Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation and Removal of Cobalt and Zinc from Chloride Solution by Indion BSR—A Chelating Resin

Archana Agrawal[a]; K. K. Sahu[a]; B. D. Pandey[a]
[a] Non Ferrous Process Division, National Metallurgical Laboratory, Jamshedpur, India

Online publication date: 08 July 2010

To cite this Article Agrawal, Archana , Sahu, K. K. and Pandey, B. D.(2005) 'Separation and Removal of Cobalt and Zinc from Chloride Solution by Indion BSR—A Chelating Resin', Separation Science and Technology, 39: 10, 2373 — 2388
To link to this Article: DOI: 10.1081/SS-120030783
URL: http://dx.doi.org/10.1081/SS-120030783

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 10, pp. 2373–2388, 2004

Separation and Removal of Cobalt and Zinc from Chloride Solution by Indion BSR—A Chelating Resin

Archana Agrawal,* K. K. Sahu, and B. D. Pandey

Non Ferrous Process Division, National Metallurgical Laboratory, Jamshedpur, India

ABSTRACT

Ion-exchange removal of zinc and cobalt from aqueous solutions on Indion BSR, an indigenous chelating resin, was studied in detail. The percentage removal of zinc and cobalt was examined by varying experimental conditions, viz., dosage of adsorbent, pH of the solution and contact time, metal concentration in aqueous feed, and temperature. It was found that more than 95% removal of both the metals was achieved under optimum conditions. The loading capacity for zinc and cobalt under optimized conditions was found to be 4.27 g Zn/100 g resin and 6.15 g Co/100 g resin with a feed concentration of 2 g/L each. Effect of various salts like sulfate, carbonate and chloride of sodium, and ammonium were also studied. Separation of both these metals from a

*Correspondence: Archana Agrawal, Non Ferrous Process Division, National Metallurgical Laboratory, Jamshedpur 831007, India; E-mails: archana_nml03@yahoo.com or archana@nmlindia.org.

DOI: 10.1081/SS-120030783
0149-6395 (Print); 1520-5754 (Online)

binary mixture was also studied. Under optimized condition this resin was found to have more affinity for Zn than Co, indicating the feasibility of zinc separation from cobalt. The studies showed that this chelating resin could be used efficiently for the removal and separation of cobalt and zinc from chloride solutions.

Key Words: Removal/separation; Ion-exchange resin; Cobalt; Zinc; Mixed system.

INTRODUCTION

Need of a specific system for the extraction and separation of strategic metals has led to the development of newer techniques. Thus, new solid adsorbents, liquid extractants, and ion-exchange resins were developed for different applications.[1] Ion exchange in industry is increasingly used because it requires simple equipment, has minimum problems of phase disengagement and reagent losses, and above all, it is easy to operate.[2,3] The conventional cation exchange resins have disadvantages in recovering metal ions due to their poor selectivity, and thus find limited use in metal separation. In order to overcome these difficulties, the development of various chelating and solvent impregnated resins and their applications in processes involving metal extraction, separation, and recovery with significantly improved efficiency, high selectivity, fast kinetics, high mechanical strengths and toughness of the exchanger particles for a wide range of chemical species[4–7] have been extensively investigated. In the past decade there has been a spurt in the usage of ion exchangers in the hydrometallurgy of copper, nickel, zinc, etc., and in the preparation of high purity inorganic compounds.[8–13] The most common methods for the removal of heavy metals are ion exchange and chemical precipitation. The main advantages of ion exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced, and meeting strict discharge specifications. In ion-exchange systems, polymeric resins are usually employed.[14–16] With the depletion of primary ores of cobalt, zinc, and other transition metals, recovery from secondary sources like electronic scraps, spent catalysts, industrial wastes and by products, and liquid effluents with high chloride concentrations, etc. requires the development of specific separation technology. To our knowledge systematic investigation of the effect of operating parameters on the separation characteristics of the metal ions in a batch mode using Indion BSR was not yet reported. Hence, the objective of this work is the extraction of Zn (II) and Co (II) from chloride medium using indigenously available chelating resin having a macroporous structure. It has a cross-linked polystyrene matrix containing aminophosphonic acid as the functional group. Presently this resin is being used mostly in chloralkali plants and in production of high purity brine,[17] but its application in metal separation has not been explored. Hence, this work presents some interesting studies on metal extraction in a batch mode with the synthetic solutions of zinc and cobalt at various conditions like variation in aqueous feed concentration, weight of resin, pH of the feed solution, time of resin contact with metal-containing solution, and temperature of the solution, with a view of its use in cobalt and zinc separation from cobalt cake generated during the processing of sea nodules.[18] In addition, the dependence of separation factor of zinc to cobalt on experimental conditions was also discussed.

EXPERIMENTAL

Materials and Methods

Indion BSR, a chelating resin, (M/s Ion Exchange India Ltd, Mumbai) was used in this study. The physical properties and specifications of the resin, as reported by the suppliers, are shown in Table 1. The resin as obtained was washed with distilled water and converted into sodium form using 0.1 M NaOH solution. After the conversion was complete, the resin was washed thoroughly with distilled water to remove free alkali. It was then dried at 50°C and stored in an airtight container for further use.

Table 1. Characteristics of Indion BSR cation-exchange resin.

Number	Physical/chemical characteristics	Values
1	Physical form	Uniform particle size spherical beads
2	Matrix type	Cross-linked polystyrene
3	Functional group	Amino phosphonic
4	Standard ionic form	Na^+
5	Particle size range (mm)	0.4–1.0
6	% Moisture	55–65
7	Maximum operating temperature (°C)	70
8	Total exchange capacity (meq/mL)	1.2

Source: Information provided by the manufacturer.

Stock solutions of 10 g/L of Zn(II) and Co(II) were prepared by dissolving the corresponding chloride salts (Merck, AR grade) in distilled water and were standardized by EDTA titration.[19] Other salts like NaCl, NH_4Cl, Na_2SO_4, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, and Na_2HPO_4 of AR grade chemicals (Merck) were used for the preparation of different solutions as and when required. One hundred mL of each solution containing 473 mg Co and 378 mg Zn per 100 mL was agitated with 5 g of Indion BSR ion-exchange resins in a 250 mL conical flask and the pH was adjusted using 0.1 N hydrochloric acid or dilute sodium hydroxide solutions. To study the effect of pH in alkaline range, ammonium hydroxide was used instead of sodium hydroxide since cobalt and zinc form a soluble amine complex. The solutions were agitated for a predetermined period at 30°C ± 1°C in a water bath shaker. The resins were separated by filtration and the filtrate was analyzed by atomic absorption spectrophotometry (Model: Thermo Jarrel ash SH 8000) for the residual zinc and cobalt content. Effects of various parameters were studied to optimize the conditions for maximum metal extraction. Metal separation from the binary mixture was also performed to see the feasibility of zinc and cobalt separation from a mixed solution. Rate of exchange was carried out with different initial concentrations of zinc and cobalt while maintaining the resin dosage at a constant level. Inorder to correct for any uptake of metals on the container surface, control experiments were carried out without resins. It was found that there was no adsorption by the container walls. Concentration of the metal ion in the resin phase was calculated by the difference between the aqueous phase concentration before and after equilibration. Satisfactory material balance was obtained when the eluted metal was analyzed for Co and Zn using 1.0 M HCl.

RESULTS AND DISCUSSION

The distribution ratio (k_d) of Zn and Co between the resin and aqueous phase can be obtained directly as

$$k_d = \frac{[M(II)]_r}{[M(II)]_{aq}} \tag{1}$$

where $[M(II)]_r$ denotes the total metal ion concentration (g) in the resin phase and $[M(II)]_{aq}$ is the metal ion concentration in the aqueous phase at equilibrium. From the mass balance, Eq. (1) can be expressed as

$$k_d = \frac{[M(II)]_i - [M(II)]_f X(V/m)}{[M(II)]_f} \tag{2}$$

where $[M(II)]_i$ and $[M(II)]_f$ are the initial and final concentration (g) of metal in the aqueous phase; *V*, the volume of the aqueous phase; and m is the mass of dry resin in Na form. Loading of cobalt and zinc from the aqueous chloride solution using the resin in protonated form was low due to the change in equilibrium pH, hence further experiments were carried out with the resin in the Na^+ form. Thus, the exchange of bivalent metals M(II) [Co(II) and Zn(II)] can be represented by the following reaction:

$$M(II) + 2R{-}CH_2{-}NH{-}CH_2{-}PO_3{-}Na_2 \longrightarrow (R{-}CH_2{-}NH{-}CH_2{-}PO_3)_2 \times MNa_2 + 2Na \qquad (3)$$

Elution with HCl and regeneration of resin to the sodium form can be represented as:

$$(RCH_2NHCH_2PO_3)_2M \cdot Na_2 + 4HCl \longrightarrow 2RCH_2NHCH_2PO_3 \cdot H_2 + MCl_2 + 2NaCl \qquad (4)$$

$$RCH_2NHCH_2PO_3H_2 + 2NaOH \longrightarrow RCH_2NHCH_2PO_3Na_2 + 2H_2O \qquad (5)$$

Influence of Initial Metal Concentration of the Feed Solution

To study the effect of aqueous metal concentration on its loading over a fixed amount of resin, metal content in the aqueous feed was varied from 2–10 g/L. It was observed that the loading of metal ion in the resin phase increased almost linearly for Co up to 10 g/L (Fig. 1), whereas for Zn, the loading increased up to about 8 g/L of aqueous feed concentration and remained almost constant thereafter. Although, with the increase in initial metal-ion level of aqueous feed, loading on the resin increased, but percentage extraction with respect to feed metal content decreased. In the case of zinc at the lower feed concentration of 4 g/L, loading was about 95% and then a gradual decrease in percent loading was seen, whereas in the case of cobalt, percent loading was almost 99% for aqueous feed up to 10 g/L. Hence, there is a possibility of zinc separation from cobalt at higher feed concentration. Saturation loading capacity of the resin (100 g) with a feed concentration of 2 g/L of zinc and cobalt was 4.72 g and 6.15 g per 100 g resin, respectively.

Influence of Particle Size of the Resin

Resin was segregated into three different particle size ranges viz., +500 μm, 250–200 μm, 200–150 μm and its extraction efficiency for both

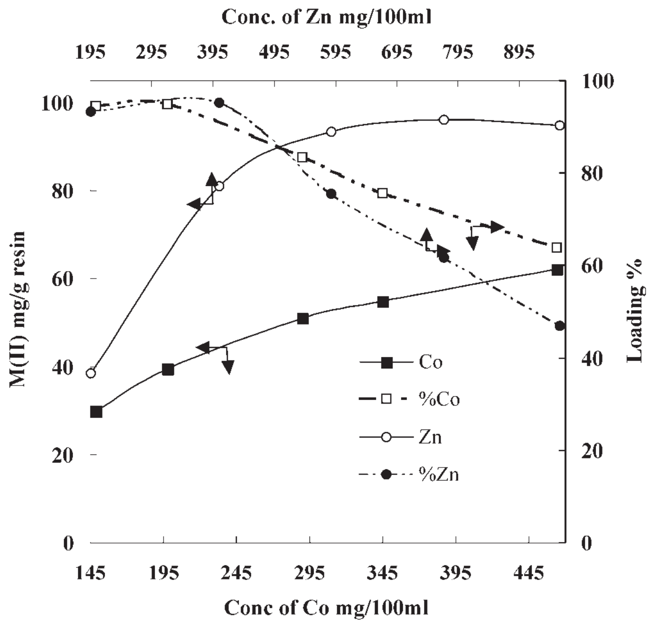

Figure 1. Effect of initial Co and Zn concentration on extraction by Indion BSR.

the metals was calculated. Figure 2 reveals that cobalt loading varies from 35.8 to 38.7 mg Co/g resin for particle size variation from $-420\,\mu m$ to $-200 + 150\,\mu m$, whereas loading of zinc increases from 54.9 to 75.8 mg/g resin with the fineness of the resin. But for particles of $-420\,\mu m$ percent loading was 67.77% for Zn and 89.41% for Co, and at the resin particles of 200–150 μm loading percentage was 93.5% for Zn and 96.0% for Co. As for column operation, finer particles might create a problem due to poor percolation and choking, the use of mixed particles may be considered for separation of metals.

Effect of Time on Metal Loading

Uptake of both the metals was found to increase with time and attained equilibrium in 15 min for cobalt and 60 min for zinc as shown in Fig. 3. Beyond this time, the loading was constant. Figure 3 also shows that in 5 min, loading of zinc was 42% and loading of cobalt was about 12.9%. Hence, separation of the two metals by adjusting the time of contact with the resin could be possible.

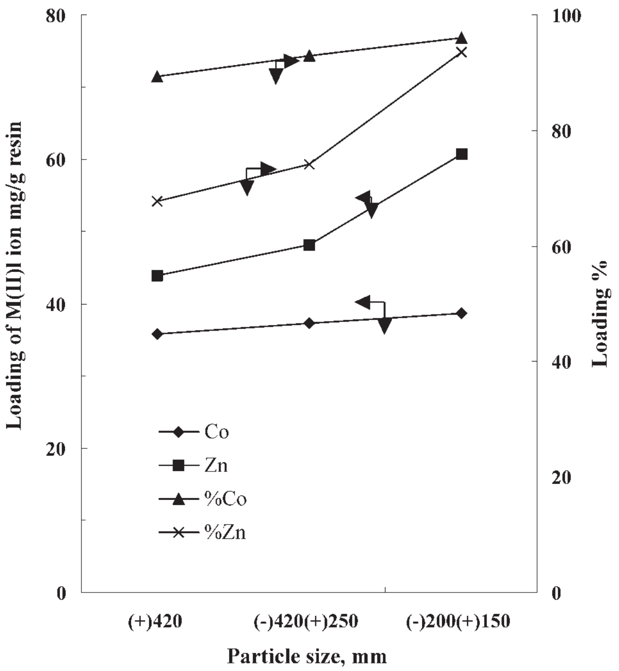

Figure 2. Effect of particle size of the resin on the extraction of M(II).

Effect of pH

Extraction of cobalt and zinc was carried out within the equilibrium pH range 1.0–10.0. Although metal hydrolysis takes place in the presence of sodium or potassium hydroxides, since cobalt and zinc form soluble complexes in ammonium hydroxides, pH of zinc- and cobalt-containing solutions was raised using ammonia solution. It is evident from Fig. 4 that the percentage extraction increased with increasing equilibrium pH for both the metal ions. At pH 5 the loading percentage for Co was 95.5% and that for Zn was 91.4%. It was observed that loading percentage for cobalt is still higher at about pH 10 (not shown in Fig. 4) but the exchange is irreversible due to some complex formation within the resin causing resin poisoning and making it ineffective for reuse. Hence, the effective pH range for Zn separation from Co is 1–6. The plot of $\log D$ vs. $\log \mathrm{pH}$ for both the metal ions (Fig. 5) shows the slope of 1.98 for zinc and 1.7 for cobalt, indicating the formation of 1 : 2 complexes with the resin. The general form of these curves is typical of nonferrous metal ion exchange on chelating resins.[20]

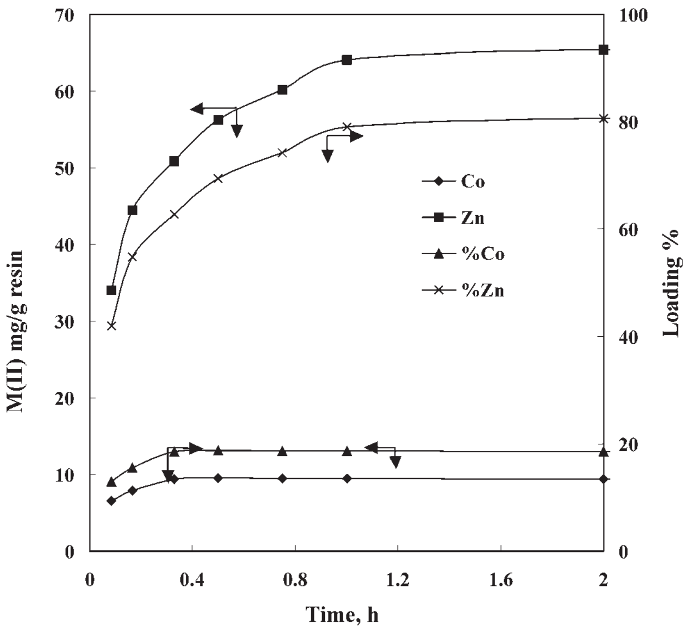

Figure 3. Rate of exchange of cobalt and zinc on Indion BSR.

Influence of Resin Dosage on Extraction

Loading pattern of metal ions was investigated with varying amounts of resin in the range 0.5–6.0 g. The results plotted in Fig. 6 infer that the percentage extraction of both the metals increased with increase in amount of resin. Thus, extraction of zinc increased from 34.0% to 99.9% when the amount of resin was varied from 0.5–6 g, whereas cobalt recovery obtained was 3.0% to 99.9% under the same experimental conditions. It is interesting to note that at the resin : aqueous feed ratio (S/L) of 1 : 200, zinc loading (34.0%) was 10 times higher than that of cobalt (3.0%), which decreased with decrease in S/L ratio. At resin : aqueous feed ratio of 1 : 20 loading was almost 99.9% for zinc and 97% for cobalt. Thus, it can be inferred that the resin has more affinity for zinc than cobalt.

Effect of Salt Addition on Loading

The influence of addition of salts such as NaCl, NH_4Cl, Na_2SO_4, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, and Na_2HPO_4 in the aqueous feed on the extraction

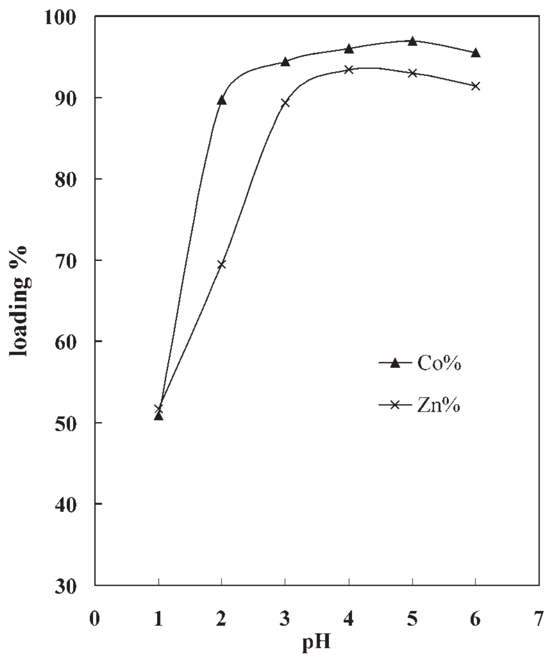

Figure 4. Effect of pH on metal loading on Indion BSR.

efficiency for cobalt and zinc was studied because any of these salts may be present in the feed solution used during leaching. Experiments were carried out for an aqueous solution containing 4 g/L of cobalt and zinc separately while varying the amount of salts. In the presence of NaCl and NH_4Cl, there was no effect on the loading of zinc but the loading of cobalt decreased from 98% to 83% and 88.0%, respectively. Presence of sulfates has a negative effect on the loading of zinc more than that of cobalt. The Na_2HPO_4 was extremely deleterious for cobalt loading, whereas it can be tolerated up to 100 g/L by zinc, beyond this level even zinc loading was affected. The presence of ammonium carbonate in the aqueous feed retarded the uptake (Figs. 7 and 8) of the two metals by the resin, zinc being more affected than cobalt, this may be due to the precipitation of carbonates of cobalt and zinc.

Stripping of Loaded Co and Zn Using H_2SO_4

Though the results obtained on loading show the possibility of the separation of these metal ions, however, the studies on selective elution

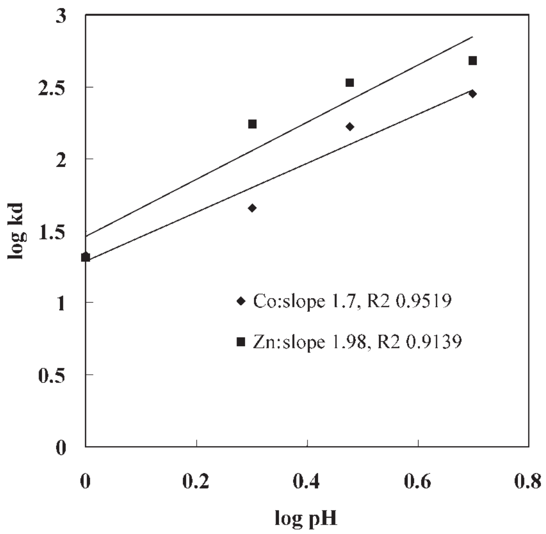

Figure 5. Plot of $\log k_d$ vs. log pH.

may eventually guide the metal recovery. Since these metals can be electrolyzed to get pure metal sheet or powder in sulfate medium, their elution from the loaded resin was done using varying concentration of H_2SO_4. An amount of 5 g of the resin was loaded with 2 g/L of each metal ion. The metal laden resin was filtered and washed with distilled water to remove the surface adhered metal ion and was stirred with varying concentrations of sulphuric acid in three contacts at room temperature ($35 \pm 0.5°C$). The results plotted in Fig. 9 shows that 99.9% of Co was eluted with 0.2 M of H_2SO_4. Beyond this acid concentration, the percent elution decreases to 75%, whereas maximum Zn removal under the same loading condition was found to be 90% at an acid concentration of 0.5 M and thereafter decreased to 84% with the increase in acid concentration up to 1.5 M.

Separation of Co and Zn from Their Mixture

This approach may be finally utilized for processing the acidic leach solution of cobalt cake in the treatment of Indian ocean nodules. It may be mentioned that the cake contained almost equal amounts of Co (20.5%) and Zn (17.7%) and their recovery from chloride leach solution is contemplated to get pure products meeting a certain specification. Therefore, synthetic mixtures of the chloride salts of Co and Zn containing 4.73 g/L of Co and

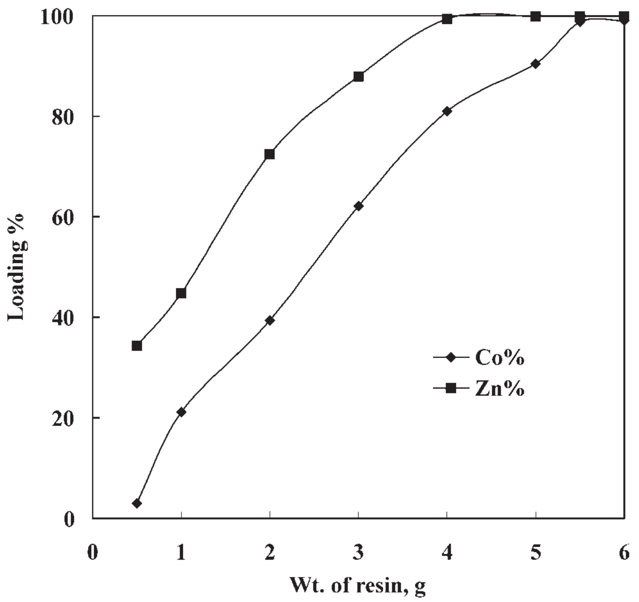

Figure 6. Effect of weight of resin on Zn and Co loading.

3.78 g/L of Zn were prepared for studying the separation of cobalt and zinc from a mixed solution.

Extraction of cobalt and zinc was carried out within the equilibrium pH range 1.0–6.0 as beyond this pH the metal hydrolysis was prevalent. It is evident from Fig. 10 that the percentage extraction increased with increasing equilibrium pH for both the metal ions. $pH_{0.5}$, i.e., pH for 50% extraction of zinc was at 1.9 and that for cobalt was found beyond pH 6.0. Separation factor (α) for zinc and cobalt can be expressed as

$$\alpha_{Co}^{Zn} = \frac{D_{Zn}}{D_{Co}} \tag{6}$$

The values of separation factor (α_{Co}^{Zn}) were plotted against pH (Fig. 10) and were found to be 8.51 at pH 1.9 and about 35 in the pH range of 4–6. Thus the difference in pH for 50% extraction of metal ions and separation factor values vividly indicates the possibility of separation of the two metal ions under consideration during the loading stage, which can be effectively achieved by pH control.

Similarly variations in resin dosage from 0.5 to 5.5 g (Table 2) show that Zn extraction is more favorable than that of Co within the weight variation

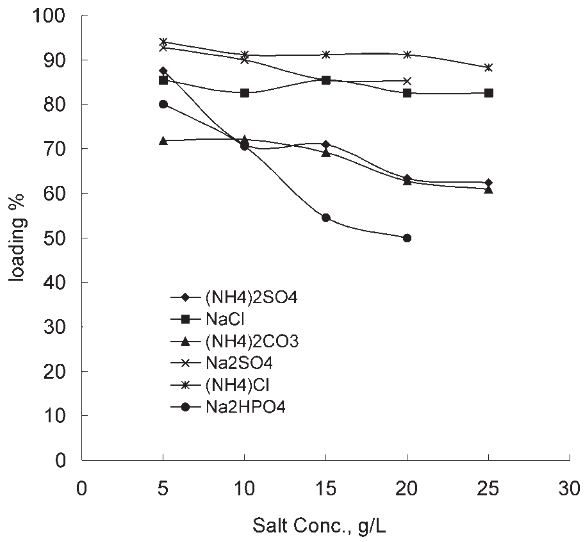

Figure 7. Effect of salt concentration on Co loading on Indion BSR.

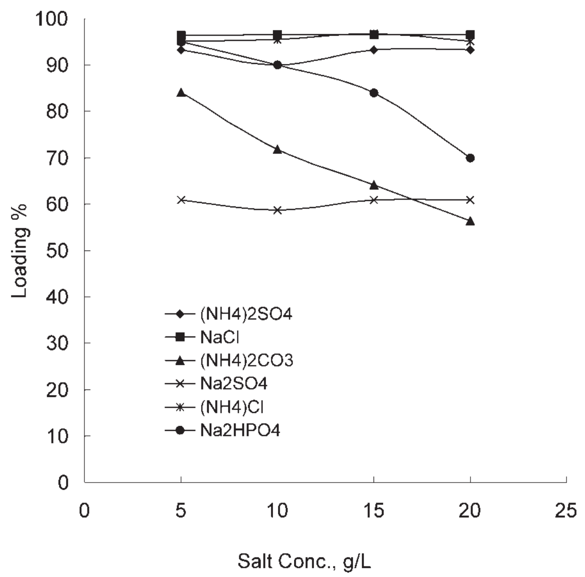

Figure 8. Effect of salt concentration on Zn loading on Indion BSR.

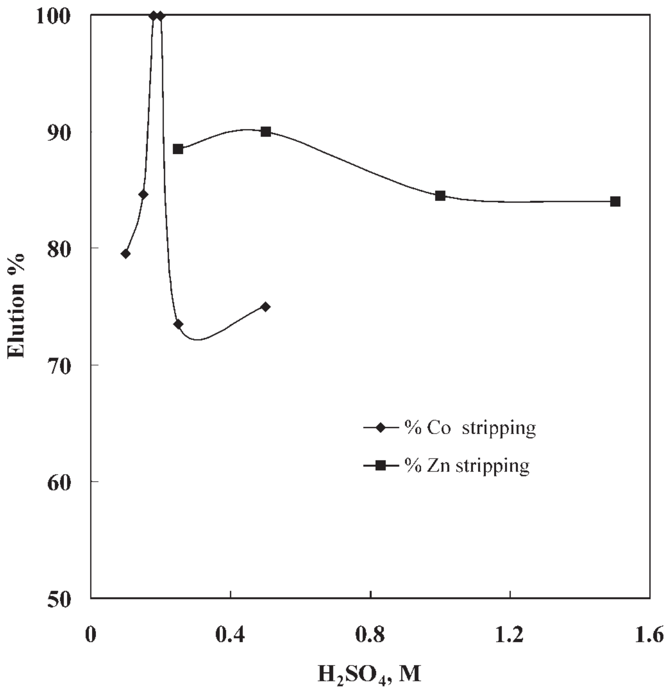

Figure 9. Effect of H_2SO_4 concentration on stripping of the loaded metal.

studied. However, at resin : aqueous feed ratio of 1 : 33 separation factor was 85.7, which was highest, with cobalt loading up to 1.45% and zinc loading up to 55.04% indicating that at this S/L ratio there is a possibility of complete separation of zinc from cobalt in a cyclic operation.

CONCLUSIONS

The extraction of cobalt and zinc on Indion BSR from the chloride medium has the following features:

1. Metal loading increased with the increase in equilibrium pH up to 6.0. Loading of cobalt and zinc also increased with the increase in metal concentration in the aqueous feed but percentage loading decreased in the case of zinc and was almost constant for cobalt.
2. The finer the size of the resin the more was the loading of zinc, but cobalt loading was independent of the particle size. Maximum

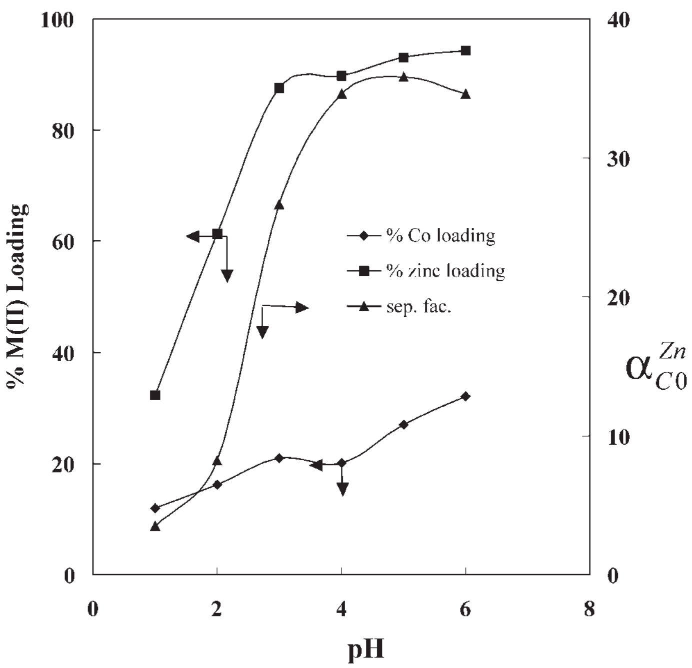

Figure 10. Effect of pH on the separation of Co and Zn from the mixed chloride solution.

loading capacity of resin (100 g) for cobalt and zinc with an aqueous feed of 2 g/L metal ions were 4.72 g and 6.15 g, respectively.

3. Equilibrium was attained in 1 hr for zinc and in 15 min for cobalt.
4. Extraction increased with the increase in resin dosage and was maximum at a resin : aqueous feed ratio of 1 : 20 for zinc and 1 : 18 for

Table 2. Effect of resin dosage on separation of cobalt and zinc in solution.

Weight of resin (g)	Ratio of resin (wt.) : aqueous feed (vol)	Equilibrium pH	D_{Zn}	D_{Co}	α_{Co}^{Zn}
0.5	1 : 200	4.58	32.95	11.11	2.96
1.0	1 : 100	4.60	35.25	6.32	5.57
2.0	1 : 50	4.60	40.11	1.25	32.10
3.0	1 : 33	4.94	40.39	0.476	85.7
4.0	1 : 25	5.20	57.65	4.08	14.13
5.0	1 : 20	5.60	148.3	3.35	44.31
5.5	1 : 18	5.60	172.63	6.38	27.05

cobalt in single salt solution. However, in a binary mixture of zinc and cobalt, at a resin : aqueous feed volume ratio of 1 : 33, the separation factor for Zn over Co was maximum and was found to be 85.7.
5. Chloride salts had no effect on loading of zinc but cobalt loading decreased. The presence of other salts, viz., sulfates, carbonates, and phosphates adversely affected the loading of the two metals. Resin exhibited preference for zinc loading rather than cobalt under the similar conditions.

Hence, separation of zinc from cobalt is possible from an aqueous chloride system.

ACKNOWLEDGMENTS

The authors are thankful to the Director, NML, Jamshedpur, for giving permission to publish the paper. Gift sample received from M/S Ion Exchange India Ltd., Mumbai, is also duly acknowledged.

REFERENCES

1. Grossi, G.; Cecille, L. *New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications*; Cecille, L., Casarci, Pietrelli, Eds.; Elsevier, Amsterdam, 1991, 11–19.
2. Tavarides, L.L.; Bae, J.H.; Lee, C.K. Solvent extraction, membranes, and ion exchange in hydrometallurgical dilute metals separation. Sep. Sci. Technol. **1987**, *22*, 581–617.
3. Cloete, F.L.D. *Ion Exchange Technology Soc. Chem. Ind.*; Naden, D., Streat, M., Eds.; Ellis Horwood: Chichester, 1984.
4. Paterson, J.W. *Metal Speciation, Separation and Recovery*; Lewis Publishers Eds. Inc; 1990; Vol. 1, 272.
5. Warshawsky, A.; Kaliv, R.; Berkovitz, H. Solvent impregnated resin incorporating phosphoric compounds. Trans. Ins. Min. Met. **1979**, *88*, C31.
6. Villasscusa, I.; Salvato, V.; Depablo, J.; Valiente, M.; Aguilar, M. Liquid–solid extraction of gold(III) from aqueous chloride solutions by macroporous resins impregnated with triisobutyl phosphine sulfide (Cyanex 471). React. Polym. **1992**, *17*, 69–63.
7. Paterson, J.W. *Metal Speciation, Separation and Recovery*; Lewis Publishers Eds. Inc.; 1987; Vol. 1, 63.

8. Krynicki, J.; Kurpas, M.; Lyszyna, K. Investigations on application of ion exchange membrane for processing of electrolyte from electrorefining of copper. Pr. Nauk. Inst. Technol. Org, Tworzyw Sztucznych Politech Wroclaw, 1973, 13, 399 (in Polish).
9. Green, B.R.; Hancock, R.D. Useful resins for the selective extraction of copper, nickel and cobalt. J. S. Afr. Inst. Min. Met. **1982**, *82* (10), 303–307.
10. Grinstead, R.R. Selective adsorption of copper, nickel, cobalt and other metal ions from sulphuric acid solution with chelating ion-exchange resin XES-4195. Hydrometallurgy **1984**, *12*, 387–400.
11. Rosato, L.; Harris, G.B; Stanley, R.W. Separation of nickel from cobalt in sulphate medium by ion-exchange. Hydrometallurgy **1984**, *13*, 33–44.
12. Strong, B.; Henry, R.P. The purification of cobalt advance electrolyte using ion-exchange. Hydrometallurgy **1976**, *1*, 311–317.
13. Bogoczek, R.; Surowiec, J. Ion exchange processes in chemical technology. Przem, Chem. **1978**, *57*, 2179 (in Polish).
14. Tiravanti, G.; Petruzzelli, D.; Passino, R. Pre-treatment of tannery waste water by an ion exchange process for Cr(III) removal and recovery. Water Sci. Tech. **1997**, *36*, 197–207.
15. Chiarle, S.; Ratto, M.; Rovatti, M. Mercury removal from water by ion exchange resins adsorption. Water Res. **2000**, *34*, 2971–2978.
16. Miller, G.P.; Norman, D.I.; Frisch, P.L. A comment on arsenic species separation using ion exchange. Water Res. **2000**, *34*, 1397–1400.
17. Pie, P. Ion exchange India Ltd.: Mumbai, Private communication, 1996.
18. Pandey, B.D.; Kumar, V. Extraction of copper and nickel from ammoniacal leach liquor of Indian Ocean sea nodules. Hydrometallurgy **1991**, *26* (1), 35–45.
19. Reilley, C.N.; Schmid, R.W.; Sadek, F.S. Chelon approach to analyses. I survey of theory and application. J. Chem. Education **1959**, *36*, 555–561.
20. Kholmogorov, A.G.; Kononova, O.N.; Patrushev, V.V.; Mikhlina, E.V.; Kononov, Y.S.; Pashkov, G.L. Ion exchange purification of manganese sulphate solutions from cobalt. Hydrometallurgy **1997**, *45*, 261–269.

Received July 2003
Accepted January 2004