

Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel–cadmium, batteries using Cyanex 923 and 272

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Abstract

Studies are conducted on the leaching and solvent extraction separation of metals from chloride leach liquor of spent nickel–cadmium batteries with Cyanex 923 and 272 diluted in kerosene as the extractants. Dissolution of the metals increases with increase in acid concentration and time but decreases with the solids-to-liquid ratio. Complete dissolution of Cd, Co and Ni can be achieved with 1.5 M HCl at 85 °C for 8 h and a solids-to-liquid ratio of 4. Treatment of leach liquor for the separation of metals with Cyanex 923 shows that increase of extractant and chloride ion concentration increases the percentage extraction of cadmium. The plot of $\log[\text{distribution coefficient}]$ versus $\log[\text{extractant}]/[\text{Cl}^-]$ is linear with a slope of 2, which indicates that the extraction follows a solvation mechanism with the extracted species as $\text{CdCl}_2 \cdot 2\text{S}$ (S, Cyanex 923). Moreover, Cyanex 923 enables a clear separation of Cd from Co and Ni. Extraction of cobalt with Cyanex 272 involves a cation-exchange mechanism with the formation of a 1:2 metal-to-ligand complex in the organic phase. Based on the distribution data, extractant concentration and equilibrium pH of the aqueous phase, a possible separation process is proposed for the recovery of cadmium, cobalt and nickel with >99% efficiency. © 2006 Elsevier B.V. All rights reserved.

Keywords: Spent nickel–cadmium batteries; Chloride leaching; Solvent extraction; Metal recovery; Cyanex 923, 272

1. Introduction

Rechargeable nickel–cadmium (Ni–Cd) batteries have been used since the 1950s in applications that require high specific energy, long lifetime and high discharge rates. Spent Ni–Cd batteries are classified as hazardous waste because nickel and cadmium are heavy metals and suspected carcinogens [1]. Given the risk associated with uncontrolled disposal, directions for issuing legislation on disposal and recycling of spent batteries have been made in industrialized countries. To the best of our knowledge, there have been no reports on the recycling of spent Ni–Cd batteries in India.

A literature search revealed that both pyrometallurgical and hydrometallurgical processes have been investigated [2–4] for the recycling of spent batteries. Recycling by a pyrometallurgical process is not appropriate due to the emission of toxic gases which can contaminate the environment. Recycling of spent batteries by a hydrometallurgical process is an alternative solution

for the environmental problem. The hydrometallurgical process involves crushing the battery followed by physical separation of structural elements, and dissolution and separation of valuable metals. Xue et al. [5] reviewed several methods for the recovery of cadmium and nickel from wastes. Flow sheets for the recovery of Cd, Ni and Co from synthetic sulfate solutions have involved the use of D2EHPA, Cyanex 272 [6] and 923 [7] extractants. Freitas and Rosalem [8] recovered cadmium as metal from the anode and collector of spent batteries by electrochemical methods. Bio-leaching of spent Ni–Cd batteries using acidophilic *Thiobacilli* organisms on sulfur to produce H_2SO_4 and leaching of metals has also been investigated [9,10]. These methods suffer from slow reaction that ranges from 50 to 90 days and the recoveries are not quantitative. Hydrometallurgical methods of leaching/dissolution of spent batteries with mineral acids/bio-organisms results in leach liquors that contain cadmium and nickel in major amounts along with impurities such as cobalt and iron. Using classical methods, such as precipitation, oxidation and crystallization, it is difficult to separate metals in a simple and economical way. For example, the separation of cadmium and nickel from other commonly associated metals requires the development of efficient methods. Solvent

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extraction (SX) offers a convenient route and has been used widely for the separation of various metal ions. The selection of an appropriate extracting agent is an important determinant of the success of SX separation. In earlier investigations [11–17], we have applied organophosphorus-based extractants for solvent extraction separation and determination of metal ions such as cadmium, nickel and cobalt.

This study examines the leaching of spent batteries with dilute hydrochloric acid followed by solvent extraction separation of metals from leach liquor with commercial organophosphorus extractants. The parameters studied are: (i) leaching with different acid concentrations, time, solids-to-liquid ratio; (ii) solvent extraction of metals from leach liquor with different extractants, equilibrium pH values of aqueous phase, extractant concentration, aqueous-to-organic phase ratio and stripping of metals from loaded organic.

2. Experimental

2.1. Apparatus and materials

A Perkin-Elmer Model A 300 atomic absorption spectrophotometer (AAS) and a digital Digisun pH meter (model DI 707) were used.

The spent Ni–Cd batteries were prismatic-shaped batteries supplied by HBL-NIFE Industries, Hyderabad, India. These were low-rate 1.2 V cells with a capacity of 7 A for use in radio military communications. The cell dimensions were 10 cm × 6 cm × 2 cm and weight was 280.4 g. The Ni–Cd cells were packed in a plastic case. The positive and negative electrodes were housed in a plastic casing and separated by a polyamide separator. The battery package was dismantled to remove the battery materials. The break-down of the battery components was: 53.7 g plastic casing, 49.2 g KOH electrolyte solution, 22.3 g metallic parts, 14.7 g polyamide separator, 13.9 g electrode substrate (wire mesh), 59.6 g negative electrode material, 67 g positive electrode material. The dismantled electrodes were washed thoroughly with distilled water and dried overnight in an oven maintained around 100 °C. The powdery materials were removed from the wire mesh and ground to –100 μm. Chemical analysis of the spent battery sample indicated: 77 wt.% Ni, 22.4 wt.% Cd and 0.5 wt.% Co.

2.2. Reagents

Cyanex 923 and 272 (Cytec Canada Inc.) were used as-received without purification. Distilled kerosene (bp 160–200 °C) was used as the diluent. It was colourless, and the aliphatic and aromatic contents were 96.2 and 3.8%, respectively. All other chemicals were Analar Reagent grade.

2.3. Leaching studies

Leaching experiments were conducted by taking 100 mL HCl of given concentration (1–2 M) in a 250 mL flask that was fitted with water-cooled condenser and stirrers, and immersed in oil bath maintained at 85 ± 1 °C. As soon as the tempera-

ture of flask reached 85 ± 1 °C, a weighed amount of the given sample (2–4 g) was added. Samples of the solution were withdrawn at different time intervals until completion of the reaction. Analyses of cadmium, nickel and cobalt metal contents were determined, after proper dilution, by means of AAS to estimate the percentage leaching.

2.4. Solvent extraction procedure

Suitable volumes of aqueous (leach liquor) and organic phases were contacted for 5 min (initial experiments showed that equilibrium was reached within 1 min) at room temperature (30 ± 1 °C). The phases were then separated and the metal concentration in the aqueous phase (raffinate) was estimated directly or after suitable dilution; pH adjustment was performed by addition of dilute NaOH/HCl. The distribution ratio, *D*, was calculated as the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium.

3. Results and discussion

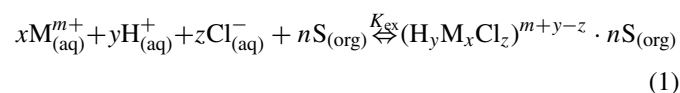
3.1. Leaching studies

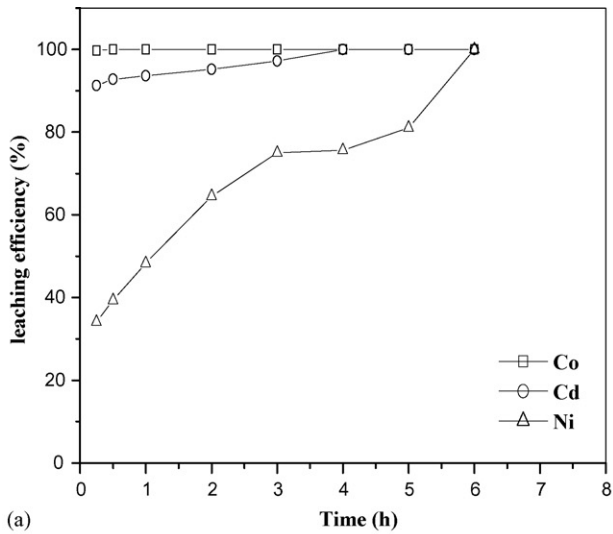
Leaching experiments on the dissolution of metals from spent battery samples were carried out with varying concentrations of HCl (1–2 M), solids-to-liquid (S:L) ratios (2 and 4%, w/w) and time (1–8 h). Dissolution rates vary with the change in conditions as expected. The results of these tests (Figs. 1 and 2) indicate that the percentage dissolution of metals increases with increase in concentration of both acid and time, and decrease with increase in the S:L ratio. Further, the results demonstrate that longer durations are necessary to achieve quantitative dissolution of samples at higher S:L ratios. Based on the leaching results and considering better utilization of acid, maximum throughput of the material and utilization of equipment, a S:L ratio of 4 and 1.5 M HCl was selected for the generation of a sufficient quantity of leach liquor for further processing to separate cadmium, nickel and cobalt metals. The composition (g L⁻¹) of leach liquor was: cadmium, 8.96; nickel, 30.8; cobalt, 0.20. Initial tests of the extraction of metals from the leach liquor using 0.5 M Cyanex 923 diluted in kerosene at a phase ratio of unity results in the formation of a third phase. As a result, the leach liquor was diluted by about 1.43 times. The pH of the diluted leach liquor was 0.95.

3.2. Solvent extraction studies

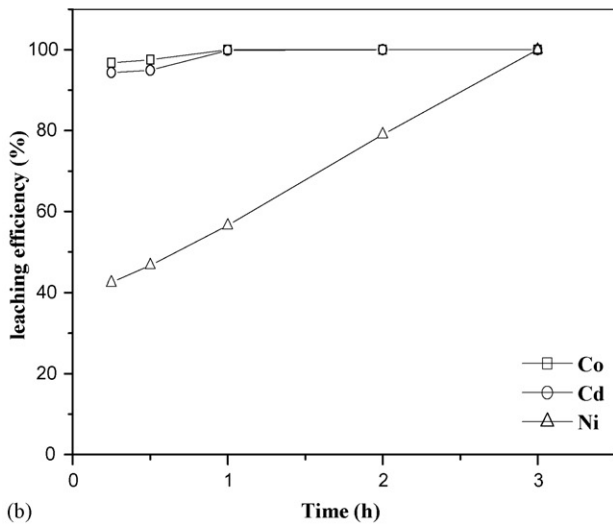
3.2.1. Cadmium extraction mechanism and species

The distribution coefficient, *D*, for the extraction of metal ions from the acidic chloride medium into an organic phase following ion-pair mechanism [18] may be expressed as a function of metal ion concentration [M^{m+}], [H⁺], [Cl⁻] and ligand concentration [S], i.e.,

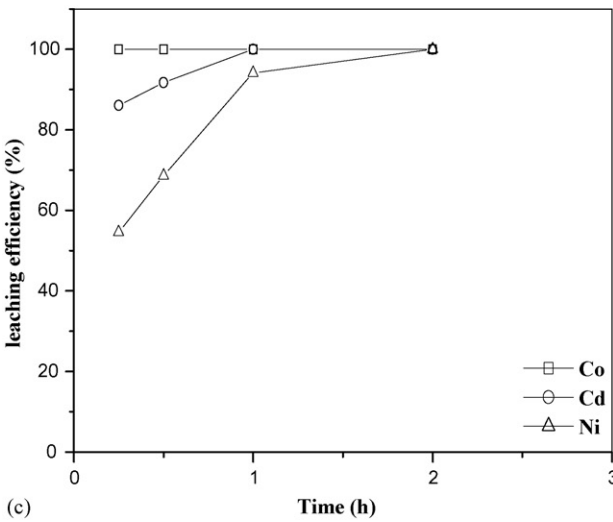




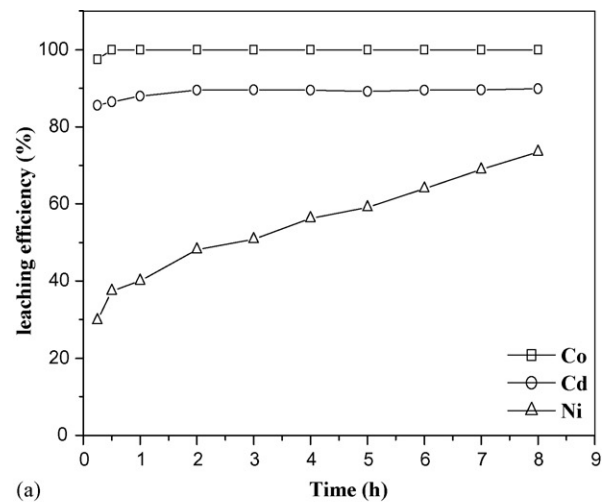
(a)



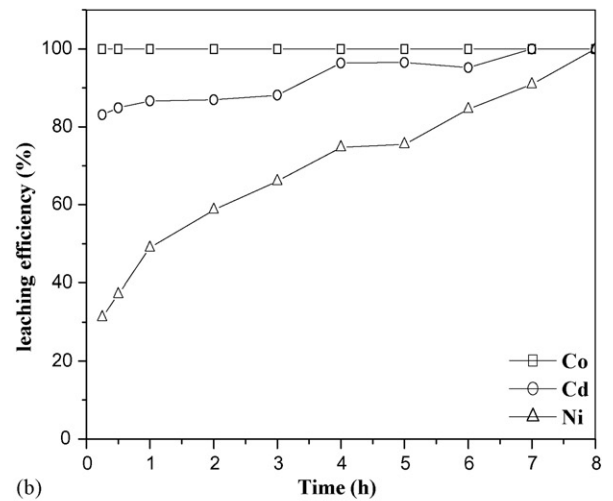
(b)



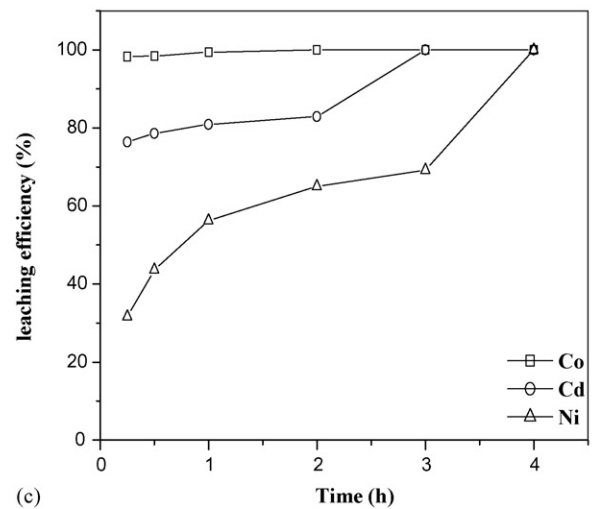
(c)



(a)



(b)



(c)

Fig. 2. Effect of reaction time vs. percentage leaching. Leaching conditions: (a) 1 M HCl; (b) 1.5 M HCl; (c) 2 M HCl; temperature: 85 °C; solids-to-liquid ratio: 4.

Fig. 1. Effect of reaction time vs. percentage leaching. Leaching conditions: (a) 1 M HCl; (b) 1.5 M HCl; (c) 2 M HCl; temperature: 85 °C; solids-to-liquid ratio: 2.

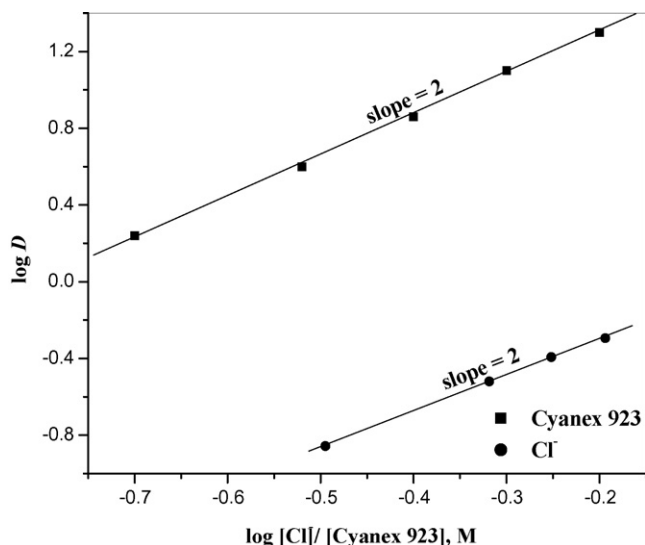


Fig. 3. Plot of $\log D$ vs. $\log[\text{Cl}^-]/\log[\text{extractant}]$, M for cadmium(II). Extraction conditions: Cd(II), 6.27 g/L; (●) $[\text{Cl}^-]$, 0.32–0.72 M, Cyanex 923, 0.1 M; (■) Cyanex 923, 0.1–0.6 M.

where M^{m+} is the metal ion and S is the extractant. The equilibrium constant, K_{ex} for the extraction process is represented by:

$$K_{\text{ex}} = \frac{[\text{complex}]}{[M^{m+}]^x [H^+]^y [Cl^-]^z [S]^n} \quad (2)$$

where x , y , z and n represent, respectively, the number of metal, hydrogen, chloride ions and ligand molecules involved with the extracted species. The distribution of metal between the aqueous phase and the organic phase may be expressed by the familiar equation:

$$D = \frac{[\text{complex}]_{(\text{org})}}{[M^{m+}]_{(\text{aq})}} \quad (3)$$

Under the present conditions of leach liquor at low acidities, the association of H^+ ions can be neglected. Considering the extraction of monomer metal complex species, substituting D , and rearranging and taking logarithms, Eq. (2) takes the form:

$$\log D = \log K_{\text{ex}} + z \log[\text{Cl}^-] + n \log[S] \quad (4)$$

By analyzing the extraction data as a function of Cl^- and S, the nature of extracted species can be elucidated.

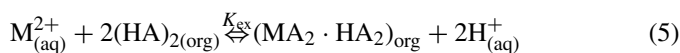
3.2.2. Effect of Cyanex 923 and chloride concentration

Variation of Cyanex 923 concentration in the range 0.1–0.6 M indicated an increase in the percentage extraction of cadmium from 29 to 96.5%. The plot of $\log D$ versus $\log[\text{extractant}]$, M is linear (Fig. 3) with a slope of 2. This indicates the association of two moles of extractant with the extracted species. Variation of Cl^- concentration in the range 0.32–0.72 M was carried with 0.1 M Cyanex 923. The extraction of metal increases from 11.5 to 39.3%. Further, the plot of $\log D$ versus $\log[\text{Cl}^-]$ is linear with a slope of 2, see Fig. 3. Thus, the species extracted appears to be $\text{CdCl}_2 \cdot 2\text{S}$ (S, Cyanex 923). On the other hand, it is interesting that there is zero co-extraction of nickel and cobalt,

which demonstrates specific separation of cadmium with the Cyanex 923 extractant. The results for a single-stage extraction suggests that about 99% cadmium can be recovered in two stages.

3.3. Cobalt extraction mechanism

The extraction equilibrium of M^{2+} ($\text{Ni}^{2+}/\text{Co}^{2+}$) ions from chloride solutions in the pH region with a cation-exchange extractant such as Cyanex 272 may be represented as:



where K_{ex} denotes the equilibrium constant and $(\text{HA})_2$ refers to the dimeric form of the extractant (Cyanex 272). It has been reported elsewhere [12,19,20] that this extractant exists as a dimer under the present experimental conditions.

$$K_{\text{ex}} = \frac{[\text{MA}_2 \cdot \text{HA}_2][\text{H}^+]^2}{[M^{2+}][(\text{HA})_2]^2} \quad (6)$$

$$K_{\text{ex}} = \frac{D[\text{H}^+]^2}{[(\text{HA})_2]^2} \quad (7)$$

$$\text{where } D = \frac{[\text{MA}_2 \cdot \text{HA}_2]}{[M^{2+}]} \quad (8)$$

Taking the logarithm of Eq. (7) and rearranging:

$$\log D = \log K_{\text{ex}} + 2 \log[(\text{HA})_2] + 2\text{pH} \quad (9)$$

Analysis of the experimental data for the distribution ratio (D) as a function of equilibrium pH and extractant concentration for constant values of other parameters allows estimation of the number of extractant molecules associated with the extracted metal complex.

3.3.1. Effect of equilibrium pH and Cyanex 272 concentration on cobalt extraction

From the cadmium raffinate, extraction was carried out at a 1:1 phase ratio in the pH range 1.57–6.03 using 0.03 M Cyanex 272. Increase in the equilibrium pH increases the extraction of cobalt from 1.1 to 96.9% up to a pH of 5.7, but the level remains constant thereafter. This shows that the transfer of cobalt by Cyanex 272 follows a cation-exchange mechanism. The co-extraction of nickel is at a minimum ($\sim 0.4\%$) under the present conditions. The plot of $\log D$ versus equilibrium pH (Fig. 4) has a slope of 2, i.e., two moles of H^+ ions are exchanged with one mole of metal during the extraction process. The influence of Cyanex 272 concentration on metal extraction was studied in the range 0.01–0.04 at an equilibrium pH of 5.7. The percentage extraction is found to increase with increasing extractant concentration, viz., from 11.6 to 62.3%. The plot of $\log D$ versus $\log[\text{extractant}]$, M (Fig. 4) is linear with a slope of 1.9, which indicates the association of two moles of extractant per mole of metal ion with the extracted species.

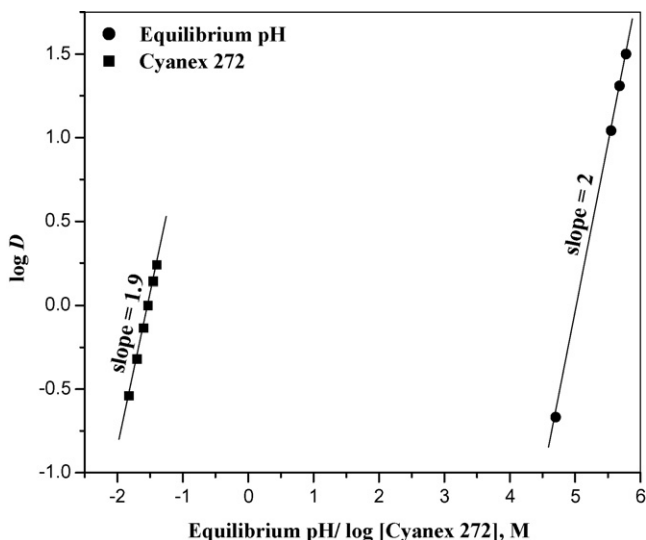


Fig. 4. Plot of $\log D$ vs. equilibrium pH/log[extractant], M for cobalt(II) extraction. Extraction conditions: Co(II), 0.14 g/L; (●) Cyanex 272, 0.03 M; (■) Cyanex 272, 0.01–0.04 M.

3.4. Nickel extraction

3.4.1. Effect of equilibrium pH and Cyanex 272 concentration

Extraction of nickel was carried out over the equilibrium pH range of 1.3–6.83 using 0.8 M Cyanex 272 at a phase ratio of unity. As expected, the percentage extraction of metal increases with rise in the equilibrium pH of the aqueous phase; it reaches a maximum (97.5%) at around pH 6.83 and remains constant thereafter. The plot of $\log D$ versus equilibrium pH is a straight line with a slope 2 (Fig. 5). The effect of variation of extractant concentration in the range 0.1–0.6 M on the extraction of nickel was studied. The plot of $\log D$ versus log[extractant], M is linear

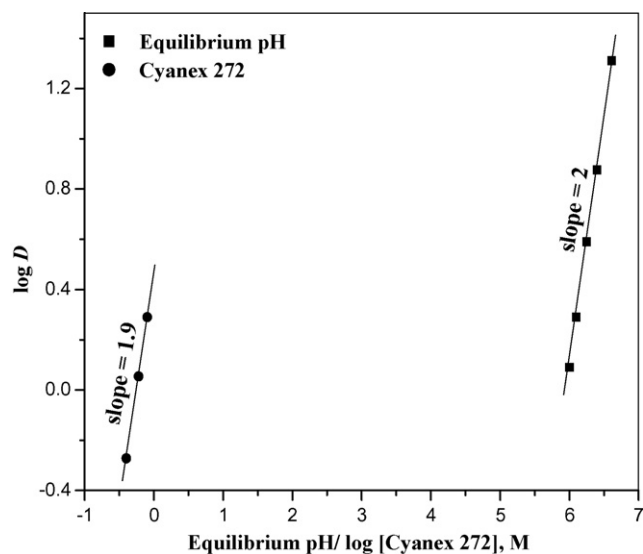


Fig. 5. Plot of $\log D$ vs. equilibrium pH/log[extractant], M for Ni(II) extraction. Extraction conditions: Ni(II), 21.56 g L⁻¹; (■) Cyanex 272, 0.8 M; (●) Cyanex 272, 0.1–0.6 M.

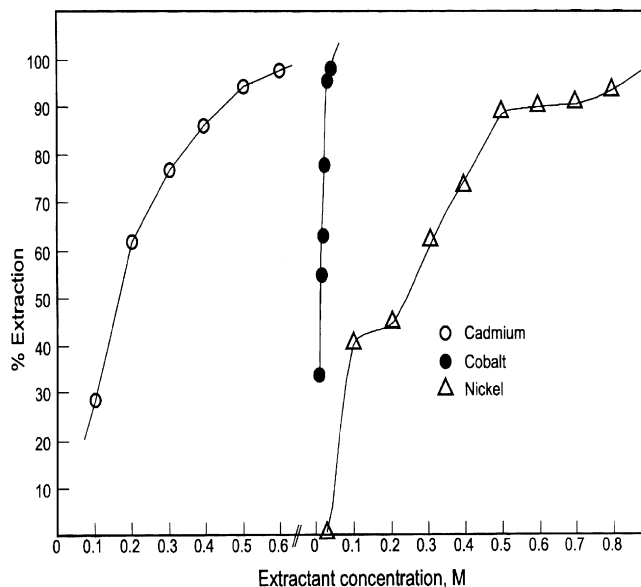


Fig. 6. Extraction behaviour of metals as function of extractant concentration. Extraction conditions: Cd(II), pH 0.95; Cyanex 923 0.6 M; Co(II), pH 5.7; Cyanex 272 0.03 M; Ni(II), pH 5.7; Cyanex 272 0.8 M.

with a slope of 1.9 (Fig. 5). This observation suggests that nickel is extracted as NiA₂ species.

3.5. Separation scheme for Cd, Co and Ni from leach liquor

Based on previous studies of the solvent extraction of metals with Cyanex 923 and 272, extraction curves in the form of extractant concentration versus percentage extraction were obtained at specified pH values of the aqueous phase (Fig. 6). The results indicate the separation of cadmium, nickel and cobalt from the leach liquor with change in the concentration of extractant.

A process for the solvent extraction separation of cadmium, cobalt and nickel from a leach liquor containing 6.27 g L⁻¹ Cd(II), 0.14 g L⁻¹ Co(II) and 21.56 g L⁻¹ Ni(II) and a pH of 0.95 was tested (Fig. 7). A two-stage, counter-current extraction simulation (CCES) test for cadmium was carried out for a A:O phase ratio of unity. Results show selective separation of cadmium at more than 99.95% efficiency when using 0.6 M Cyanex 923, with the entire cobalt and nickel being left in the raffinate. Cadmium was then recovered from the organic phase (Cd L.O = 6.267 g L⁻¹) with distilled water of pH 6.12 as the stripping agent in two stages at a A:O ratio of 1:3 that can yield a stripping efficiency of >99% cadmium. The raffinate from the cadmium extraction circuit, containing Co at 0.14 g L⁻¹ and Ni at 21.56 g L⁻¹, was used for optimizing the conditions for cobalt recovery. Cobalt can be recovered with 0.03 M Cyanex 272 at an equilibrium pH of 5.8 in three stages. Co-extracted nickel is scrubbed with a cobalt solution of 0.09 g L⁻¹ (pH 4.0) in single stage at a phase ratio of unity. The cobalt-loaded organic phase was then stripped with acidified distilled water of pH 1.0 at an A:O ratio of 1:1 in a single stage to recover more than 99.9% of the metal. Finally, the cobalt raffinate contains nickel, which can be recovered as a salt or as a hydroxide.

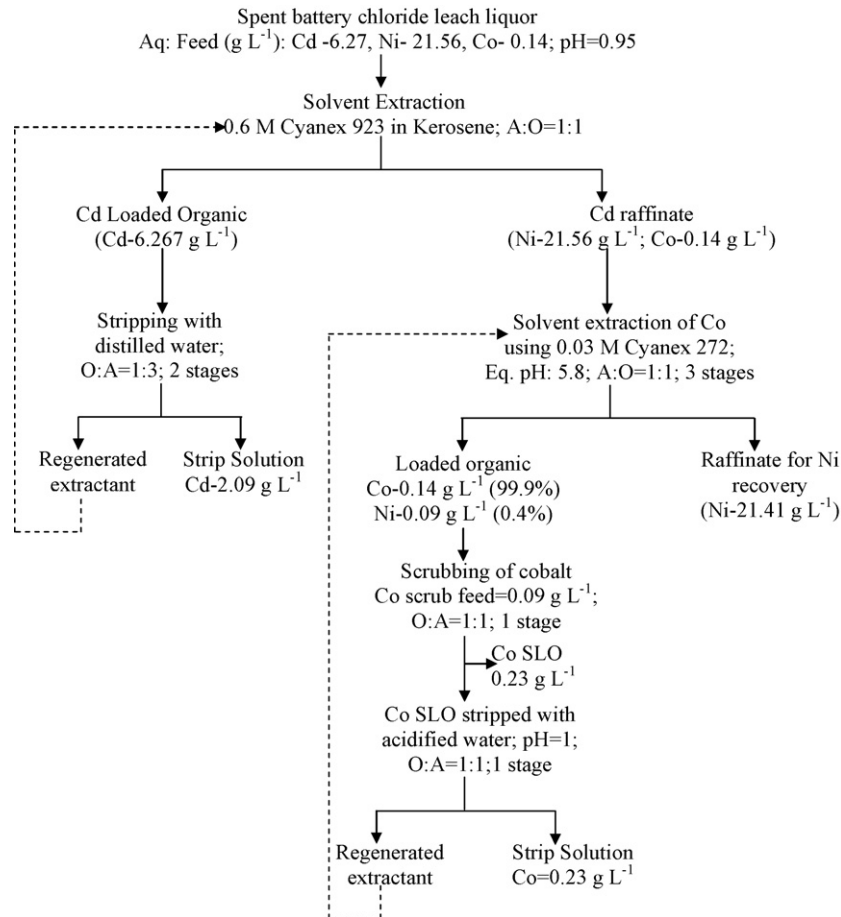


Fig. 7. Process for separation of Cd(II), Co(II) and Ni(II) from chloride leach liquor.

4. Conclusions

Leaching of spent batteries with dilute hydrochloric acid leads to complete dissolution of valuable metal ions. The generated leach liquors contain macro concentrations of cadmium and nickel. Solvent extraction studies reveal that the transfer of cadmium by Cyanex 923 follows a solvation mechanism in which extraction of cobalt and nickel by Cyanex 272 involves cation-exchange mechanism. Cyanex 923 extractant has been applied successfully for the clear separation of cadmium from cobalt and nickel. The separation and recovery of metals is more than 99.9% efficient during the extraction and stripping stages. Based on the extraction data, a scheme for the separation and recovery of cadmium, nickel and cobalt is presented. In summary, the results demonstrate the applicability of the present hydrometallurgical approach to the treatment of waste batteries and thereby its potential for the amelioration of environmental-related issues.

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