

Useful resins for the selective extraction of copper, nickel, and cobalt

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SYNOPSIS

The loading and selective properties of a number of commercial and experimental resins developed for the extraction of base metals were evaluated. Particular applications that were considered included the extraction of copper from artificial dump liquors, the treatment of low-grade copper, nickel, and cobalt liquors, and the removal of nickel from a cobalt electrolyte. Reagents that showed promise were two experimental resins developed at Mintek containing pyridyl imidazole active groups and two Dow resins, XF 4195 and XF 4196.

SAMEVATTING

Die laai- en selektiewe eienskappe van 'n aantal kommersiële en eksperimentele harse wat vir die ekstraksie van onedelmetale ontwikkel is, is geëvalueer. Besondere gebruike wat oorweeg is, sluit in die ekstraksie van koper uit kunsmatige hoopvloeistowwe, die behandeling van laaggraadse koper-, nikkel- en kobaltvloeistof en die verwydering van nikkel uit 'n kobaltelektroliet. Reagense wat belofte ingehou het, was twee eksperimentele harse wat by Mintek ontwikkel is en die aktiewe groepe piridielimidiasool bevat, en twee Dow-harse, XF 4195 en XF 4196.

Introduction

Much interest has been shown lately in the presence of base metals – especially cobalt, nickel, and copper – in mine wastes and low-grade ores. The recovery of copper by the use of LIX and KELEX-type reagents from liquors obtained from dump leaching is well known. Recently¹ the successful separation of cobalt from nickel was achieved by the use of di(2-ethylhexyl) phosphoric acid. Although the solvent-extraction reagents work well for certain applications, problems may be encountered when the metals are to be recovered from liquors of low concentration, and the use of an ion-exchange technique may offer some advantages. The loss of reagents through entrainment – a drawback of solvent-extraction processes – is not a consideration in an ion-exchange process. The use of high-density resins in countercurrent ion-exchange (CIX) or resin-in-pulp processes would allow unclarified liquors to be treated.

The work described here was aimed originally at the development of resins selective for copper over iron(III) that could be used as an alternative to solvent extraction. More recently, cobalt and nickel have also received attention. A number of resins developed at Mintek and elsewhere may be of interest. The performance of the more suitable resins that were tested for particular applications will be discussed. The various factors that determined the approach to the design of selective resins for the extraction of base metals have been described elsewhere².

Experimental

Resins were obtained from suppliers or were prepared as previously described²⁻⁴.

Equilibrium Isotherms

Samples of the resin were contacted with different volumes of copper sulphate solution at a pH value of

2 (Fig. 1) or in 120 g/l H₂SO₄ or 100 g/l NH₃ (Fig. 2). The resins were washed with water and eluted completely with 10 per cent ammonia. The depleted copper solutions and eluates were analysed for copper.

In another set of tests (Fig. 3), the methods were similar to that described except that 0,02 M copper, nickel, or cobalt solution containing 0,5 M Na₂SO₃ was used and the pH value was maintained at 4 with NaOH.

Separation Factors

For the determination of $\alpha_{Cu/Fe(III)}$, samples of resin were contacted for 24 hours with an excess of a solution containing 1 g/l copper, 3 g/l iron(III), and 10 g/l magnesium as sulphates and with a pH value of 2. The resins were eluted completely with 120 g/l H₂SO₄ and 100 g/l NH₃ after being washed with 20 ml of water adjusted to pH 2 with H₂SO₄. Copper and iron in the eluate were determined, and the separation factors were calculated from the formula

$$\alpha_{Cu/Fe} = \frac{[\overline{Cu}][Fe]}{[Cu][\overline{Fe}]}$$

where $\overline{[M]}$ refers to metal on the resin and $[M]$ refers to metal in solution at equilibrium.

For the determination of α values for the other base metals, the procedure was similar to that described except that the solutions contained metals at a concentration of 1 g/l as sulphates and 10 g/l of total sulphate. For $\alpha_{Ni/Co}$, all except copper were present, and for $\alpha_{Co/Zn}$, $\alpha_{Co/Fe^{2+}}$ and $\alpha_{Co/Mn}$, only cobalt, zinc, iron(II), and manganese were present.

Removal of Nickel from Cobalt Electrolyte

In these tests, 0,44 g of resin was shaken with 50 ml of advance electrolyte containing 36,4 g/l of cobalt and 0,82 g/l of nickel. Samples of the solution were taken at intervals, and the nickel and cobalt values were determined. After a contact time of about 20 h, the resin was removed and eluted with 120 g/l H₂SO₄, and the cobalt and nickel values in the eluate were determined. The resin was then returned to the partially extracted solution, and the procedure was repeated until the nickel concentration was reduced to below 0,2 g/l.

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During the extractions, the pH values were maintained at between 4 and 5.

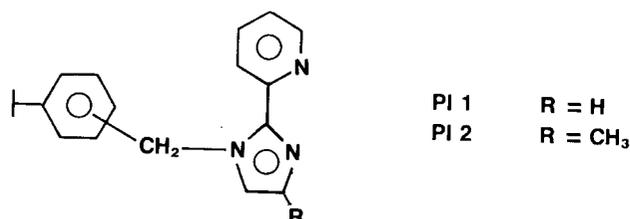
Results and Discussion

Copper from Dump-leach Liquors

The liquors dumped from the dump leaching of low-grade oxide ores contain copper at a concentration of about 0,5 to 5 g/l and iron(III) at similar or slightly higher levels. Sulphuric acid, which is normally used to leach this material, produces a liquor with a pH value in the region of 2. The required resin should therefore be able to load copper well at that pH value and have a good selectivity for copper against iron(III).

Where a solvent-extraction process is used to upgrade copper values, an electrolyte is obtained from which high-purity copper can be electrodeposited directly. It is therefore desirable that elution of the resin should also produce a suitable electrolyte. As the eluant (depleted electrolyte) will contain about 20 g/l of copper in sulphuric acid (120 g/l), it is necessary that the resin should be stripped by this solution and, furthermore, that the copper content of the electrolyte should be increased to more than 45 g/l during elution. If the maximum ferric ion content is 6 g/l in the electrolyte (to achieve a current efficiency of 77 per cent⁵) and the ratio of ferric ions to copper in the leach liquor is 3, a resin selectivity of 23 would be required.

Fig. 1 gives equilibrium isotherms for two experimental resins developed at Mintek⁴: PI 1 and PI 2. Copper sulphate solutions were used, and the pH value was maintained at 2. An attractive feature of the resins is that good loading is obtained at relatively low concentrations.



In order to obtain an idea of the loading behaviour of the resins in a typical plant solution they were contacted with an artificial pregnant liquor with a pH value of 2 that contained 1 g/l Cu²⁺, 3 g/l Fe³⁺, and 10 g/l Mg²⁺ as

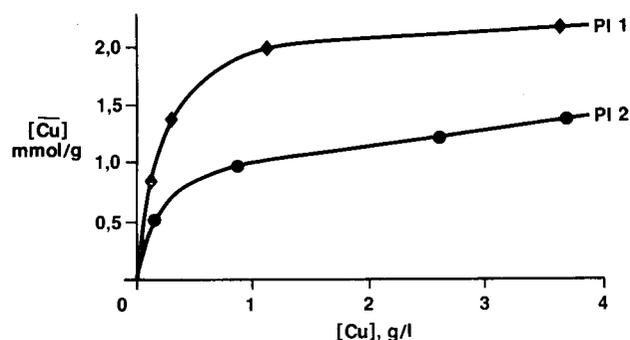
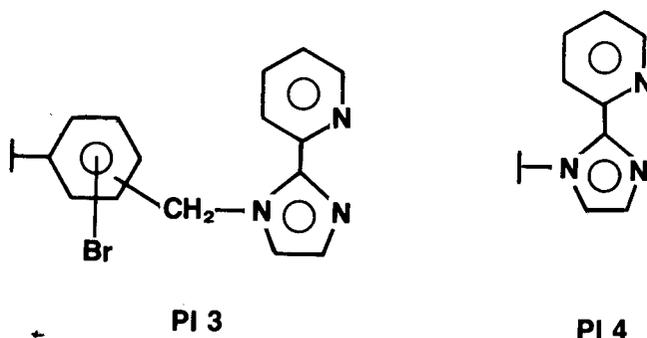


Fig. 1—Equilibrium isotherms for copper on pyridyl imidazole resins (pH = 2)

sulphates. A large excess of solution was used so that these concentrations also represented the equilibrium values. Table I gives the quantities of copper and iron(III) loaded, and the separation factors (α) for copper over iron for the same two resins and also a commercial DOW resin, XF 4196, a heavy resin, PI 3, and a more recently developed polyvinyl-based resin, PI 4.



The separation factors are sufficiently good to produce an electrolyte with 6 g/l ferric ions. However, if a better selectivity is required, the Fe³⁺ can be removed selectively by scrubbing with water. Copper is chelated to the resin, whereas iron as Fe(SO₄)₂⁻ forms an ion pair with the protonated amine groups. Water destroys the iron complex, allowing it to be eluted. An effective selectivity of 60 can be achieved in this way. A change in the physical nature of the resin matrix can also vary the

TABLE I
LOADING BEHAVIOUR OF COPPER-SELECTIVE RESINS

Resin	Metals absorbed at equilibrium		$\alpha = \frac{[\text{Cu}^{2+}][\text{Fe}^{3+}]}{[\text{Cu}^{2+}][\text{Fe}^{3+}]}$	Metal absorbed at equilibrium, mmol/g (20g/l Cu, 120g/l H ₂ SO ₄)
	mmol/g			
	Cu [mmol/g (mmol/ml)]	Fe [mmol/g]		
PI 1	1,4	(0,48)	27	1,6
PI 2	1,0	(0,28)	22	0,5
PI 3	0,7	(0,35)	25	—
(high density)				
XF 4196	1,3	(0,40)	14	0,5
PI 4	2,6	(0,80)	22	1,2

selectivity by a factor of more than 2. For example, various resins of the PI 1 type that were chemically identical but differed in porosity were found to possess different separation ratios. Table II illustrates this phenomenon. The porosities of the resins were changed by the use of different quantities of porogen during the preparation of the matrices.

TABLE II
EFFECT OF MACROPOROSITY ON THE SEPARATION RATIOS
OF COPPER-SELECTIVE RESINS

Porogen content ml/g	Separation factor $\alpha_{Cu/Fe}$
1,22	19
0,99	27
0,85	32

It may be desirable for a high-density resin to be used in a CIX process in which unclarified liquor is used. PI 3 (Table I) is such a reagent in which the active group is attached to a heavy-polymer matrix. This particular resin has a relative density of 1,31.

Fig. 2 illustrates the equilibrium isotherms for the PI 1, PI 2, and XF 4196 resins in 120 g/l sulphuric acid, and for PI 1 in 100 g/l ammonia. These results give an idea of how the resins will behave under elution conditions. PI 2 and XF 4196 behave similarly. A copper concentration in the electrolyte of at least 60 g/l can be achieved in a countercurrent elution. However, the copper content of the resins cannot be reduced to below 0,5 mmol/g if the eluant enters the column with more than 20 g of copper per litre.

Some workers⁶, using XF 4196 in a Higgins loop to recover copper from a dump-leach liquor, avoided this problem by first contacting the freshly loaded resin with copper-free eluant or barren acid, which is employed as a barrier to prevent copper in the spent electrolyte from being carried with the resin during a pulse-back in the loading section. In this way, the resin can be completely eluted.

The elution of PI 1 with sulphuric acid is poor. In fact, the PI 1 resin would probably load more copper from a depleted electrolyte solution (containing about 20 g of

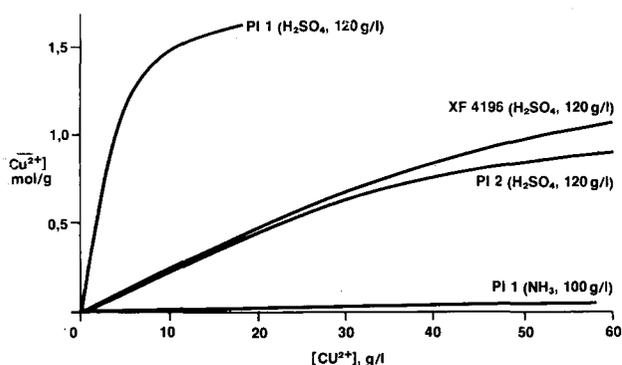


Fig. 2—Equilibrium isotherms for copper-selective resins in possible eluant solutions

copper and 120 g of sulphuric acid per litre—Table I) than it would from a pregnant solution. When the same active group is attached to a polyvinyl matrix (see PI 4 in Table I), the elution properties are greatly improved.

Good elution of PI 1 is possible with 100 g/l ammonia solution. Furthermore, the eluate is pure in copper since iron is not eluted by ammonia. There are a number of possibilities for the subsequent treatment of the ammoniacal solution for the recovery of copper.

- (i) The copper solution can be treated with sulphur dioxide to precipitate Cu(I) ammonium sulphite or similar intermediates. The precipitate can then be thermally disproportionated in water to copper powder⁷. If Chevreul's salt is precipitated from the ammonia liquor, it can be dissolved in water with acetonitrile and Cu(II), and the removal of acetonitrile by distillation yields copper powder⁸.
- (ii) The ammonia solution can be treated with hydrogen at $3,45 \times 10^3$ kPa and 190 °C, thereby reducing Cu(II) to copper powder⁹.
- (iii) Copper(II) ammine sulphate can be obtained and heated to remove NH_3 . The resulting copper sulphate is reduced to the metal either by electrowinning or by hydrogen reduction to copper powder¹⁰.
- (iv) Copper can be extracted from ammine solutions with LIX and KELEX-type reagents, which, in turn, can be stripped with sulphuric acid to yield a solution suitable for a subsequent electrowinning step¹¹.

Base Metals in Mine Wastes

Some interest has been shown recently in copper, nickel, and cobalt in mine wastes. Although the last two metals are the more valuable, there is no resin that is selective for nickel and cobalt over copper. Any copper in solution has therefore to be recovered as well. The requirements that should be met by a resin depend on the nature of the liquor. The type of solution of interest in the present work contained copper, nickel, cobalt, zinc, manganese, iron(II), and uranium at levels between 0,2 and 0,8 g/l in a sulphate medium at a pH value of 2. However, it was acceptable for this value to be raised.

Uranium can be removed by a strong-base resin in the conventional way, after which the liquor can be treated in two ways.

- (i) Copper, nickel, and cobalt can be extracted together by the use of a non-selective resin. The eluted metals can then be separated by solvent extraction or with selective resins.
- (ii) Selective resins can be used to remove the metals consecutively. This is the approach that was taken in the present investigation.

Of the resins that were available for testing, an iminodiacetate type (Bayer TP 207), DOW XF-4195, XF 4196, and three of the resins developed at Mintek (DETA, PI 1, and PI 4) were found to be the most suitable.

From the stability constants for the metal-ligand complexes that are expected to be formed on absorption, it can be predicted that TP 207, XF 4195, XF 4196, PI 1, and PI 4 will load copper well at the pH value of the liquor. However, if the pH is raised to 4, DETA should load well and give a much better selectivity than the

others. In practice, it was found, from the equilibrium loading of the resins at a solution concentration of 1 g of the metals per litre and at a pH value of 4 (in sulphate), that DETA has a selectivity for copper over nickel of more than 100 (Table III). The capacity of DETA is not as high as that of the other resins, but it should be borne in mind that DETA is an experimental resin and its capacity can probably be improved by an increase in the active-group content. PI 4 also had a fairly good selectivity with the advantage of a much higher capacity.

TABLE III
COPPER LOADING AND SELECTIVE BEHAVIOUR OF RESINS
FOR BASE METALS

Resins	Copper loading mmol/g	$\alpha_{Cu/Fe}$
DETA	1,05	130
TP 207	1,61	9
XF 4195	1,24	6
XF 4196	2,00	12
PI 1	1,54	10
PI 4	3,20	31

DETA is not suitable for the absorption of nickel and cobalt. It can be predicted that all of the other resins will absorb nickel well, but XF 4195, XF 4196, PI 1, and PI 4 should have the advantage of being more selective for nickel over cobalt. Table IV gives the results of loading experiments similar to those described in Table III, except that copper was omitted from the metal solution. The results were found to be as expected except that resin PI 4 has a better selectivity and higher capacity than the others.

TABLE IV
NICKEL LOADING AND SELECTIVE BEHAVIOUR OF RESINS
FOR BASE METALS

Resin	Nickel loading mmol/g	$\alpha_{Ni/Co}$
TP 207	0,89	3
XF 4195	1,10	13
XF 4196	1,20	10
PI 1	0,82	14
PI 4	1,30	55

Once the copper and nickel have been extracted, cobalt would have to be separated from zinc, iron(II), and manganese. Again, the results given in Table V can be qualitatively predicted. Although PI 1 has a slightly lower capacity than most of the other resins, it is the only one that is selective.

It is conceivable from the foregoing results (Tables

TABLE V
COBALT LOADING AND SELECTIVE BEHAVIOUR OF RESINS
FOR BASE METALS

Resin	Cobalt loading mmol/g	$\alpha_{Co/Zn}$	$\alpha_{Co/Fe^{2+}}$	$\alpha_{Co/Mn}$
TP 207	0,82	1	5	4
XF 4195	0,82	1	—	41
XF 4196	0,78	3	5	115
PI 1	0,59	23	35	590
PI 4	0,50	6	21	168

TABLE VI

THE REMOVAL OF NICKEL FROM COBALT ADVANCE ELECTROLYTE WITH RESINS XF 4195 AND PI 4

Duration h	Metal in electrolyte, g/l*				Metal on resin, mg/g			
	XF 4195		PI 4		XF 4195		PI 4	
	Ni	Co	Ni	Co	Ni	Co	Ni	Co
First extraction								
1,5	0,78	35,5	0,66	36,8				
4	0,71	35,2	0,56	35,9				
19	0,65	36,1	0,47	35,9	19	84	34	48
					19†		39†	
Second extraction								
1,5	—	—	0,31	34,0				
4,5	0,47	33,0	0,28	34,0				
20	0,40	32,7	0,23	33,3	23	76	27	68
					28†		27†	
Third extraction								
4,5	—	—	0,09	31,3				
21	0,20	30,5	0,07	31,2	—	—	14	70
							18†	
Fourth extraction								
4,5	—	—	0,03	30,0				
24	—	—	0,03	30,0				
Fifth extraction								
4,5	—	—	0,015	28,1				

*At time 0, Ni = 0,82 g/l, Co = 36,4 g/l

†Values obtained from the analysis of Ni removed from solution

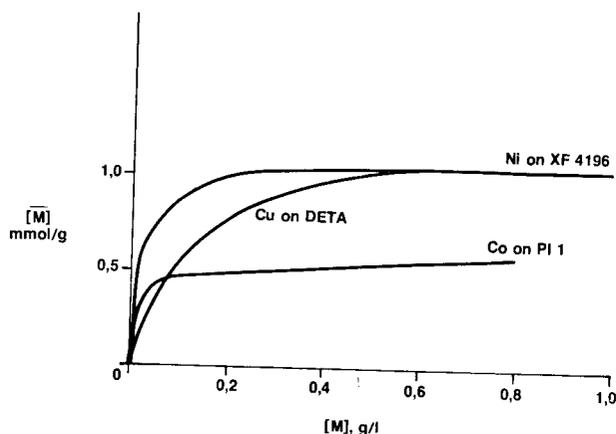


Fig. 3—Equilibrium isotherms for copper on DETA, nickel on XF 4196, and cobalt on PI 1 (pH = 4)

III, IV, and V) that the separation of copper, nickel, and cobalt from one another and from other base metals can be carried out in a series of columns by the use of the resins DETA or PI 4 for copper, PI 4 for nickel, and TP 207, XF 4195, XF 4196, or PI 1 for cobalt. The eluates, which should all be considerably more than 90 per cent pure, would probably require to be upgraded further by ion exchange, solvent extraction, or selective precipitation if the metals are to be electrowon. Equilibrium isotherms on some of the more suitable resins for copper, nickel, or cobalt at pH 4 are given in Fig. 3. Relatively good metal loadings were obtained at low concentrations.

Removal of Nickel from Cobalt Electrolyte

For the electrowinning of cobalt it may be necessary to reduce the concentrations of nickel in the advance electrolyte in order to achieve the required purity of cobalt metal.

From the foregoing work (Table IV), resins PI 4 and XF 4195 would appear to be candidates for this purpose. In a comparative test, equal quantities of resins were

used to extract nickel from a real electrolyte solution. After a contact time of one day, the resin was eluted and returned to the partially extracted solution. This procedure was repeated until the nickel content of the electrolyte was reduced to less than 0,2 g/l with XF 4195 and 0,02 g/l with PI 4 to obtain sufficiently pure cobalt deposits.

The results of the tests are given in Table VI. The superior performance of PI 4 compared with XF 4195 can be ascribed to the higher inherent capacity of the resin and its greater selectivity. The average particle size of PI 4 was somewhat smaller than that of XF 4195. This could be important if the kinetics of loading are diffusion controlled.

Conclusion

Of the resins tested, two experimental resins developed at Mintek containing pyridyl imidazole active groups and two DOW resins, XF 4195 and XF 4196, showed most promise for the selective extraction of copper, nickel, and cobalt.

Acknowledgements

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