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Ion exchange studies on zinc-rich waste liquors

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Abstract

This paper reports on the use of ion exchange resins for the recovery of zinc, in a relatively pure form, from a zinc-rich industrial waste liquor and from model zinc-rich solutions. Lewatit OC-1026 resin was found to have good zinc selectivity, whilst the chelating resins Purolite S-930, Metalfix Chelamine and Metalfix Chelosolve showed greater selectivity for the major contaminant ions, Cu, Cd and Pb. These resins however, showed some loss of their functional groups after a small number of repeat cycles. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal separation and recovery is used mainly for either obtaining metals from low grade ores or for purification of water systems [1,2]. Both of these are essentially low concentration systems and a number of methods have been developed for the separation and recovery of the required metals, generally based upon hydrometallurgical (both chemical and biological) and electrometallurgical methods [3,4].

A third area with very different requirements is that of the recovery of metals from industrial wastes [5,6] with the aim of recycling one or more of the metal components. This entails separation of a relatively pure form (requirements vary) of a metal from media which are metal-rich, generally highly acidic and variable in composition, both in terms of cations and anions. Examples include copper-rich etchant waste from the electronics industry and waste acids from the metal finishing industry, containing metals such as copper, chromium, iron, nickel and zinc [7–9]. This field has been less well addressed than the other two, but the rising costs and challenges of waste disposal, for

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example introduction of landfill taxes and increasing restrictions on environmental disposal, makes this an area demanding urgent attention.

For metal recovery from acidic metal-rich liquors, aspects that must be addressed are the overall costs involved and the minimisation and fate of any wastes generated [10]. For any separations developed to be commercially viable three key factors need to be considered. Firstly, whether the method is robust enough to cope with variations in impurity ion levels between batches of waste liquor. By the very nature of these wastes, it is not unusual for the levels of metal ions in the system to fluctuate over wide ranges. Secondly, whether the separation process produces the metal in a form that is commercially useful. Finally, whether the overall process is cost effective, taking into account the balance between the cost of recovery against the cost of conventional disposal and the market value of the recovered metal. This paper reports on studies aimed at the recovery of zinc, in as pure a form as possible, from industrial zinc-rich waste liquors. Solvent extraction probably offers the best selectivity, and zinc selective reagents have been developed [11,12]. For many companies, however, the cost of installing plant for large scale solvent extraction and subsequent recovery of the solvent makes this an expensive procedure. For this reason we have re-investigated ion exchange as an alternative method. The initial work reported here was carried out using model solutions to screen and identify the best ion exchange and chelating resins to be used. This generated selectivity ratios for the various metals for each of the resins. From these data, work then progressed to using the resins and electrowinning to investigate the separation and purification of zinc from a zinc-rich waste liquor.

2. Experimental

2.1. Reagents and solutions

All model solutions were prepared from the metal chloride salts, i.e., zinc chloride (Fisher, AR grade), copper(II) chloride dihydrate (BDH, AR grade), lead chloride (BDH, Laboratory reagent), cobalt(II) chloride hexahydrate (BDH, General purpose reagent), nickel(II) chloride hexahydrate (BDH, AR grade), cadmium chloride (Aldrich, 99.99 + %) and iron(II) chloride (BDH, Technical grade). Solutions were made with fresh double-distilled water. The zinc-rich waste liquor was an industrial zinc chloride liquor donated by a European-based company; details of its composition are given in Table 1.

The resins used were chosen to cover a range of the different types available, i.e., strong and weak acid cation exchangers, various chelating resins and a Levextrel resin [13]. Details of the resins are given in Table 2.

2.2. Ion exchange procedure

The resins were packed into glass columns (typical dimensions: 30 cm length, 1 cm internal diameter) and washed through thoroughly with doubly distilled water prior to use. Elution of metals was achieved by the addition of 2 M hydrochloric acid to the

Table 1
Composition of the zinc-rich waste liquor sample[a]

Metal	Concentration (mg l^{-1})
Zn	480 000
Pb	563
Cu	3
Ni	58
Co	1
Cd	9
Fe	1

[a] Measured pH of 1.82 (expected pH in range of 2 to 4).

column followed by doubly distilled water. These combined washings were collected for analysis in each case. Flow rates of approximately 5 ml min^{-1} were used. All resins were used in the ionic form as supplied, except Purolite S-930 which required conversion to the H^+ form before use. For each experiment the approximate volume of resin required was first calculated from the respective metal concentrations so as to achieve full capacity loading.

2.3. Electrowinning

The electrowinning studies were performed using a single compartment cell arrangement, based on a design published elsewhere [14], with stainless steel as the cathode and graphite sheet as the anode. The total cathode surface area was 9×10^{-3} m^2, with an anode–cathode spacing of 2.5 cm. A total deposition time of 8 h was used, with an electrolyte volume of 500 ml, an air sparge over the cathode surface of ~ 1 l min^{-1} and a current density of 100 A m^{-2}. The studies were carried out at room temperature. This

Table 2
Summary of resins used in this work

Resin	Supplier	Type	Functional Group
Chelex 100	Sigma	chelating	iminodiacetic
Duolite C-467	Supelco	chelating	aminophosphonic
Duolite GT-73	Supelco	chelating	thiol
Diaion CR-20	Supelco	chelating	polyamine
Lewatit OC-1026	Bayer	Levextrel	DEHPA[a]
Lewatit TP-207	Bayer	chelating	iminodiacetic
Metalfix Chelamine	Fluka	chelating	polyamine
Metalfix Chelosolve	Fluka	chelating	polyamine–acetic
Purolite C-100H	Purolite	strong acid	sulfonate
Purolite C-105	Purolite	weak acid	carboxylic
Purolite C-160	Purolite	strong acid	sulfonate
Purolite S-930	Purolite	chelating	iminodiacetic

[a] Di(2-ethylhexyl)phosphoric acid.

procedure was repeated with solutions which had been pretreated by ion exchange to reduce the amount of some of the metal impurities. It has been claimed that such pretreatments can improve the current efficiency of the electrowinning process [15].

2.4. Analyses

Analysis by atomic absorption spectroscopy (AAS) was performed using an Instrumentation Laboratory 151 spectrometer, with an air/acetylene flame and the appropriate hollow cathode lamps. The wavelengths used for determining the various elements were (in nm): Zn 213.9, Cu 324.7, Pb 217.0, Ni 232.0, Co 240.7, Cd 228.8 and Fe 248.3. Calibration solutions were prepared from 1000 mg l^{-1} stock solutions of the appropriate elements (BDH Spectrosol or equivalent).

Analysis by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was performed using a Perkin-Elmer Plasma 40 spectrometer. The emission wavelengths used for the determining the various elements were (in nm): Zn 213.856, Cu 324.754, Pb 261.418, Ni 221.647, Co 238.892, Cd 214.438 and Fe 238.204 nm. Calibration solutions were the same as used for the AAS measurements.

X-ray fluorescence (XRF) measurements were made using an Oxford Instruments ED-2000, operating in semi-quantitative mode. Samples were pressed into briquettes using boric acid (BDH, AR grade).

3. Results and discussion

3.1. Model solutions

A model solution containing zinc (480 g l^{-1}) and copper (300 mg l^{-1}) was prepared from the corresponding metal chloride salts. This model solution accounted for the two components of the zinc-rich waste liquor that present the greatest challenge in separation. The metal ions bound by the resins were eluted and the eluate composition determined by AAS. From the results, the mole ratios of zinc to copper were calculated to give an indication of the selectivity, if any, of each resin towards the metals. The ratios are summarised in Table 3; for no selectivity towards either zinc or copper Zn/Cu = 1555/1. From this study the best resins, in terms of selectivity for zinc, were Lewatit OC-1026, Purolite C-105 and Purolite C-160.

A second model solution containing zinc (480 g l^{-1}), lead (1000 mg l^{-1}) and copper (300 mg l^{-1}) was prepared. This model solution accounted for the three highest concentration metals in the zinc-rich waste liquor. The metal ions bound by the resins were eluted and the eluate composition determined by AAS. From the results, the mole ratios of zinc to copper and zinc to lead were calculated to give an indication of the selectivity, if any, of each resin towards the metals. The ratios are summarised in Table 4; for no selectivity towards any one of the metal ions Zn/Cu = 1555/1 and Zn/Pb = 1521/1. From this study the best resins, in terms of selectivity for zinc, were Lewatit OC-1026, Purolite C-100H and Purolite C-160.

Table 3
Mole ratios of metals bound from high zinc-low copper model solution[a]

Resin	Zn/Cu
Chelex 100	101
Diaion CR-20	135
Duolite C-467	243
Duolite GT-73[b]	578
Lewatit OC-1026[c]	∞
Lewatit TP-207	151
Metalfix Chelamine	129
Metalfix Chelosolve	341
Purolite C-100H	790
Purolite C-105	2342
Purolite C-160	1715
Purolite S-930	65

[a] Initial ratio Zn/Cu = 1555.
[b] Incomplete copper recovery.
[c] Copper level below limit of detection.

3.2. Zinc-rich waste industrial liquor

The composition of the liquor determined by AAS is given in Table 1. These data are for one sample of waste liquor, however, since waste by its very nature is variable, other batches will differ in composition. The upper limits for impurity levels in these waste liquors are (in mg l^{-1}): lead 1000, copper 300, nickel 150, cobalt 100, cadmium 1000 and iron up to 5 mg l^{-1} (these figures were quoted by the industrial company that supplied the waste liquor).

Table 4
Mole ratios of metals bound from zinc–lead–copper model solution[a]

Resin	Zn/Cu	Zn/Pb
Chelex 100	55	199
Diaion CR-20	43	410
Duolite C-467	448	655
Duolite GT-73[b]	113	50
Lewatit OC-1026[c]	∞	∞
Lewatit TP-207	105	578
Metalfix Chelamine	5	5
Metalfix Chelosolve	54	48
Purolite C-100H	1033	2000
Purolite C-105	53	87
Purolite C-160	749	742
Purolite S-930	45	171

[a] Initial ratios Zn/Cu = 1555, Zn/Pb = 1521.
[b] Incomplete copper recovery.
[c] Copper and lead levels below limits of detection.

Table 5
Mole ratios of metals bound from zinc-rich waste liquor by the more zinc selective resins[a]

Resin	Zn/Pb	Zn/Ni	Zn/Cd
Lewatit OC-1026[b]	51 533	∞	∞
Purolite C-100H	5153	13 225	658 198
Purolite C-160	6549	20 402	356 575

[a] Initial ratios Zn/Pb = 2716, Zn/Ni = 7181, Zn/Cd = 82 538.
[b] Nickel and cadmium levels below limits of detection.

The first approach towards purification of the zinc-rich waste liquor was to attempt to quantitatively remove the zinc to leave behind a solution of the impurity metals. This was deemed to be the most straightforward approach since it focused on the separation of a single metal ion. Using the three resins showing the most selectivity for zinc, the approximate volume of each required to remove the zinc content from an aliquot of the zinc-rich waste liquor was calculated. The metal ions bound by the resins were eluted and the eluate composition determined by AAS. From the results, the mole ratios of zinc to the three highest level impurity ions (lead, nickel and cadmium) were calculated. The ratios are summarised in Table 5; for no selectivity towards any one of the metal ions, Zn/Pb = 2716/1, Zn/Ni = 7181/1 and Zn/Cd = 82 538/1. From this study, the resin showing the greatest zinc selectivity over lead, nickel and cadmium was Lewatit OC-1026.

The second approach towards purification of the zinc-rich waste liquor was to attempt removal of the majority of the impurity metals to leave behind a relatively pure zinc chloride liquor. The outcome of this approach was less predictable since the effect of variation in impurity levels between samples of the liquor on the selectivities towards the metals by the resins was not known. Using the four resins showing the least zinc selectivity, the approximate volume of each resin required to remove the impurity metal content from an aliquot of the zinc-rich waste liquor was calculated. The metal ions bound by the resins were eluted and the eluate composition determined by AAS. From the results, the mole ratios of zinc to the three highest level impurity ions (lead, nickel and cadmium) were calculated. The ratios are summarised in Table 6; for no selectivity towards any one of the metal ions, Zn/Pb = 2716/1, Zn/Ni = 7181/1 and Zn/Cd = 82 538/1. From the results, Purolite S-930 shows the least selectivity for zinc over lead. Metalfix Chelamine and Metalfix Chelosolve show similar low selectivities, however

Table 6
Mole ratios of metals bound from zinc-rich waste liquor by the least zinc selective resins[a]

Resin	Zn/Pb	Zn/Ni	Zn/Cd
Chelex 100	1540	4178	52 172
Metalfix Chelamine	354	3210	51 812
Metalfix Chelosolve	699	936	63 416
Purolite S-930[b]	210	1873	∞

[a] Initial ratios Zn/Pb = 2716, Zn/Ni = 7181, Zn/Cd = 82 538.
[b] Cadmium level below limit of detection.

Table 7
Mole ratios of metals bound by resins from modified zinc-rich waste liquor[a]

Resin	Zn/Pb	Zn/Cu	Zn/Co	Zn/Ni	Zn/Cd
Lewatit OC-1026[b]	3716	1857	10 555	∞	235 197
Purolite S-930[c]	691	48	∞	∞	22 282

[a] Initial ratios Zn/Pb = 2716, Zn/Cu = 1555, Zn/Co = 4326, Zn/Ni = 7181, Zn/Cd = 82 538.
[b] Nickel level below limit of detection.
[c] Cobalt and nickel levels below limits of detection.

both gave rise to coloured eluates and subsequent analysis indicated the partial loss of the chelating group from each resin.

The sample of zinc-rich waste liquor supplied for this work had copper and cobalt levels towards the lower limits of the possible ranges. To study the effect of varying impurity levels, copper and cobalt levels were increased to 300 and 100 mg l^{-1}, respectively, by the addition of the corresponding metal chlorides to the zinc-rich waste liquor.

Lewatit OC-1026 and Purolite S-930 were studied with the modified process liquor with the aim of investigating how the binding of the various metals would be affected. The same procedures were adopted as for the studies with the zinc-rich waste liquor as supplied. The mole ratios of each of the impurity metals to zinc were then calculated and the results are summarised in Table 7. For no selectivity towards any one of the metal ions, Zn/Pb = 2716/1, Zn/Cu = 1555/1, Zn/Co = 4326, Zn/Ni = 7181/1 and Zn/Cd = 82 538/1. Overall, Lewatit OC-1026 still shows a selectivity for zinc over the impurity metals, and Purolite S-930 shows a preference for lead, copper and cadmium over zinc although no cobalt or nickel were detected. Not surprisingly, it can be seen that increasing levels of impurity ions in the zinc-rich waste liquor causes the mole ratios of metals bound by the two resins to change due to the presence of additional competing ions.

3.3. Ion exchange as a pretreatment stage for zinc electrowinning

For this study, the previous methods were combined to investigate the effect of using an ion exchange step for the pretreatment of an electrolyte prior to electrowinning to

Table 8
Composition of the simulated zinc-rich waste liquor[a]

Metal	Concentration (mg l^{-1})
Zn	31 200
Pb	575
Cu	230
Ni	80
Co	50
Cd	73
Fe	3

[a] Measured pH of 1.86.

Table 9
Composition of electrowon deposits: no pretreatment of electrolyte

	Time (h)	Concentration of metal in electrowon deposit (wt.%)							
		Zn	Pb	Cu	Cd	Ni	Co	Fe	Total
Study 1	4	80.07	10.83	3.60	0.11	1.15	0.03	0.02	95.82
	8	93.98	1.04	1.14	a	0.12	0.03	0.11	96.42
Study 2	4	77.30	11.03	3.43	0.11	1.10	0.03	0.05	93.06
	8	87.41	0.92	0.41	a	627	0.02	0.06	88.88

[a] Levels below 0.01%.

remove impurity metals. It was initially decided to use a simulated industrial waste liquor, containing the same impurity metals as the zinc-rich waste liquor but with lower levels of zinc. The liquor was prepared using the metal chloride salts. Analysis of the simulated waste liquor using ICP–AES gave the data shown in Table 8.

3.3.1. *Electrowinning without pretreatment*

Samples of deposited material were collected after 4 and 8 h electrowinning of the simulated waste liquor. The study was carried out twice under the same conditions to investigate the reproducibility of the electrowinning process. The composition of the deposits, as determined by XRF analysis, are given in Table 9. Current efficiencies for the electrowinning were calculated as 71.2% for study 1 and as 64.8% for study 2.

3.3.2. *Electrowinning with pretreatment*

For the pretreatment step, the simulated zinc-rich waste liquor was passed through a column containing Purolite S-930 (H^+ form) prior to electrowinning. Purolite S-930 was selected on the basis of its low selectivity towards zinc as demonstrated previously. As before, samples of deposited material were collected after 4 and 8 h and the study was carried out twice under the same conditions to investigate the reproducibility of the combined ion exchange-electrowinning process. The composition of the deposits, as determined by XRF analysis, are given in Table 10. Current efficiencies for the electrowinning were calculated as 64.2% for study 1 and as 74.4% for study 2.

Table 10
Composition of electrowon deposits: ion exchange pretreatment of electrolyte

	Time (h)	Concentration of metal in electrowon deposit (wt.%)							
		Zn	Pb	Cu	Cd	Ni	Co	Fe	Total
Study 1	4	77.58	7.81	0.03	0.11	0.15	0.02	0.03	85.72
	8	81.19	0.23	0.02	a	0.07	a	0.04	81.55
Study 2	4	82.01	9.55	0.06	0.13	0.16	0.02	0.10	92.04
	8	95.58	0.49	0.01	a	0.11	a	0.04	96.24

[a] Levels below 0.01%.

4. Conclusions

Of all the resins studied, Lewatit OC-1026 showed the greatest selectivity for zinc. Fortunately, the waste liquor has low levels of iron which would otherwise be extracted in preference [16]. The selectivity for zinc mirrors work carried out by others using resins containing DEHPA [17,18].

For impurity removal, Purolite S-930 performed well, although the removal of such a range of impurity metal ions would benefit more from a mixed resin bed, rather than using a single resin. Metalfix Chelamine and Metalfix Chelosolve were also found to be efficient but suffered from loss of their chelating groups, Lewatit OC-1026 was also found to lose some of the DEHPA content after a few repeat cycles; these observations possibly reflect the hostile nature of these metal-rich liquors.

The introduction of an ion exchange pretreatment stage for the simulated zinc waste liquor prior to electrowinning, although removing the majority of the copper content and reducing levels of lead and cadmium, did not produce any large gain in current efficiency as has been suggested elsewhere [15]. An unfortunate side effect of using a stainless steel cathode was the observation of higher iron levels in the deposited material and electrolyte, indicating corrosion of the cathode by the simulated waste liquor. An advantage of using ion exchange resins over solvent extraction in connection with zinc electrowinning is the removal of the carry-over of any organic reagents or impurities to the electrowinning cell which themselves can affect the quality of deposition [19,20].

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