

Separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquors of spent Ni–Cd batteries using phosphorus based extractants

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Abstract

Solvent extraction separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquor of spent Ni–Cd batteries was investigated using phosphorus based extractants such as TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302 and Cyanex 301 diluted in kerosene. The composition of the leach liquor used for the present study contains (g/L): Cd, 2.40; Ni, 5.94; Co, 0.05. Among the phosphorus based extractants screened at 0.1 M concentration as a function of aqueous phase equilibrium pH, Cyanex 301 showed selective separation of Cd(II) from Co(II) and Ni(II). On the other hand, stripping of metal from Cd–Cyanex 301 loaded organic (LO) phase needs high acid solution. Two-stage counter-current extraction with 0.06 M Cyanex 301 at unit phase ratio and three-stage stripping of the metal from LO with 6 M HCl at an aqueous to organic (A:O) phase ratio of 2 yielded >99.9% Cd(II) extraction and stripping efficiency. However, Cd(II) concentration in strip solution was reduced to half. Cobalt(II) extraction efficiency of ~99% was achieved from cadmium raffinate at an equilibrium pH of 6.25 with 0.03 M Cyanex 272 in two counter-current stages at an A:O ratio of 2:1. Complete stripping of metal from LO containing 0.15 g/L Co(II) was carried out using a strip solution pH of 1.0 in two stages at an O:A ratio of 1.75. The enrichment of cobalt during extraction and stripping operations was ~5.2 times. Complete process flowsheet for the separation and recovery of Cd(II), Co(II) and Ni(II) was proposed.

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1. Introduction

Batteries are popular source of portable energy. The principal applications include illumination, communication and entertainment. Nickel–cadmium batteries represent the kind of secondary batteries that are used in many portable electronic devices, military and defense applications. Nickel is a useful metal whereas cadmium is toxic and poisoning occurs through inhalation and ingestion. Discarded waste Ni–Cd batteries into the environment results in pollution of soil and water. As a result, these are being replaced with nickel–metal hydride batteries to some extent. Recycling of spent batteries will be important, both from an environmental and economic point of view. In several European countries, the collection rates of spent batteries vary between 32 and 54% of battery sales. To the best of our knowledge, data on

disposal and recycling of spent Ni–Cd batteries is not available in India.

Several methods to recover metal values from spent batteries are already reported in the literature but industrial routes generally employ either pyrometallurgical/hydrometallurgical processes such as the SNAM-SAVAN, SAB-NIFE and INMETCO [1–3], which employ basically selective volatilization of metals at elevated temperatures around 900 °C followed by condensation to recover cadmium. High pure cadmium (>99%) is obtained, but most valuable metals such as nickel and cobalt are not usually recovered. Therefore, hydrometallurgical methods such as solvent extraction (SX) are found more economical and efficient which are characterized by low energy consumption, higher metal selectivity, high purity products and avoid effluent emissions.

A number of hydrometallurgical methods involving acid leaching of battery active materials followed by recovery of Cd, Ni and Co by precipitation, ion exchange and solvent extraction methods were reported. Bartolozzi et al. [4] reported hydromet-

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allurgical methodology for the recovery of cadmium and nickel from spent batteries by chemical and electrochemical methods. Xue et al. [5] proposed a method with initial acid leaching followed by precipitation of iron and manganese hydroxides; nickel was precipitated as a double salt at first and finally recovered as nickel hydroxide and cadmium was then precipitated as carbonate. The BATENUS [6] process provides a solution for the treatment of mixed battery waste, using sulphuric acid leaching and a combination of ion exchange and solvent extraction for metal recycling and purification. Solvent extraction flow-sheet for the recovery of Cd, Co and Ni from synthetic sulphate solutions using D2EHPA, Ionquest 801 and Cyanex 272 was reported. Cd extraction with D2EHPA involves co-extraction of both Ni and Co, which needs scrubbing stage with pure Cd solution [7]. Solvent extraction studies of cadmium with possible stoichiometry of extracted species from acidic chloride media using Cyanex 302 [8], selective extraction of Zn from Co from sulphate solutions by organophosphorus acidic extractants [9] and Co–Ni separation by Cyanex 301 and Cyanex 302 was studied [10], but the stripping behavior of these metals has not been reported. Application of phosphorus based extractants such as D2EHPA, PC 88A, Cyanex 272 for the solvent extraction studies of Ni at macro-level concentrations from sulphate/chloride solutions [11], separation studies of Co(II)/Ni(II) from synthetic chloride solutions containing 0.5 g/L Co and 0.5/2 g/L Ni concentrations by the sodium salts of extractants and their mixtures [12], separation of Co and Ni from sulphate solutions of Indian Ocean nodules using Cyanex 272 [13], solvent extraction studies of Cd from sulphate solutions [14] and separation of Cd(II), Ni(II) and Co(II) from chloride leach liquor of spent batteries [15] were explored in our earlier studies.

In this paper we report, studies carried out on the screening of suitable extractant and development of a hydrometallurgical route for the separation and recovery of Cd(II), Co(II) and Ni(II) from sulphate leach liquor of spent nickel–cadmium batteries using phosphorus based extractants, Cyanex 301, Cyanex 272 and TOPS 99 diluted in kerosene. The parameters studied for optimization of process are: leaching, effect of equilibrium pH, selection of extractant and its concentration, phase ratios, extraction and stripping isotherms, counter-current extraction and stripping simulations.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Model A300 Atomic Absorption Spectrophotometer (AAS) and a digital Digisun pH meter (model DI 707) were used for the measurement of metal concentration and pH in the aqueous phase.

2.2. Reagents

The spent Ni–Cd batteries used in this work were prismatic shaped batteries supplied by HBL-NIFE Industries, Hyderabad, India. These are low rate cells with a capacity of 7 A and 1.2 V used in radio military communications. The dismantled elec-

trodes were washed thoroughly with distilled water and dried overnight around 100 °C. The powdery materials from the wire mesh were scrapped and ground to $-100\ \mu\text{m}$. Chemical analysis of the spent Ni–Cd battery powder indicated 61.3% Ni, 21.4% Cd and 0.5% Co.

Cyanex 301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid; Cyanex 302, bis(2,4,4-trimethylpentyl)monothiophosphinic acid; Cyanex 923, a mixture of four trialkylphosphine oxides ($\text{R}_3\text{P}=\text{O}$, $\text{R}_2\text{R}'\text{P}=\text{O}$, $\text{R}'_3\text{P}=\text{O}$, $\text{R}'_2\text{R}\text{P}=\text{O}$, where $\text{R}=\text{hexyl}$ and $\text{R}'=\text{octyl}$); Cyanex 272, bis(2,4,4-trimethylpentyl)phosphinic acid obtained from Cytec Canada Inc.; TOPS 99 (an equivalent of di-2-ethylhexyl phosphoric acid) from Heavy Water Plant, Talchar, India, were used as such with out purification. Distilled kerosene (b.p.: 160–200 °C) mostly aliphatic (96.2%) was used as the diluent. All other chemicals used were analar grade.

2.3. Leaching studies

Leaching experiments were conducted by taking 200 mL H_2SO_4 (2.5 M) in a 500 mL round bottom flask fitted with water cooled condenser and stirrer, which is immersed in oil bath maintained at $85 \pm 1\ ^\circ\text{C}$. As soon as the temperature of flask reached $85 \pm 1\ ^\circ\text{C}$, weighed amounts (2 g) of sample was added and samples were with drawn periodically at different time intervals till the sample gets dissolved totally. It was observed that 8 h time is required for the total dissolution of the sample. Analysis of Cd, Ni and Co metal contents was determined after proper dilution by AAS to estimate the percentage leaching. The composition of leach liquor with H_2SO_4 under optimum conditions (H_2SO_4 : 2.5 M, temperature: 85 °C, solid/liquid ratio: 1, time: 8 h) was (g/L): Cd, 2.40; Ni, 5.94; Co, 0.05. pH of the liquor was 0.3.

2.4. Solvent extraction procedure

Suitable volumes of aqueous (leach liquor) and organic phases were contacted in separating funnels for 5 min (initial experiments showed that equilibrium was reached within 1 min), the phases were separated and the metal concentration in the aqueous phase (raffinate) was estimated directly or after suitable dilution. pH adjustment was performed by the addition of dilute $\text{NaOH}/\text{H}_2\text{SO}_4$. The loaded organic (LO) phases were stripped with respective $\text{HCl}/\text{H}_2\text{SO}_4$ acid concentrations after which the strip solutions were diluted to the required concentration and analyzed for metal values by AAS. All the experiments were carried out at room temperature ($30 \pm 1\ ^\circ\text{C}$). The distribution ratio, D , was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium.

3. Results and discussion

3.1. Influence of equilibrium pH and extractant concentration on Cd(II) extraction

Preliminary experiments on effect of equilibrium pH in the range from 1 to 7 on the extraction of metals with 0.1 M of TOPS 99 and Cyanex 923 showed low extraction efficiencies and non-

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