolar amount of 2-ethylhexanal oxime. Subsequently, a study[3] was made of the extraction of nickel and cobalt by a range of carboxylic acids in the presence of such non-chelating oximes. Carboxylic acids themselves, in contrast to organophosphorus acids, show a slight selectivity for nickel over cobalt, but have not found commercial application on account of the small separations of the nickel and cobalt extraction curves (up to 0,2 pH unit). However, it was found that, in the presence of aliphatic aldoximes, much greater separations of the extraction curves were obtained (up to 1,1 pH units in favourable cases).

The following paragraphs illustrate the use of such reagents in the selective separation of nickel from cobalt in sulphate solutions.
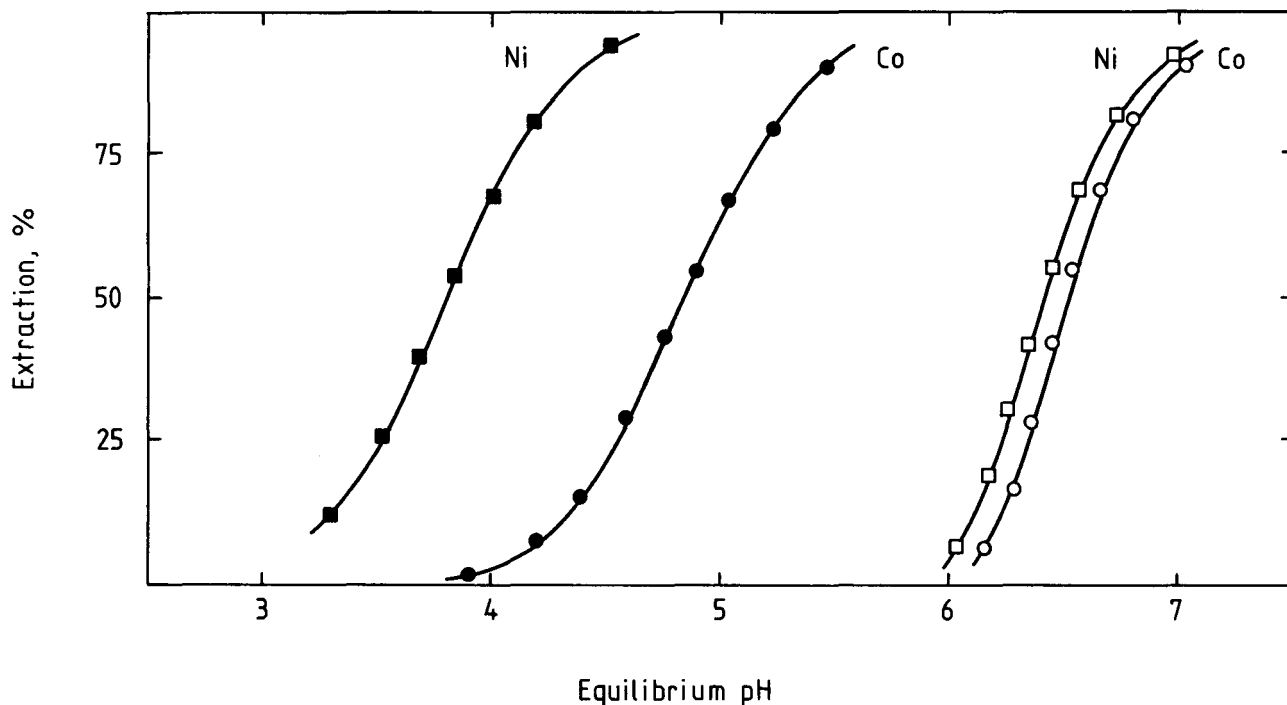
The extraction of nickel and cobalt from ammonium

Fig. 7—Extraction of nickel and cobalt by 0,50 M naphthenic acid (unshaded symbols) and by 0,50 M naphthenic acid plus 1,0 M isotridecanal oxime (shaded symbols) in xylene at 20° C. Initial aqueous phase: Ammonium sulphate, 40 g/l. Cobalt or nickel as sulphate, 3 g/l
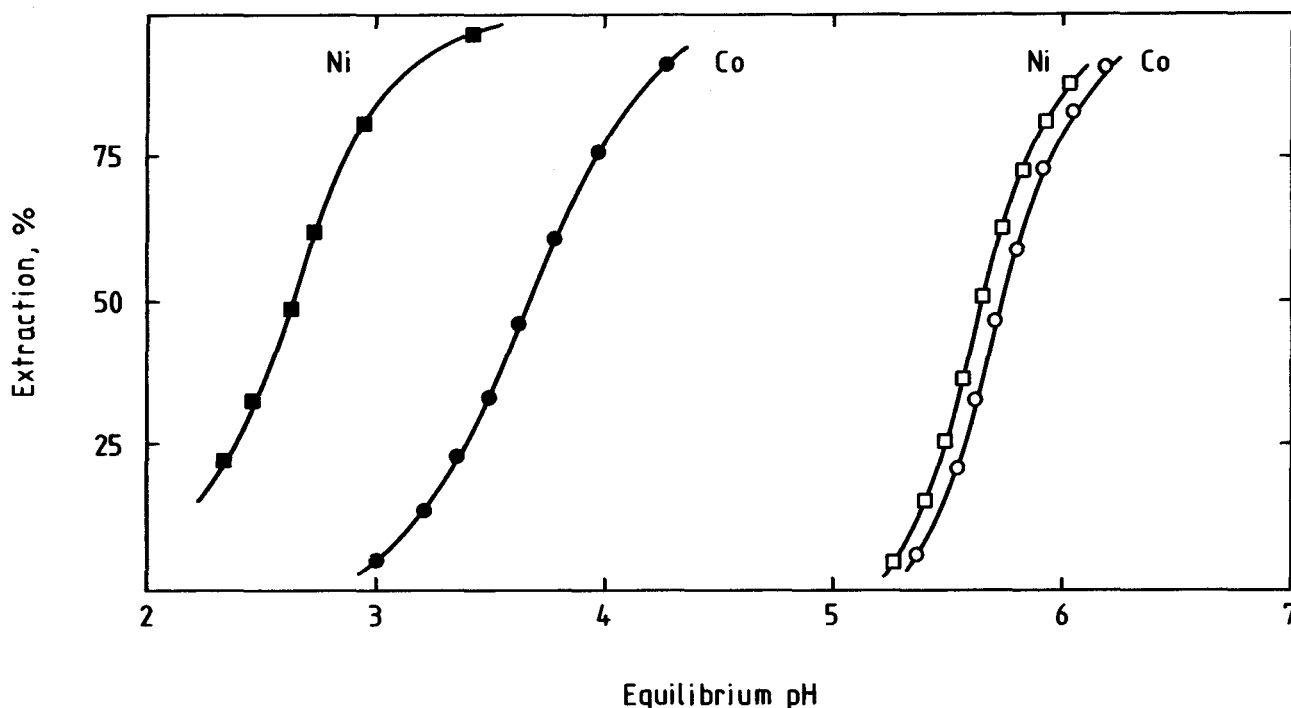
Fig. 8—Extraction of nickel and cobalt by 0,50 M di-isopropyl-salicylic acid (unshaded symbols) and by 0,50 M di-isopropyl-salicylic acid plus 1,0 M isodecanal oxime (shaded symbols) in xylene at 20°C. Initial aqueous phase: Ammonium sulphate, 40 g/l. Cobalt or nickel as sulphate, 3 g/l

sulphate solution by 0,50 M naphthenic acid (a cycloaliphatic carboxylic acid derived from crude petroleum) in xylene at 20°C is shown in Fig. 7. A very small separation (0,1 pH unit) between the extraction curves for the two metals is evident. In contrast, the corresponding curves in the presence of 1,0 M isotridecanal oxime show that the mixed extractant displays considerable selectivity for nickel over cobalt, a separation of 1,03 pH units being observed. Further advantage accrues from the use of the mixed-extractant system in that metal extraction occurs under considerably more acidic conditions than is the case when the carboxylic acid alone is used; for example, a shift of 2,6 pH units in the extraction curve for nickel is observed on the addition of 1,0 M isotridecanal oxime. It is known[8] that solubility losses of carboxylic acids to the aqueous phase are strongly dependent on pH. These losses become large at pH values where the degree of neutralization of the carboxylic acid (i.e. its conversion to the more soluble sodium or ammonium salt form) is appreciable. It is evident, therefore, that the use of non-chelating oximes in conjunction with carboxylic acids exerts a beneficial effect on the solubility losses of the latter by permitting metal extraction in a pH region in which the extent of neutralization of the carboxylic acid is negligible.

Further, variation of the carboxylic acid component of the extractant mixture enables metal extraction to be carried out under a wide range of pH conditions. Thus, for example, the use of a somewhat more acidic carboxylic acid such as di-isopropylsalicylic acid (pK_a=4,59

in 50 volume per cent propan-2-ol compared with pK_a=6,69 for naphthenic acid[3]) in conjunction with a suitable non-chelating oxime allows efficient extraction of nickel to be carried out at pH values in the region of 3,0, in contrast to the pH value of about 4,5 required for systems using naphthenic acid and an oxime (Fig. 8). Although di-isopropylsalicylic acid has been patented as a general metal extractant[9,10], it is clear from the extraction curves in Fig. 8 that this reagent is of no use on its own for the separation of nickel from cobalt.

TABLE IV

EXTRACTION OF NICKEL AND COBALT BY MIXTURES OF 0,50 M CARBOXYLIC ACIDS AND 1,00 M NON-CHELATING OXIMES IN XYLENE AT 20°C

Initial aqueous phase:
Ammonium sulphate, g/l   40
Nickel or cobalt as sulphate, g/l 2,95

Carboxylic acid	Oxime	$pH_{0,5}$		
		Ni	Co	Co–Ni
Naphthenic	Octanal	3,82	4,84	1,02
Naphthenic	Isotridecanal	3,81	4,84	1,03
Naphthenic	None	6,41	6,51	0,10
Di-isopropylsalicylic	Isodecanal	2,64	3,67	1,03
Di-isopropylsalicylic	Isodecanal*	3,12	4,14	1,02
Di-isopropylsalicylic	None	5,65	5,74	0,09

*0,50 M

The extraction results for the examples of mixtures of carboxylic acids and non-chelating oximes mentioned

above are presented in Table IV in terms of the $pH_{0,5}$ values for nickel and cobalt.

The results of experiments involving batch countercurrent extraction at 20°C with mixtures of naphthenic the cobalt product 0,48 and 0,24 per cent nickel for the systems based on naphthenic acid and on di-isopropylsalicylic acid respectively. Again, these specifications could readily be improved in practice by the inclusion of additional extraction or scrubbing stages.

TABLE V

BATCH COUNTERCURRENT EXTRACTION OF NICKEL BY 0,50 M NAPHTHENIC ACID PLUS 1,0 M ISOTRIDECANAL OXIME IN XYLENE AT 20°C

Initial aqueous phase:
Ammonium   sulphate, g/l   40
Cobalt   as   sulphate, g/l   5,15
Nickel   as   sulphate, g/l   5,20
Equilibrium pH in stages 2 to 4 4,3

Stage	Metal concentrations p.p.m.			
	Aqueous phase		Organic phase	
	Ni	Co	Ni	Co
1	5054	5245	5325*	50*
2	1441	5696	5179	145
3	125	5432	1600	536
4	27†	5001†	240	698

*Loaded organic phase
†Raffinate

TABLE VI

BATCH COUNTERCURRENT EXTRACTION OF NICKEL BY 0,50 M DI-ISOPROPYLSALICYLIC ACID PLUS 1,0 M ISODECANAL OXIME IN XYLENE AT 20°C

Initial aqueous phase:
Ammonium   sulphate, g/l   40
Cobalt   as   sulphate, g/l   3,00
Nickel   as   sulphate, g/l   2,89
Equilibrium pH in stages 2 to 4 3,25

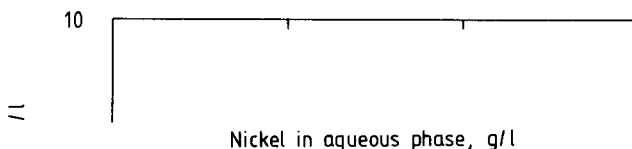| Stage	Metal concentrations p.p.m.			
	Aqueous phase		Organic phase	
	Ni	Co	Ni	Co
1	2630	3103	5710*	62*
2	930	3047	5453	163
3	136	3081	1980	438
4	7†	2889†	214	753

*Loaded organic phase
†Raffinate

Fig. 9—McCabe–Thiele construction for the extraction of nickel from ammonium sulphate (40 g/l) solution into 0,50 M naphthenic acid plus 1,0 M isotridecanal oxime in xylene at 20° C using an aqueous-to-organic ratio of 1:1 and an equilibrium pH value of 4,3

Nickel-stripping curves were drawn for a solution containing sulphuric acid (60 g/l), nickel (40 g/l) as sulphate, sodium sulphate (100 g/l), and boric acid (10 g/l), in simulation of a spent nickel electrolyte. The McCabe–Thiele construction for the system using naphthenic acid and isotridecanal oxime (Fig. 10) shows that complete stripping of nickel-loaded organic phases can be effected in two stages at an organic-to-aqueous ratio of 6:1. Advance electrolytes with a nickel content of up to 78 g/l at a pH value of 3,0 were obtained, indicating that only a small adjustment of pH would be required prior to electrowinning.
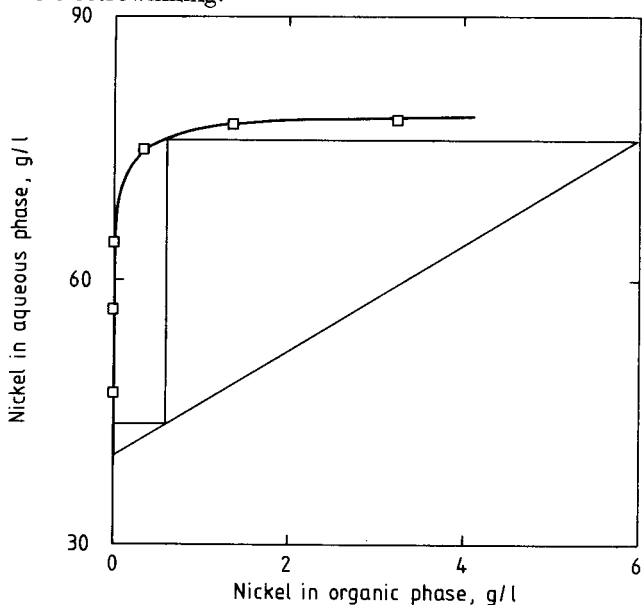

Fig. 10—McCabe–Thiele construction for the stripping of nickel from 0,50 M naphthenic acid plus 1,0 M isotridecanal oxime in xylene into a solution of sulphuric acid (60 g/l), sodium sulphate (100 g/l), boric acid (10 g/l), and nickel (40 g/l) as sulphate at 20° C using an organic-to-aqueous ratio of 6:1

As a further example of the potential usefulness of the novel nickel-selective systems, an investigation was made of the extraction of nickel (1,08 g/l) from a concentrated cobalt sulphate solution (53,2 g/l cobalt) in a simulation of a 'clean up' operation on a cobalt electrolyte. In a three-stage countercurrent process using a mixture of naphthenic acid (0,5M) and isotridecanal oxime (1,0 M) in xylene at an equilibrium pH value of 4,0 for each stage and an organic-to-aqueous ratio of unity, a raffinate containing nickel (0,01 g/l) and cobalt (51,6 g/l) was obtained. Such an electrolyte would be adequate for the electrowinning of cobalt cathodes of at least 99,98 per cent purity. Because of the very high aqueous cobalt concentration, a considerable amount of cobalt (1,65 g/l) was extracted into the loaded solvent together with the nickel (1,08 g/l), although this represents only a 3 per cent loss of cobalt in the initial electrolyte. The loaded metals could be stripped together and returned to the primary cobalt–nickel separation stage in the process. Alternatively, if no other outlet for nickel is incorporated in the flowsheet, the mixed-metal solution can be separated as in the example shown in Table V.

Finally, it is interesting to note that the mixed-extractant systems described here do not suffer from the slow extraction of nickel noted with previously reported systems based on mixtures of carboxylic acids and commercial chelating hydroxyoximes[11,12]. A further significant disadvantage of systems that incorporate chelating oximes[11,13] is the now well-known irreversible extraction of cobalt(III) complexes[14,15], which causes gradual 'poisoning' of the extractant. In contrast, the mixed-ligand complexes containing non-chelating oximes do not display any propensity towards oxidation, and cobalt-loaded organic phases were completely stripped, even after they had stood several months in contact with air.

Conclusions

Recently developed organophosphorus acid reagents (PC-88A, Cyanex 272) permit a more efficient separation of cobalt from nickel in sulphate solutions than was possible with the established extractant D2EHPA. Operation at ambient temperatures appears to be feasible with the new reagents, in contrast to the requirement of elevated temperatures for D2EHPA.

Novel reagents developed at Mintek and based on mixtures of carboxylic acids and non-chelating oximes show considerable potential in processes that require the selective extraction of nickel in the presence of cobalt.

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