Solvent extraction of cobalt and zinc from sulphate solutions using phosphoric, phosphonic and phosphinic acids

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Received 10 April 2002; accepted 15 January 2003

ABSTRACT

Extraction and separation of cobalt and zinc was studied from a sulphate solution using NaD2EHPA, NaPC88A and NaCyanex 272 of 0.04M concentration. The percentage extraction and DZn values increased with increasing equilibrium pH. Of the three extractants studied, NaD2EHPA was found to be the most suitable extractant for the separation of metal ions. Separation factor for cobalt and zinc increased with increasing equilibrium pH and was the highest (3394) at pH 5.65. Quantitative extraction (at equal phase ratio) and stripping (at A:O=1:5) of zinc could be achieved in two counter-current stages. Between H2SO4 solution and zinc spent electrolyte (containing the same concentration of H2SO4), the former was found to be a better stripping agent for zinc. Extraction (>99%) of cobalt could be achieved in two counter current stages at equal phase ratio and the metal could be stripped quantitatively in two counter-current stages from the loaded solvent with H2SO4 solution of 2.0kg/m³ concentration. © 2003 SDU. All rights reserved.

Keywords: Solvent extraction; Cobalt; Zinc; Counter current simulation

1. INTRODUCTION

Regional Research Laboratory, Bhubaneswar has developed a number of processes to extract metal values from manganese nodules of Indian Ocean origin. One of the processes is based on reductive ammoniacal leaching using sulphur dioxide (Nathsarma, 1989). The leach liquor obtained by the above process consists of ammine complexes of Cu, Ni, Co, Zn and minor amounts of iron and manganese. After removal of the iron and manganese impurities, co-extraction of Cu and Ni using a LIX type of reagent leaves cobalt and zinc in the raffinate. The concentration of cobalt and zinc in the raffinate was ~0.1kg/m³ along with nearly 80kg/m³ of ammonium sulphate. A considerable amount of work has been carried out on the extraction and separation of manganese (Hoh et al., 1984; Devi et al., 1997), zinc (Devi et al., 1997; Hancil et al., 1990), cobalt (Hoh et al., 1984; Preston, 1983; Devi et al., 1994), and nickel (Preston, 1982; Sarma et al., 1987) from aqueous solutions using the organophosphorus based extractants. With a view to find out the possibility of separating cobalt and zinc from aqueous solutions similar to those described above, attempts were made using the sodium salts of D2EHPA, PC 88A and Cyanex 272 and results of these studies are incorporated in this paper.

2. MATERIALS AND METHODS

2.1. Reagents

Stock solutions (containing ~5kg/m³ of metal ion) of cobalt sulphate and zinc sulphate were prepared from reagent grade chemicals in distilled water and were made slightly acidic with H2SO4 to prevent hydrolysis of metal ions on storage. A stock solution of 1.0M Na2SO4 was prepared in distilled water. The cobalt and zinc solutions were standardised against 0.1M EDTA solution (Vogel, 1962) using Xylenol Orange as indicator. From the stock solutions, a working solution containing ~1kg/m³ each of cobalt, zinc and 0.1M Na2SO4 was prepared. From D2EHPA, PC 88A and Cyanex 272 obtained respectively from Mobil, Diahachi and Cyanamid, stock solutions (1.0M NaD2EHPA, 1.0M Na PC 88A and 0.5M NaCyanex 272)

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were prepared using kerosene (b.p. 160-220°C) as the diluent. Neutralisation of the extractants was carried out using NaOH solution by mixing the phases intimately to form a single phase. From the stock solutions, lower concentrations of the extractants were obtained by dilution using distilled kerosene. TBP (5 vol.%) was added as the phase modifier.

2.2. Extraction procedure

The aqueous phase containing ~1kg/m³ each of cobalt, zinc, and 0.1M Na₂SO₄ was adjusted to the desired pH value using dilute solutions of H₂SO₄/NaOH and was equilibrated for five minutes in a separating funnel with an appropriate volume of the organic phase. After complete phase disengagement, the aqueous and organic phases were separated and equilibrium pH of the aqueous phase was measured. A suitable aliquot of the organic phase (after filtration through phase separating paper) was contacted three times with 2M HCl solution to ensure complete metal stripping. Both the raffinate and the combined organic strip solutions were suitably diluted with M HCl and analysed with the Perkin Elmer Model 3100 Atomic Absorption Spectrophotometer.

All the extraction and stripping studies were carried out at ambient temperature (30±1°C) and at equal phase ratio excepting those involving McCabe-Thiele constructions. The pH measurements were made with a Systronics Model 324 pH meter.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

Extraction of cobalt and zinc was studied in the equilibrium pH range of 1.05-5.00 from a sulphate solution containing about 1.0kg/m³ each of the metal ions and 0.1M Na₂SO₄ using 60% neutralised 0.04M Na D2EHPA, Na PC 88A and Na Cyanex 272. The data are plotted in Figure 1 as percentage extraction versus equilibrium pH. The percentage extraction of cobalt and zinc increased with increasing equilibrium pH; however, the increase was much more for zinc than for cobalt. With all the extractants, the percentage extraction was much higher for zinc than that of cobalt indicating preferential extraction of zinc. At any equilibrium pH, zinc extraction followed the order NaD2EHPA > NaPC 88A > NaCyanex 272. For example, as read off from the graph, the extraction of zinc at pH 4.0 is 71, 48 and 32%, respectively with 0.04M NaD2EHPA, Na PC 88A and Na Cyanex 272. Further, to attain a desired percentage of extraction, Na Cyanex 272 requires the highest equilibrium pH value, NaD2EHPA requires the lowest equilibrium pH value while Na PC 88A requires an equilibrium pH value falling in between. For example, to attain 60% extraction the required equilibrium pH values were 3.75, 4.1 and 4.75, respectively for NaD2EHPA, NaPC 88A and NaCyanex 272. Extraction of cobalt by all the extractants was very low, the maximum ranging between 6-9%. The plots of log D_Zn versus equilibrium pH (Figure 2) were straight lines with slope values of 1.11, 0.80 and 0.91, respectively for NaD2EHPA, Na PC 88A and NaCyanex 272 indicating the release of one mole of H⁺ ion per mole of Zn ion. The highest separation factors (β= D_Zn/D_Co) achieved for zinc-cobalt system were 101.3, 60.6 and 60.6, respectively for Na D2EHPA, Na PC 88A and Na Cyanex 272 at the equilibrium pH values of 4.10, 4.15 and 4.90. For the extractants Na D2EHPA, Na PC 88A and Na Cyanex 272, the highest distribution coefficient value were 3.565 (eq. pH 4.25), 3.20 (eq. pH 4.55) and 1.917 (eq. pH 4.90) for zinc and 0.0653 (eq. pH 4.25) 0.0888 (eq. pH 4.60) and 0.0653 (eq. pH 5.0) for cobalt.

Figure 1. Effect of equilibrium pH on cobalt and zinc extraction using 0.04M 60% neutral extractants
The maximum extraction achieved for zinc with Na D2EHPA, Na PC 88A and Na Cyanex 272 was 78.1% (eq. pH 4.25), 78.1% (eq. pH 4.60) and 65.7% (eq. pH 5.0), respectively. Thus, Na D2EHPA appeared to be more potent compared to the other two extractants taking into consideration the extraction efficiency and reagent cost. It is logical to think that fully neutralised D2EHPA would give still higher extraction due to complete utilization of the extractant. In view of this, completely neutralised 0.04M Na D2EHPA was prepared and the effect of pH on zinc and cobalt extraction was studied again.

The equilibrium pH was varied in the range 1.47-6.55 during metal extraction from a feed solution containing about 1.0kg/m³ each of cobalt and zinc, and 0.1M Na₂SO₄. Extraction was carried out by equilibrating the aqueous and organic phases at equal phase ratio. As expected, the percentage extraction was higher for both cobalt and zinc with the completely neutralised extractant. The plot of percentage extraction versus equilibrium pH (Figure 3) shows a sigmoidal curve for zinc. The figure shows an increase in percentage extraction with increase in equilibrium pH for both cobalt (2.0-22.01%) and zinc (0.99-99.8%). The total metal concentration of about 1.23kg/m³ (obtained through 99.8% zinc and 22.01% cobalt extraction) in the organic phase indicates 100% utilisation of the extractant. The percentage extraction and distribution coefficient values for zinc increased with increasing equilibrium pH whereas the percentage extraction and distribution coefficient values for cobalt did not increase significantly. The Dₗ values increased significantly after equilibrium pH 4.5. For example, Dₗ value was 9.15 at pH 4.5 which increased by about 14 times to 125.9 at pH 5.3. The logarithmic values of Dₗ are plotted against equilibrium pH (Figure 4) and a straight line having a slope of 1.05 was obtained indicating the release of one mole of H⁺ ion per mole of Zn ion extracted. The slope value obtained was close to the value (1.11) obtained with 60% neutral Na D2EHPA (Figure 2).
Figure 4. Plot of Log $D_{Zn}$ versus equilibrium pH

The separation factor ($\beta = D_{Zn} / D_{Co}$) increased with increasing equilibrium pH and attained the maximum value of 3394 at equilibrium pH 5.70. With further increase in equilibrium pH, the value of $\beta$ decreased due to increase in cobalt extraction and consequent increase in $D_{Co}$ value (zinc extraction having already reached the maximum value) as shown in Figure 5. For example, at equilibrium pH 6.55 the value decreased to 1796.

Figure 5. Plot of separation factor versus equilibrium pH

3.2. Selective extraction of zinc

Completely neutralized 0.04M Na D2EHPA was used to recover zinc values from the binary solution containing 0.995kg/m$^3$ of zinc, 0.95kg/m$^3$ of cobalt and 0.1M Na$_2$SO$_4$. The equilibrium isotherm (Figure 6) for the extraction of zinc was obtained by equilibrating the aqueous and organic phases in the phase ratios ranging between 1:5 and 5:1. The McCabe-Thiele construction in Figure 6 predicts two counter-current stages for complete extraction of zinc at the A:O ratio of 1:1 which was confirmed by carrying out a two stage counter-current simulation. Analysis of the representative aqueous and organic phases indicated that the loaded organic contains 0.9995kg/m$^3$ zinc and 3.8g/m$^3$ cobalt whereas the raffinate contains 0.21g/m$^3$ zinc and 0.944kg/m$^3$ cobalt. Required quantity of zinc loaded organic phase was generated under the above conditions for further studies.
Figure 6. McCabe-Thiele plot for zinc extraction

3.3. Effect of sulfuric acid concentration on zinc stripping

To optimise the H₂SO₄ concentration required for stripping of zinc from the loaded organic phase, H₂SO₄ solutions of varying concentrations (0.1-5.0 kg/m³) were prepared and used in single stage stripping tests. For comparison, spent zinc electrolyte solutions containing 60 kg/m³ Zn and H₂SO₄ (in the concentration range 0.1-5.0 kg/m³) were also prepared and used in single stage zinc stripping studies. Equal volumes of the zinc loaded organic and H₂SO₄/spent zinc electrolyte solutions were equilibrated for five minutes. The aqueous and organic phases obtained after complete phase disengagement were analysed and percentage zinc stripping was plotted against H₂SO₄ concentration. The data shown in Figure 7 illustrate that H₂SO₄ alone is a better stripping agent than zinc spent electrolyte (ZnSE) having an equal concentration of H₂SO₄. For example, H₂SO₄ solution of 1.0 kg/m³ concentration can effect 97.4% stripping whereas ZnSE having the same concentration of H₂SO₄ can give only 50% stripping efficiency. Further stripping studies were carried out using H₂SO₄ alone.

Figure 7. Effect of [H₂SO₄] on zinc stripping using H₂SO₄ and spent electrolyte

As the loaded organic phase contains only about 1.0 kg/m³ of zinc, stripping at 1:1 phase ratio results in strip solution having only about 1.0 kg/m³ of zinc. To enrich zinc values in the strip solution, studies were carried out using a more concentrated (5.0 kg/m³) H₂SO₄ solution. The stripping isotherm was obtained using zinc-loaded organic and H₂SO₄ solution (5.0 kg/m³) by varying the A:O phase ratio between 1:5 to 5:1. The Plot of [Zn]ₐq versus [Zn]ₐ₉ (Figure 8) suggests two counter-current stages for complete metal stripping at A:O ratio of 1:5. To confirm the predicted stripping data, a two stage counter-current simulation study was carried out at A:O ratio of 1:5. The representative spent organic phase showed no zinc value and thus the stripping efficiency was cent percent.
Figure 8. Mc Cabe-Thiele plot for zinc stripping using 5kg/m$^3$ H$_2$SO$_4$

3.4. Effect of pH on cobalt extraction

Extraction of cobalt from the Zn-free raffinate was carried out in the equilibrium pH range 2.15-7.65 using 0.04M Na D2EHPA. The aqueous and organic phases were equilibrated for five minutes at equal phase ratio. The plot of cobalt extraction versus equilibrium pH (figure 9) obtained from the analysis of aqueous/organic phases shows increased extraction with increasing equilibrium pH. The cobalt extraction was 32.4% at pH 4.75 and increased up to 97.99% at pH 7.65. The distribution coefficient increased with equilibrium pH from a value of 0.1256 (pH 4.15) to 48.83 (pH 7.65). The plot of log $D_{Co}$ versus equilibrium pH (figure 10) is a straight line with a slope of 0.91 indicating release of one mole of H$^+$ ion per mole of cobalt ion extracted.

Figure 9. Effect of equilibrium pH on cobalt extraction
3.5. Cobalt extraction

Recovery of cobalt from the zinc-free solution containing 0.944 kg/m³ of cobalt was studied with 0.04M NaD2EHP. The equilibrium isotherm was obtained by varying the A:O ratio in the range 1:5 to 5:1. The plot of [Co]_{org} versus [Co]_{aq} (Figure 11) shows that two counter-current stages at equal phase ratio is the prerequisite for complete metal recovery and to confirm this, a two-stage counter-current simulation study was carried out. The representative raffinate showed the presence of 8.2 g/m³ of cobalt indicating 99.13% recovery of the metal. Sufficient quantity of cobalt loaded organic phase was generated to optimise the stripping conditions.

3.6. Stripping of cobalt

Stripping studies of cobalt from the loaded Na D2EHP were carried out with H₂SO₄ solutions of varying concentrations (0.1–5.0 kg/m³) by equilibrating the two phases for five minutes at 1:1 ratio. The data are plotted in Figure 12 which shows that the percentage stripping increases linearly with H₂SO₄ concentration up to 0.6 kg/m³ after which the percentage stripping slowly reaches maximum at 2.0 kg/m³ sulphuric acid concentration. Accordingly, H₂SO₄ solution of 2.0 kg/m³ concentration was chosen to strip cobalt from the
loaded organic phase. The McCabe-Thiele plot for stripping of cobalt (Figure 13) predicted two counter-current stages for complete stripping at 1:1 phase ratio where 94.7% stripping has taken place in the first stage and 5.3% stripping has taken place in the second stage. A two-stage counter-current simulation study at equal phase ratio was carried out and the spent organic contained no cobalt and the strip solution contained all the cobalt values indicating quantitative stripping.

Figure 12. Effect of $[\text{H}_2\text{SO}_4]$ on cobalt stripping

Figure 13. McCabe-Thiele plot for cobalt stripping using 2kg/m$^3$ $\text{H}_2\text{SO}_4$

4. CONCLUSIONS

Extraction of cobalt and zinc and their separation from a sulphate solution has been studied using sodium salts of D2EHPA, PC 88A and Cyanex 272. Of the three extractants, NaD2EHPA appeared more promising. Extraction of metal ions increased with increasing equilibrium pH. Of the three extractants, NaCyanex 272 required a higher equilibrium pH while NaD2EHPA the lowest to achieve a desired extraction efficiency but the pH value for Na-PC 88A falls in between. Between the two metal ions, zinc was extracted in preference to cobalt by all the three extractants. Separation factor for zinc and cobalt increased with equilibrium pH and the highest $\beta$ value was achieved at pH 5.70. Complete extraction of zinc (with 0.04M completely neutralised D2EHPA) could be achieved in two counter-current stages at equal phase ratio. Stripping studies of zinc from the loaded organic phase with $\text{H}_2\text{SO}_4$ and zinc spent electrolyte (containing the same concentrations of $\text{H}_2\text{SO}_4$) showed that $\text{H}_2\text{SO}_4$ is a better stripping agent than the spent electrolyte. Quantitative zinc stripping could be achieved in two counter-current stages at the A:O phase ratio of 1:5 using $\text{H}_2\text{SO}_4$ solution of 5.0kg/m$^3$ concentration. Extraction of cobalt from the Zn-free raffinate
was also studied using 0.04M Na D2EHP as the extractant and as expected the extraction of cobalt increased with increasing equilibrium pH. Quantitative (>99%) extraction of cobalt could be achieved in two counter-current stages at equal phase ratio. Stripping efficiency of cobalt from the loaded organic phase increased with increasing H2SO4 concentration. The stripping isotherm for cobalt predicted two counter-current stages for quantitative stripping at equal phase ratio with H2SO4 solution of 2.0kg/m³ concentration and the data was confirmed by the counter-current simulation study.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Hydrometallurgy Department and the Director, Regional Research Laboratory, Bhubaneswar for giving permission to publish this work.

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