

Recovery of metal values from spent nickel–metal hydride rechargeable batteries

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Abstract

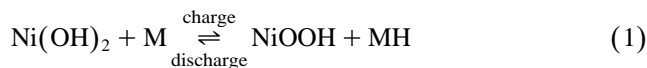
A hydrometallurgical process is developed for the separation and recovery of metal values such as nickel, cobalt and rare earths from spent nickel–metal hydride (Ni–MH) rechargeable batteries. After removal of the external case, the electrode materials are dissolved in 2 M sulfuric acid solution at 95°C. The resulting liquor contains typically (g l^{-1}), 10.6 Ni, 0.85 Co, 1.70 Fe, 0.36 Zn, 0.21 Al, 0.54 Mn, 1.73 La, 0.10 Ce, 0.33 Pr, 1.10 Nd and 0.032 Sm. The pH is around 0.4. The rare earth values are recovered from the liquor by means of a solvent extraction circuit with 25% bis(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene, followed by precipitation with oxalic acid. A mixed rare earth oxide of about 99.8% purity is obtained after calcination of the precipitate. The total yield of rare earths approaches 93.6%. The cobalt and nickel in the raffinate are effectively separated by solvent extraction with 20% bis(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272) in kerosene. The individual cobalt and nickel are then recovered as oxalates by the addition of oxalic acid. Cobalt and nickel oxalates with purities close to 99.6% and 99.8%, respectively, are obtained. The overall recoveries are over 96% for both cobalt and nickel. A total flowsheet of the process for recovery of rare earths, cobalt and nickel from spent Ni–MH batteries is proposed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Nickel–metal hydride batteries; Nickel; Cobalt; Rare earths; Recovery

1. Introduction

The practical success of electric vehicles will depend considerably upon the choice of power source. Novel rechargeable batteries such as lithium-ion (Li-ion) and nickel–metal hydride (Ni–MH) batteries are considered to be strong candidates for battery-powered electric vehicles, as well as for other mobile applications. This is because the systems have specific energies and design flexibility. Ni–MH batteries were developed in 1989 and commercialized primarily in Japan in 1990. The positive electrodes comprise porous Ni plate with nickel hydroxide as the activating agent. The negative electrodes consist of a hydrogen storage alloy powder such as Mm–Ni–Co (Mm = Misch metal) on a metal-mesh substrate. The two electrodes are separated by an inert insulating layer. The

overall cell reaction for charging and discharging can be simply illustrated by:



where M represents the alloy to be hydrided.

The Ni–MH rechargeable batteries have high electrochemical capacity (1.5 to 2 times that of Ni–Cd batteries), as well as safety and good environmental compatibility, i.e., no hazardous materials are used, such as cadmium and lead which are utilized in Ni–Cd and lead–acid batteries, respectively. In addition, Ni–MH batteries are found to function efficiently within a wide range of temperatures (–20 to +60°C) and to possess long lives (500 to 1000 cycles) and low self-discharge rates. In recent years, advanced Ni–MH batteries have been commonly adopted in portable electronic applications such as personal computers, video-recorders and mobile telephones. The output of Ni–MH batteries in Japan has been increasing year after

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year at a high rate, as shown in Fig. 1 [1]. The estimated consumption of Ni–MH batteries in the year 2000 will comprise approximately 50% of the total market for rechargeable batteries (Li-ion batteries will probably command a 30% share and Ni–Cd batteries 20%). Thus, it is expected that an appreciable amount of spent Ni–MH batteries will be generated in the near future. The anticipated tonnages of both primary and secondary raw materials are potentially very large. As a consequence, recycling and treatment of the waste batteries have become an important issue. From an economic incentive, Ni–MH batteries contain significant quantities of valuable metal resources like nickel, cobalt and rare earths. Additionally, recycling will be important due to the likelihood that environmental regulations for nickel may become more stringent. The present work is aimed at developing an efficient process for the recovery of nickel, cobalt and rare earths from spent Ni–MH batteries by hydrometallurgical techniques.

A literature survey reveals that there is little information available with regard to the hydrometallurgical treatment of spent Ni–MH rechargeable batteries [2–5], although a number of investigations have been reported or patented on the separation and recovery of a variety of metallic values from other spent batteries such as lead [6,7], alkaline manganese [8,9], nickel–cadmium [10–15] and lithium batteries [16–18]. Lyman and Palmer [2,3] systematically investigated leaching of Ni–MH battery scrap with mineral acids such as sulfuric acid, hydrochloric acid and nitric acid, and developed a coarse filtration technique which produced a concentrated solution of rare earths while maintaining much of the remainder of the scrap in metallic form. For example, over 99% of the original iron content of the rolls could be prevented from dissolving into the leach solution. They found that 4 M HCl was the best acid medium for this process. Lanthanum and cerium were reported to be recovered as phosphate precipitates from the resulting rare-earth bearing chloride solution by the addition of H_3PO_4 after the pH was adjusted to 1 with either NaOH or NH_4OH . Both HNO_3 and H_2SO_4 systems were

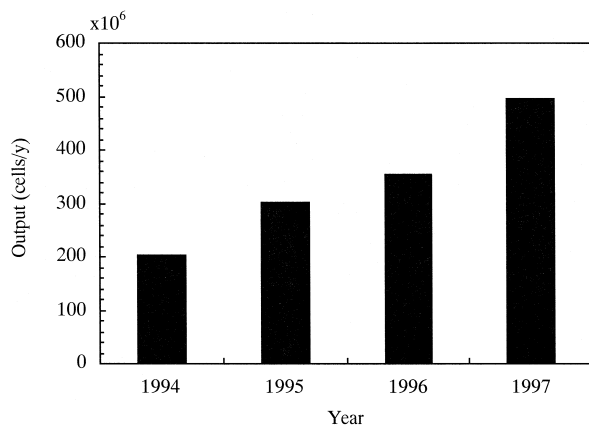


Fig. 1. Production of Ni–MH batteries.

considered to be inadequate for phosphate precipitation due to incomplete rare earth recovery and contamination from iron which also precipitated with the use of the former acid, and the formation of mixed rare earth sulfate and phosphate salts with the latter acid. Studies on the separation and recovery of nickel and cobalt from the remaining solution were not reported. Lyman and Palmer [4] also examined iron removal from acid leach solutions by solvent extraction. They found that solvent extraction using D2EHPA was very effective for iron removal from nitric acid system when the acid concentration was 6 M. Once the iron was removed, cobalt and nickel were reported to be precipitated from the raffinate with oxalic acid while leaving lanthanum and cerium in solution. Similarly, solvent extraction with D2EHPA was found to be very effective in removing the iron from leach solutions of either 4 M, 6 M, or 8 M hydrochloric acid. Nevertheless, no further studies on the treatment for the remaining metals were conducted. For the sulfuric acid system, iron removal by solvent extraction was reported to be problematic due to poor selectivity. Yoshita et al. [5] have proposed a basic recycling process for used Ni–MH rechargeable batteries, in which the nickel, cobalt and rare earth elements are recovered through a combination of mechanical processing and hydrometallurgical processing that includes leaching of battery material by sulfuric acid, recovery of rare earths using a double salt method, separation of impurity elements from cobalt and nickel by solvent extraction or sulfide precipitation as well as electrowinning of nickel and cobalt. Unfortunately, however, no detail technological data were disclosed in this paper.

In recent work [19], we described a hydrometallurgical process for the recovery of cobalt and lithium from spent Li-ion batteries. The current paper extends the work to the development of a hydrometallurgical process for recycling of spent Ni–MH rechargeable batteries. The general experimental route leaches the electrode materials of the batteries with sulfuric acid, recovers the rare earths from the leach solution by solvent extraction with D2EHPA as well as precipitation with oxalic acid, and then separates and recovers cobalt and nickel from the raffinate by solvent extraction with Cyanex 272.

2. Experimental

2.1. Materials

Cylinder-shaped Ni–MH batteries (Toshiba TH-3A type) were used. The cells weighed an average of 24.8 g each and contained an AB_5 -type (rare earth metal system) negative electrode. In the cell, the weight of the positive electrode was 7.27 g and that of the negative electrode was 10.57 g, in which the alloy powder accounted for 87.6% and the metal-mesh, 12.4%. The chemical components of

the electrode materials were analyzed separately by total dissolution in aqua regia. The results showed that the positive electrode was composed basically of about 88 wt.% nickel, 6 wt.% cobalt and 5.6 wt.% zinc. The negative electrode consisted mainly of about 48 wt.% nickel, 29 wt.% rare earths (lanthanum 15.4 wt.%, cerium 1.0 wt.%, praseodymium 3.0 wt.%, neodymium 9.7 wt.% and samarium 0.3 wt.%), 13 wt.% iron and 3.5 wt.% cobalt. The other metals (zinc, aluminum and manganese) accounted for less than 6.4 wt.%.

Two commercial extractants were employed: (i) D2EHPA containing the active component bis(2-ethylhexyl) phosphoric acid (D2EHPA) was supplied by Daihachi Chemical Industry; (ii) Cyanex 272, containing active component bis(2,4,4-trimethylpentyl) phosphinic acid was purchased from Cyanamid Canada. These extractants were utilized without any further purification. Unless otherwise noted, the concentrations of D2EHPA and Cyanex 272 in organic solution were 25% and 20% by volume, respectively. The diluent was kerosene. All other reagents were of analytical reagent grade.

2.2. Experimental procedure

2.2.1. Leaching

The Ni–MH batteries were cut in half longitudinally to separate the metallic cases from the internal battery rolls which consisted of the positive and negative electrodes plus a nylon separator. One battery roll (~ 17.8 g) from which the separator had been removed, was leached in 350 ml of 2 M sulfuric acid solution, under agitation for 4 h at 95°C. After leaching, the small amount of the insoluble residue was filtrated and washed with water. The resulting pregnant liquor was a green solution with a chemical composition (g l^{-1}) of: 10.6 Ni, 0.85 Co, 1.70 Fe, 0.36 Zn, 0.21 Al, 0.54 Mn, 1.73 La, 0.10 Ce, 0.33 Pr, 1.10 Nd and 0.032 Sm (rare earths: total 3.29). The pH was about 0.4. The leach efficiency of nickel, cobalt and rare earths was 97, 100 and 96%, respectively. From this solution, the rare earth elements, cobalt and nickel will be recovered as described in the following sections.

2.2.2. Solvent extraction

Extraction and stripping tests for obtaining equilibrium data were conducted by contacting suitable volumes of the organic and aqueous solutions in 50 ml centrifuge tubes. The batch counter-current in the solvent-extraction processes was carried out by mechanically shaking separatory funnels of suitable sizes. All experiments were performed at a temperature of $25 \pm 0.2^\circ\text{C}$. The two phases were contacted for 30 min (found to be sufficient for reaching equilibrium). The adjustment of pH was performed by the addition of a concentrated solution of sodium hydroxide. After allowing the phases to disengage completely, they were separated and subjected to analysis.

2.2.3. Precipitation of rare earths, cobalt and nickel

The mixed rare earths were precipitated from the strip liquors of the extraction circuit with D2EHPA by the addition of concentrated ammonia solution until a pH 2–3 was reached, followed by an excess of saturated oxalic acid solution. The resulting oxalate was calcined in a muffle furnace at 850–900°C to effect a conversion to a mixed rare earth oxide product. Precipitation of cobalt and nickel was performed using a similar technique to that described above.

2.3. Analysis

The concentrations of metals in the aqueous solutions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a SEIKO SPS 1200A spectrophotometer. Those in the organic phase, in principle, were calculated in the light of mass balance, unless otherwise specified. The total concentration of rare earths, which is represented by [RE] in the text, is the summation of the concentrations of the individual rare earth elements in the solution. The pH value of each aqueous solution was measured with a TOA pH meter type HM-30S.

3. Results and discussion

3.1. Recovery of rare earths

3.1.1. Separation of impurities and rare earths from cobalt and nickel

Early research into the use of acidic organophosphorus reagents for the solvent extraction of metal ions from aqueous solutions has demonstrated that D2EHPA can extract divalent transition metals such as Zn^{2+} , Cd^{2+} , Mn^{2+} [20,21] and trivalent metal cations such as Fe^{3+} [22,23], Al^{3+} [24,25], as well as trivalent rare earth elements [26,27] at relatively low pH, but does not extract cobalt and nickel. Accordingly, solvent extraction with D2EHPA was employed to eliminate rare earths and impurities from leach liquor while leaving cobalt and nickel in solution.

Initial extraction tests on the actual leach solution at different pH by a 25% solution of D2EHPA in kerosene at an equal phase ratio showed that at a pH close to 2.5, all of the rare earths and iron, as well as most of the aluminum and the zinc, could be extracted. By contrast, the extraction of cobalt was negligible and no nickel extraction took place. Moreover, the extraction of manganese was insufficient. To remove manganese entirely from the solution, it was found necessary to increase the organic-to-aqueous phase ratio (O:A) and use multi-stage counter-current operation. For this purpose, the distribution isotherm for the

extraction of manganese was determined by contacting the two phases at different phase ratios at a pH around 2.6. The equilibrium data are presented in Fig. 2. The McCabe–Thiele construction shows that an essentially complete extraction of manganese is attainable in two counter-current stages at an O:A ratio of 3:2 and an equilibrium pH of 2.6. Therefore, the aqueous feed liquor was processed in a two-stage batch counter-current test, using 120 ml of organic phase and 80 ml of aqueous phase for each contact. The equilibrium pH value for each contact was controlled at 2.56–2.60. After six cycles, the concentration of manganese in the raffinate was 0.010 g l^{-1} ; those of aluminum and zinc were 0.002 g l^{-1} and 0.042 g l^{-1} , respectively. Iron and rare earths were never detected, as expected. The incomplete extraction of zinc is attributed to the complexation of zinc ions with sulfate ions due to the presence of a large amount of sulfate ions in the leach liquor [28]. Analyses of the loaded organic phase showed that the extraction efficiencies of cobalt and nickel were less than 4.7% and 0.8%, respectively.

3.1.2. Scrubbing of cobalt and nickel

Small amounts of cobalt and nickel co-extracted into the organic phase were easily removed by scrubbing with a $0.15 \text{ M H}_2\text{SO}_4$ solution at an O:A ratio of 25:1 in a single stage. The scrub solution contained, (g l^{-1}): 0.63 Co, 1.38 Ni, 1.21 Mn, 0.027 Zn, 0.019 Al and 0.045 La, as well as 0.001 Pr. No iron and none of the other rare earths were detected in the scrub solution. In practical applications, this solution can be returned to be mixed with the leach liquor. The scrubbed organic phase contained, (g l^{-1}): 0.002 Co, 0.30 Mn, 0.21 Zn, 0.14 Al, 1.11 Fe, and 2.19 RE.

3.1.3. Stripping of rare earths

The stripping of rare earths from the scrubbed organic phase can be performed with sulfuric acid solution. Table 1 shows that almost all quantitative stripping are achieved with a $1 \text{ M H}_2\text{SO}_4$ solution in a single contact at an O:A

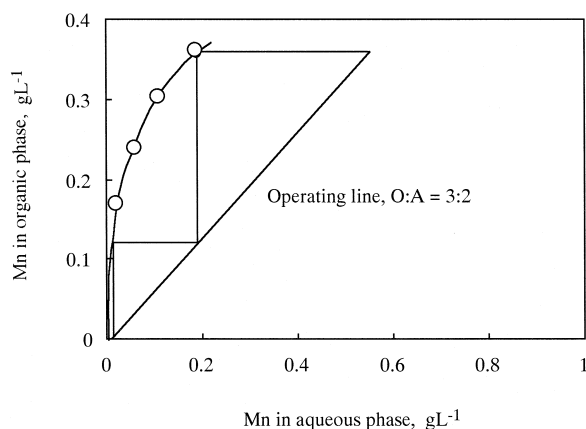


Fig. 2. McCabe–Thiele equilibrium isotherm for the extraction of manganese from leach liquor at pH 2.6 by 25% D2EHPA in kerosene.

Table 1

Effect of sulfuric acid concentration and O:A phase ratio on stripping of metal ions from the D2EHPA organic phase^a

[H ₂ SO ₄] (M)	O:A ratio	Stripping yields of metals (%)					
		RE	Co	Mn	Zn	Al	Fe
0.5	1:1	98.5	100	99.7	97.6	89.6	0.09
1.0	1:1	100	100	100	100	100	0.72
2.0	1:1	100	100	100	100	100	6.6
1.0	1:0.5	100	100	100	100	100	0.27
1.0	1:0.15	98.7	100	100	96.0	83.3	0.01
1.0	1:0.1	95.5	100	100	91.0	72.0	<0.01

^aSolvent loading (g l^{-1}): [RE] = 2.19, [Co] = 0.002, [Mn] = 0.30, [Zn] = 0.21, [Al] = 0.14, [Fe] = 1.11.

ratio of 20:3. The resulting strip liquor contains (g l^{-1}): 14.4 RE, 0.78 Al, 1.34 Zn, 2.02 Mn, 0.013 Co, and 0.001 Fe. Higher concentrations of rare earths can be obtained, if required, by the use of a multi-stage counter-current stripping operation at a greater O:A ratio. The stripping of iron by sulfuric acid is inefficient. Investigations showed, however, that iron stripping is improved considerably by employing hydrochloric acid as the strip agent. Nearly complete removal of iron from the organic phase is theoretically possible using a 6 M HCl solution in four counter-current stages at an O:A ratio of 5:1.

3.1.4. Recovery of mixed rare earth oxide product

As seen from the above results, since the partial stripping of aluminum and essentially complete stripping of zinc and manganese together with rare earths from the loaded organic phase take place, further separation is required to obtain pure rare earth product. This is achieved by selective precipitation of rare earths with oxalic acid from the strip liquor, leaving the other impurities in solution. Calcination of the oxalate gives a mixed rare earth oxide product which contains 52.9 wt.% La₂O₃, 3.3 wt.% CeO₂, 10.3 wt.% Pr₆O₁₁, 32.5 wt.% Nd₂O₃, and 0.9 wt.% Sm₂O₃. With respect to impurities other than rare earths, analyses for three samples show them to contain 0.007 wt.% CoO, 0.034 wt.% MnO, 0.052 wt.% ZnO, 0.006 wt.% Fe₂O₃, and 0.10 wt.% Al₂O₃. The loss of rare earths was approximately 1.2 wt.%.

3.2. Recovery of cobalt and nickel

3.2.1. Selective extraction of cobalt with Cyanex 272

Following the removal of rare earths and impurities from the leach solution by extraction with D2EHPA, the separation of cobalt from nickel from the raffinate is required to obtain pure products. It has been known that the cobalt–nickel separation from weakly acidic or neutral sulfate media can be achieved by solvent extraction with organophosphorus acids such as D2EHPA [29,30], PC-88A [31,32] and Cyanex 272 [33,34]. A comparison of the extent of the extraction of cobalt and nickel by these three

extractants from sulfate solution as a function of equilibrium pH is illustrated in Fig. 3 [35]. Clearly, the extraction of cobalt takes place prior to nickel (i.e., at lower pH) in all cases. Furthermore, the difference in $\text{pH}_{1/2}$ values (defined as the pH at which 50% of metal in solution is extracted) increases in the following sequence: D2EHPA < PC-88A < Cyanex 272 (Table 2). The difference in $\text{pH}_{1/2}$ reflects immediately the degree of separation between two metals. The greater the difference in $\text{pH}_{1/2}$, the higher the selectivity of the extractant, i.e., the better the separation efficiency. Consequently, in the present work, Cyanex 272 has been chosen in preference to the other two extractants because of its more excellent selectivity towards cobalt over nickel.

At a pH of about 4.5, Cyanex 272 can extract cobalt quantitatively whereas extraction of nickel is negligible (see Fig. 3). Preliminary extraction tests on the raffinate obtained previously at this pH value for one contact at an equal phase ratio with 20% Cyanex 272 in kerosene, showed that extraction of cobalt was incomplete. As a result, the distribution isotherm for extraction of cobalt from the raffinate by 20% Cyanex 272 in kerosene was determined at pH 4.75–4.80 to recover cobalt completely. The equilibrium data are presented in Fig. 4. The McCabe–Thiele construction demonstrates that it should be possible to achieve nearly complete extraction of cobalt from a solution which initially contains 0.80 g l^{-1} of cobalt in two counter-current stages at an O:A ratio of 1:1.2. To confirm this expectation, a two-stage counter-current batch simulation was conducted. After six cycles, the representative raffinate was found to contain 0.015 g l^{-1} of cobalt, which corresponds to an extraction yield of > 98%. The concentrations of other metals in the loaded organic phase were (g l^{-1}): 0.065 Ni, 0.012 Mn, and 0.002 Al. It should be pointed out that although zinc has been reported [36] to be extracted from sulfate solution at

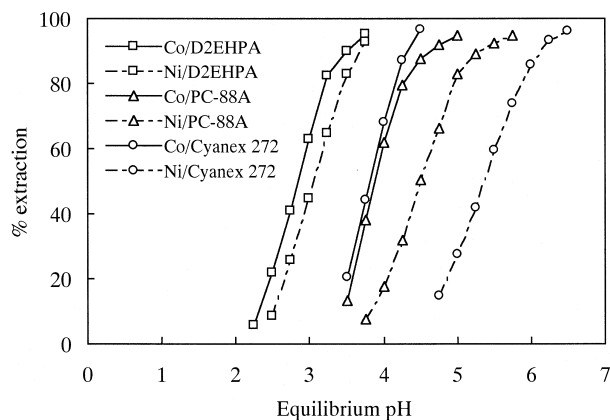


Fig. 3. Extraction of cobalt and nickel by various acidic organophosphorus extractants (HR) at 40°C. Organic phase: 20% HR in EXXSOL D80, an aliphatic commercial diluent similar to kerosene; initial feed solution: 0.3 g l^{-1} of each metal in 0.05 M sodium sulfate; O:A = 1:1.

Table 2

The $\text{pH}_{1/2}$ values for extraction of cobalt and nickel by acidic organophosphorus extractants dissolved in EXXSOL D80 at 40°C

Extractant	$\text{pH}_{1/2}$		
	Co	Ni	Ni-Co
D2EHPA	2.80	3.05	0.25
PC-88A	3.84	4.60	0.76
Cyanex 272	3.75	5.33	1.58

^aExperimental conditions are given in Fig. 3.

$\text{pH} > 2$ by Cyanex 272, only a very small amount of zinc ($< 0.001 \text{ g l}^{-1}$) was observed in the loaded organic phase in the current work.

3.2.2. Scrubbing of nickel

Trace levels of nickel co-extracted in the Co-loaded organic phase can be removed by contact with a scrub feed (19.2 g l^{-1} Co as sulfate, initial $\text{pH} = 3.65$) at an O:A ratio of 25:1 in a single stage. The concentration of cobalt in the scrubbed solvent was 1.01 g l^{-1} and the Co:Ni ratio was found to be 1530, and this indicated that nearly full elimination of nickel was achieved under the conditions. The scrub solution contained (g l^{-1}): 17.5 Co, 1.63 Ni and 0.065 Mn. In the commercial operations, the contaminated solution can be fed back to the extraction stage.

3.2.3. Stripping and recovery of cobalt

The cobalt in the scrubbed organic phase was stripped readily and completely by a 0.50 M sulfuric acid solution at an O:A ratio of 20:1.1 in one contact. The resulting strip liquor contained (g l^{-1}): 18.4 cobalt, 0.012 Ni, 0.18 Mn, 0.002 Al, and 0.005 Zn. The cobalt was further recovered as a cobalt oxalate precipitate by the addition of oxalic acid. Analyses for the products showed them to contain

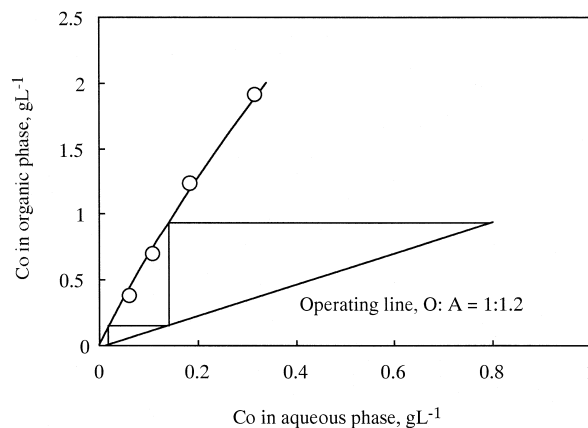


Fig. 4. McCabe–Thiele equilibrium isotherm for the extraction of cobalt from raffinate at pH 4.75–4.80 by 20% Cyanex 272 in kerosene. The raffinate contained (in g l^{-1}): 0.80 Co, 9.93 Ni, 0.042 Zn; 0.010 Mn, 0.002 Al, $\text{pH} = 2.60$.

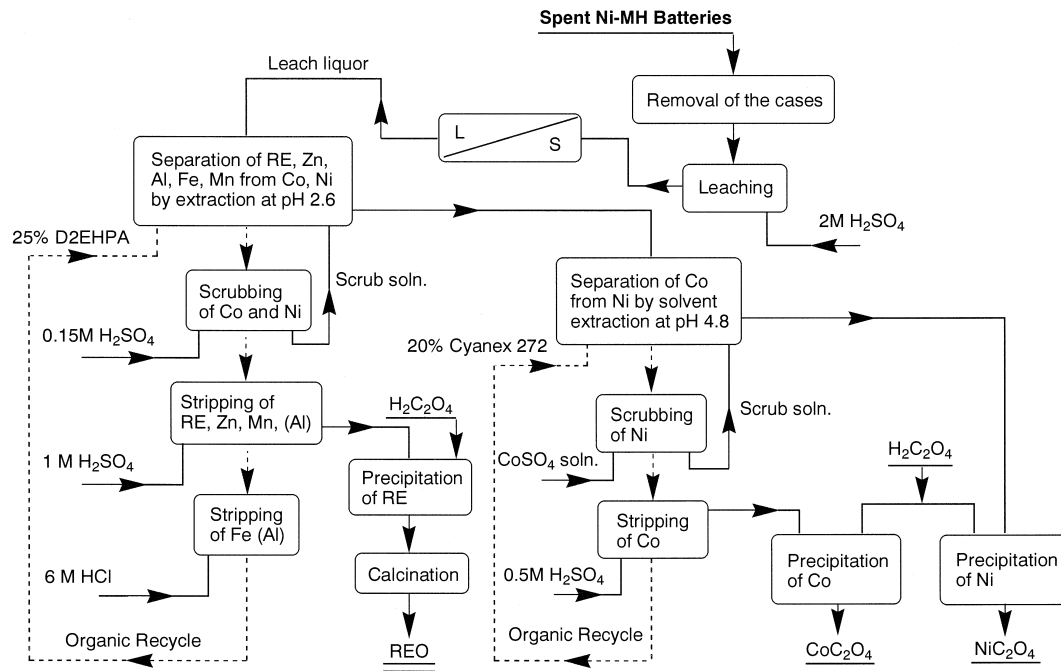


Fig. 5. Flowsheet for the recovery of metal values from spent Ni–MH rechargeable batteries (dashed lines: organic streams; solid lines: aqueous streams).

0.025 wt.% Ni, 0.01 wt.% Zn, 0.38 wt.% Mn and 0.004 wt.% Al. The percentage precipitation of cobalt was up to 98%.

3.2.4. Recovery of nickel

The nickel in the final raffinate was recovered directly as nickel oxalate by precipitation with oxalic acid. The contents of cobalt and zinc in the products were determined to be 0.058 wt.% and 0.15 wt.%, respectively. No other metal impurities were detected by ICP-AES. The precipitation yield of nickel was about 99%.

4. Conclusions

The technical feasibility of a hydrometallurgical process for the separation and recovery of rare earths, cobalt and nickel from the sulfate leach liquor of spent Ni–MH rechargeable batteries has been demonstrated by means of batch simulation trials on a laboratory scale. A mixed rare earth oxide containing 52.9 wt.% La_2O_3 , 3.3 wt.% CeO_2 , 10.3 wt.% Pr_6O_{11} , 32.5 wt.% Nd_2O_3 and 0.9 wt.% Sm_2O_3 was obtained with a yield of about 94% by a solvent extraction circuit with 25% D2EHPA in kerosene, followed by selective precipitation with oxalic acid and then calcination of the precipitate. The total content of impurities (other than rare earths) in the oxide product was found to be less than 0.2 wt.%. The separation of cobalt from nickel was achieved by preferential extraction of cobalt with 20% Cyanex 272 in kerosene. Cobalt and nickel oxalates with purities close to 99.6% and 99.8%, respectively, were obtained after precipitation with oxalic acid.

For each metal, the total recovery was over 96%. An overall flowsheet for the recovery of nickel, cobalt and rare earths from spent Ni–MH rechargeable batteries using the process described in this paper is presented in Fig. 5.

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