RECOVERY OF METAL VALUES FROM SPENT NICKEL-CADMIUM RECHARGEABLE BATTERIES BY SOLVENT EXTRACTION ROUTE

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ABSTRACT

Spent Nickel cadmium batteries are classified as hazardous waste due to the presence of toxic cadmium in high concentration. Recycling of metal value by environmentally friendly process is the best option to obtain economical advantage and prevent environmental pollution. In the present investigation, a metal separation scheme is proposed for recovery of cadmium, nickel and cobalt from the leach solution of Ni-Cd battery electrode materials. After removal of the external case, the electrodes were washed with water to remove adhered alkali and dissolve in sulphuric acid in presence of a suitable additive. The iron from the leach solution was removed by selective precipitation and the iron free leach solution of composition: Ni:18.63 g/L, Cd:17.24 g/L, and Co:1.89 g/L was subjected to solvent extraction for separation of cadmium, cobalt nickel using phosphoric acid based extractants. Initially di-(2-ethyl hexyl) phosphoric acid (D2EHPA) and cyanex 302 were used to extract cadmium selectively, followed by cobalt and nickel separation using PC 88A, Cyanex 272 of suitable composition. Effect of different parameters such as equilibration time, pH aqueous feed, solvent concentration, organic to aqueous phase ratio were studied to determine the optimum conditions for extraction, scrubbing and stripping of cadmium, cobalt and nickel. Requirement of number of stages were determined from Mc-Cabe-Thiele plot for complete extraction and stripping of specific metal and subsequently validated by counter current simulation study.

Keywords: Spent Batteries, NiCad Batteries, Solvent Extraction, D2EHPA.

INTRODUCTION

Nickel cadmium battery is specifically suitable for various applications in cellular and cordless telephones, video cameras, portable power tools, and laptop computers due to its ability to deliver high currents. After several cycle of uses these batteries can no longer hold charge and become spent.[1] Increase in the consumption of batteries for household appliances, implementation of strict environmental regulations and promoting the treatment of Ni-Cd household batteries have turned this kind of battery waste into an increasingly representative material to be recycled. A major concern with Ni-Cd batteries is the environmental pollution problem due to the presence of toxic metals such as cadmium at the same time spent batteries contain high value metals such as nickel and cobalt. This has lead to an increased interest in the recycling of used household batteries such as alkaline, zinc-carbon, mercuric oxide,[2] lead[3,4] and nickel–cadmium Ni-Cd[5–9] batteries which will not only generate revenue but also prevent environmental pollution. Both pyrometallurgical/or hydrometallurgical based processes have been tried to recover metal values

from spent batteries. The pyrometallurgical method basically consists of selective volatilization of metals at elevated temperatures (~900°C) followed by condensation to recover cadmium with 99% purity. But most valuable metals such as nickel and cobalt are usually lost.[10, 11] The hydro-metallurgical process developed are based on crushing the spent battery followed by a physical separation of the structural elements, dissolution of electrode materials in acid and separation of metals by solvent extraction/ion exchange/cementation.[6, 12] Earlier organo-phosphorus extractants have been extensively used for separation of Cd, Co and Ni from each other.[13–16] In this paper we report studies on the extraction and separation of cadmium from sulfate leach liquors of spent nickel-cadmium batteries containing nickel and cobalt using D2EHPA diluted in kerosene. The parameters studied to optimize extraction and separation conditions are: selection of extractant, effect of equilibrium pH, extractant concentration, phase ratios, extraction and stripping isotherms, counter-current extraction and stripping simulations.

EXPERIMENTAL

Materials and reagents

Cylindrical shaped Ni-Cd batteries were procured from BEL, Pune. Leach liquor was generated by leaching of the electrode material of these spent Ni-Cd batteries after mechanical separation of each component. All other chemicals used in the present study were of AR grade. Di-(2-ethylhexyl) phosphoric acid (D2EHPA), (Fluka, AG, Buchs) was used as a solvent in the present investigation without further purification. The extracting solvent was prepared by dissolving appropriate volume of D2EHPA in distilled (160–200°C fraction) kerosene oil (diluent) unless otherwise stated, to obtain organic solutions of different concentrations. 5% isodecanol was added as a phase modifier. The pH value of aqueous phase before and after extraction was measured with a pH meter (Systronics μ pH system 362). Metal analysis was done by atomic absorption spectrophotometer (Thermo SOLAAR S-2). Mass balance gives the amount of metal extracted by the solvent.

Leaching of the battery electrode material

The spent batteries were dismantled into the separate components of the cell such as the steel case, electrodes, polymeric separators and the active cell material. Anode (negative electrode) was covered by cadmium hydroxide, while the cathode (positive electrode) was covered by nickel hydroxide separated by synthetic separators impregnated with potassium hydroxide solution. After the separation, the electrode material was washed to remove alkali 100 g of electrode material of composition 40.5% Ni, 23% Cd, 0.8% Co and 13.5% Fe was dissolved in H_2SO_4 under oxidizing condition. The leach slurry was filtered and collected along with the wash solution. This solution contains sufficient amount of iron hence it was diluted to remove iron by precipitated after adjusting the pH upto 3.5. The iron free leach solution of composition: 12.45 gpl Ni, 7.3 gpl Cd, 0.212 gpl Co was further used for the selective extraction of Cd using saponified di(2-ethylhexyl) phosphoric acid(D2EHPA).

Extraction experiments

The extraction experiments were performed with a known amount of D2EHPA of a known concentration dissolved in distilled kerosene (160–200°C fraction). The appropriate volume of aqueous solution (10 ml) containing metal ion and 10 ml of pre-neutralized D2EHPA at an organic/aqueous phase ratio of 1, were mixed in a separatory funnel and shaken for 5 minutes. All

the experiment studies were carried out at 30°C. To optimize the experimental parameters a leach liquor of the composition 12.45 g/L Ni, 7.3 g/L Cd, 0.212 g/L Co respectively was used. Tests for the extraction of a known amount of Cd^{2+}, Co^{2+} and Ni^{2+} mixture were carried out, initially with unsaponified 10% D2EHPA but the extraction was not good due to decrease in pH of the raffinate at equilibrium, hence the solvent was pre-neutralized (saponified) with the stoichiometric amount of NaOH at different percentages, for the maximum extraction of the metal ions.

RESULTS AND DISCUSSION

Effect of extractant concentration on extraction of Cd, Ni and Co

The effect of initial concentration of D2EHPA on the extraction of Cd, Ni and Co from the leach solution of composition 12.45 gpl Ni, 7.3 gpl Cd, 0.212 gpl Co respectively was studied in the range of 10–40% (v/v) at O:A ratio of 1 at 30°C. Since the solvent when used without any saponification showed a poor extractability, it was saponified to 90% by adding stoichiometric amount of NaOH. Fig. 1 shows that with the increase in the concentration of 90% saponified solvent from 10 to 40%, percentage extraction of cadmium increases from 50.1 % to 95.9%, nickel from 12.7 to 45.12% and cobalt from 10.5 to 52.9% in a single contact (Fig. 1).

Separation factors $\left(\alpha_{M2}^{M1}\right)$ were calculated for the selectivity of Cd over Ni and Co in the solution and also for Ni in the presence of Co (Table 1).

Table 1: Separation factors $\left(\alpha_{M2}^{M1}\right)$ for the separation of Cd from Ni and Co and Ni from Co with different concentration of DEHPA and 90% saponification

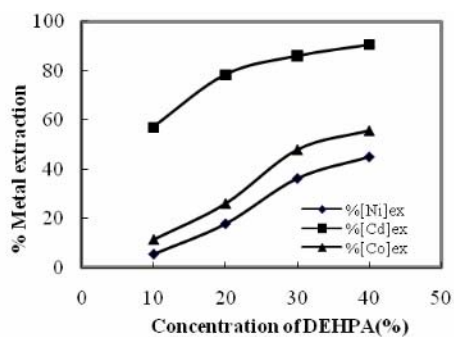| D2EHPA %	α_{Ni}^{Cd}	α_{Co}^{Cd}	α_{Co}^{Ni}
10	16.05	8.55	0.53
20	23.70	9.97	0.42
30	22.56	14.62	0.65
40	28.33	20.74	0.73

Fig. 1: Effect of D2EHPA concentration on metal extraction at 90% saponification. O:A 1:2, T 30°C, t 5 min, [Aq feed]g/L: 12.435 Ni, 7.312 Cd, 0.2324 Co.

Separation factor data indicates that selectivity for cadmium over nickel and cobalt increases with the increase in solvent concentration. However separation of Ni from Co is not possible. Since percent metal extraction was around 86.2 % for Cd along with 32.85 % Ni and 38.76% Co, at 20% solvent concentration, further experiments were conducted with 20% solvents unless otherwise stated.

Effect of equilibrium pH on extraction of Cd, Ni and Co by D2EHPA

Extraction of these metals were found to be very sensitive to pH, it was varied in the range of 2.5 to 4.0 by varying the saponification of the solvent to different concentration varying from 20% to 90% by adding stoichiometric amount of NaOH. The initial pH of the aqueous feed was 4.31. Effect of saponification of 20% D2EHPA was studied. Fig. 2 shown that with the increase in eq pH from 2.34 to 3.2 at an O/A ratio of 1:1 the percent extraction of Cd increases from 42.9 to 81.9%, Ni extraction increases from 6.8 to 41.9% and Co extraction increases from 11.4 to 38.5%. In another set of experiment effect of pH on metal extraction was studied with 20% D2EHPA at different saponification and at an O/A ratio of 1:2. In this case also the equilibrium pH varies in the range of 2.27 to 3.3 and in this pH range the percentage extraction increases from 8.3 to 17.8% for Ni, 48.75 to 78.9% for Cd and 4.5 to 19.5 % for Co (Fig. 3). Thus further experiments were performed with 20% D2EHPA at 60% saponification.
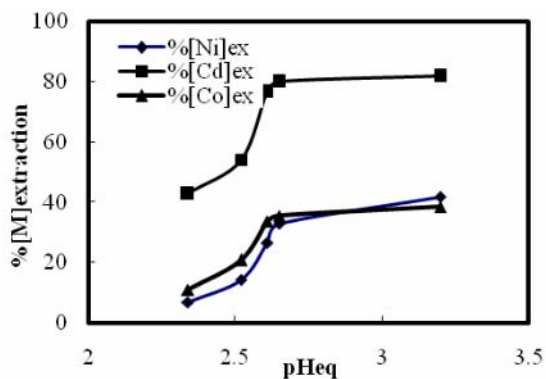

Fig. 2: Effect of equilibrium pH on metal extraction by 20% D2EHPA (varying saponification). O:A 1:1, T 30°C, t 5min, Aq feed]g/L 12.435 Ni, 7.312 Cd,0.2324 Co.
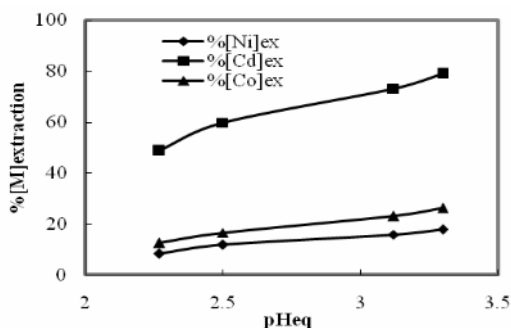
Fig. 3: Effect of equilibrium pH on metal extraction by 20% D2EHPA (varying saponification).
[O:A 1:2, T 30°C, t 5min, Aq feed]g/L 12.435 Ni, 7.312 Cd,0.2324 Co.

Effect of O : A ratio on extraction of Cd, Ni and Co

Extraction of Cd, Ni and Co from the aqueous phase were carried out at different O : A ratio using 60% saponified 20% (v/v) D2EHPA at initial pH 4.31 and a temperature of 30°C to observe the possibility to extract maximum amount of metals in a single contact. It was observed from the result (Fig. 4) that on increasing O : A ratio from 0.2 to 5, the percentage extraction of Cd increases from 34.8 to 98.3%, and for Ni and Co the extraction percentage increases from 3.8 to 85.4% and 8.14 to 89.2% respectively.
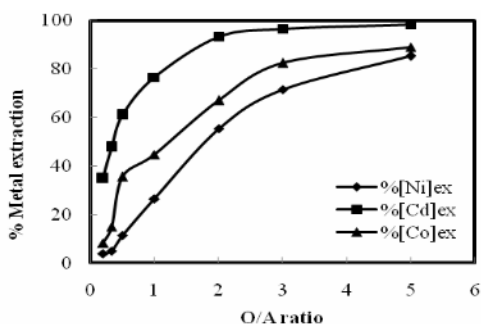

Fig. 4: Effect of O/A variation on the extraction of Cd, Ni and Co by 20% (60% saponification)
D2EHPA., T 30°C, t 5min, Aq feed(g/L) 12.435 Ni, 7.312 Cd,0.2324 Co.

To determine the number of stages required at a chosen volume phase ratio, the extraction isotherm was obtained by plotting [Metal]aq. vs [Metal]org. phases at different O/A ratios. As can be observed from Fig. 5, a quantitative Cd extraction was achievable in three counter-current stages at O/A phase ratio 1:1.
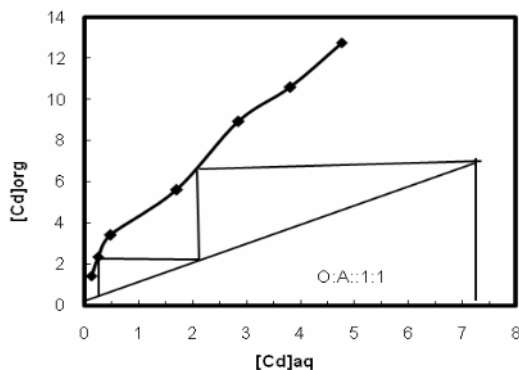

Fig. 5: Mc Cabe Thiele plot for stage determination for complete metal extraction, T 30°C,
t 5 min, Aq feed]g/L 12.435 Ni, 7.312 Cd,0.2324 Co 1.89.

Counter current batch simulation study for cadmium extraction

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To confirm the extraction isotherm prediction data, a three stage counter current extraction simulation (CCES) test was carried out at the O:A ratio of 1:1. Aqueous (Raffinate) and organic outlet stream were collected after the fourth cycle onwards and analysed for metal values. The Loaded organic contained 7.84 g/L Cd corresponding to 98.5% extraction efficiency. Co-extraction of Ni and Co was 3.29 gpl and 0.081 g/L respectively. Remaining Reffinate contains 9.49 g/L Ni,0.12 g/L Cd, 0.15 g/L Co (Fig. 6) which was used for the separation of Co and Ni.
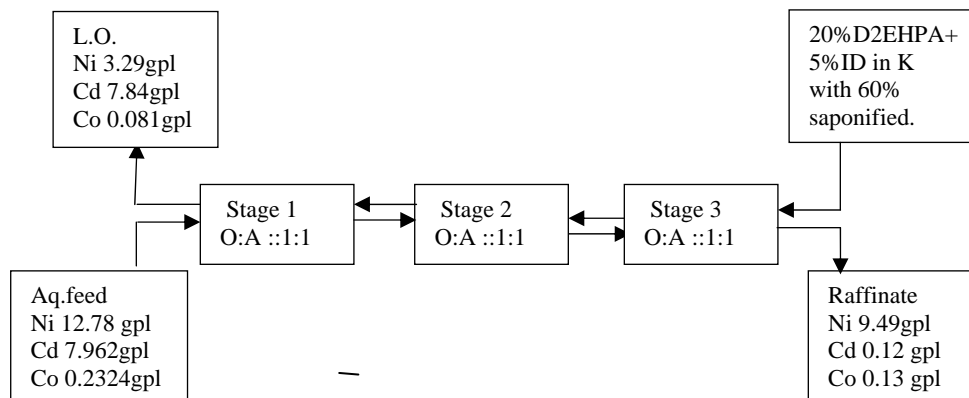

Fig. 6: Counter current flow for extraction study of Cd with 20% D2EHPA + 5% Isodecanol in kerosene with 60% saponification.

Scrubbing and stripping of loaded Organic

The loaded organic was scrubbed with different concentration of sulphuric acid in the range 3 to 10 g/L at an O/A ratio of 1 to remove the co-extracted Ni and Co. It was observed that scrubbing of Ni and Co increases with increasing acid concentration but Cd is also scrubbed with Ni and Co. With a H_2SO_4 concentration of 6 g/L, scrubbing of Ni and Co was 50.76% and 48.15% respectively and Cd scrubbing was only 9.7%, hence this acid concentration (6 g/L) was used from scrubbing studies.

After the scrubbing of Co and Ni, the loaded organic contains 0.24 g/L Ni, 7.1 g/L Cd and 0.015 g/L Co. Scrubbed Organic containing Cd was stripped with different concentration of sulphuric acid in the range 20 to 50 g/L at an O/A ratio of 1 for a period of 5 min. It was found that Cd stripping increased with increasing acid concentration and about 70% of Cd was stripped with 20 g/L of acid. Further stripping studies were performed with 20g/L H_2SO_4. Phase variation study shows that quantitative Cd stripping was possible in two stages at O/A ratio of 0.75:1. Subsiquently a Counter current batch simulation study for Cd stripping was carried at O/A ratio of 1. Fig. 7 shows that about 94% cadmium was stripped in two stage.
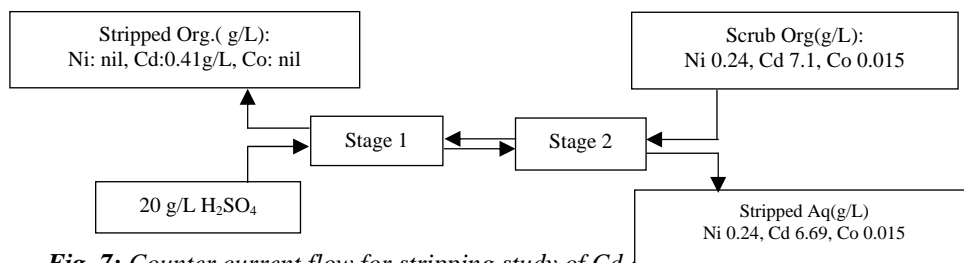
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┌─────────────────────────────┐              ┌─────────────────────────────┐
│ Stripped Org.( g/L):        │              │ Scrub Org(g/L):             │
│ Ni: nil, Cd:0.41g/L, Co: nil│              │ Ni 0.24, Cd 7.1, Co 0.015   │
└─────────────────────────────┘              └─────────────────────────────┘
              ↑                                              ↓
         ┌─────────┐        ┌─────────┐
         │ Stage 1 │ ←───── │ Stage 2 │ ←─────
         └─────────┘ ─────→ └─────────┘
              ↑                                   ┌─────────────────────────────┐
┌──────────────────────┐                         │ Stripped Aq(g/L)            │
│ 20 g/L H₂SO₄         │                         │ Ni 0.24, Cd 6.69, Co 0.015  │
└──────────────────────┘                         └─────────────────────────────┘
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Fig. 7: *Counter current flow for stripping study of Cd at O:A 1 with 20% D2EHPA + 5% Isodecanol in kerosene stripped with 20 g/L H_2SO_4.*

CONCLUSION

Following conclusions were made from the above study:

– Percent extraction of metal increases with the increase in equilibrium pH.
– At a fixed saponification percentage the percent extraction of Cd, Ni and Co increases with the increase in solvent concentration.
– Saturated loading capacity for 20% (90% saponified D2EHPA) was found to be 0.24 g/L Ni, 7.1 g/L Cd and 0.015 g/L Co.
– With the increase in O/A ratio from 0.2 to 5, the percentage extraction of Cd increases from 34.8 to 98.3%, and for Ni and Co the extraction percentage increases from 3.8 to 85.4% and 8.14 to 89.2% respectively.
– Mc Cabe thiele plot shows that a quantitative Cd extraction was achieved in three counter-current stages at O/A phase ratio 1:1.
– Scrubbing of co-extracted Ni and Co was done with 6 g/L H_2SO_4 and stripping of Cd from the scrubbed organic solvent was performed with 20 g/L of H_2SO_4.

ACKNOWLEDGEMENT

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