Recovery and Separation of Valuable Metals from Spent Nickel-Metal Hydride Batteries using some Organophosphorus Extractants

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ABSTRACT

The separation of cobalt, nickel, and rare earth elements from NiMH battery residues is evaluated in this paper. A hydrometallurgical process is developed for the recovery of metals from spent batteries and a selective separation of RE by precipitation of sodium RE double sulfate is performed. The methodology used benefits the solubility of the battery electrode materials in sulfuric or hydrochloric acids. The results obtained show that sulfuric acid is slightly less powerful in leaching (NiMH) compared to HCl acid. However, sulfuric acid was used on economic basis. Leaching solution was obtained by using 3 M H$_2$SO$_4$ at 70 + 1°C + 3% wt. H$_2$O$_2$ for 5 hours. It has been shown that it is possible to recover about 98% of the RE contained in spent NiMH batteries. The maximum recovery of nickel and cobalt metals was 99.9% and 99.4%, respectively. The effects of the main operating variables of both leaching and solvent extraction steps of nickel (II) and cobalt (II) from the leach solution using HDEHP (di-2-ethylhexyl phosphoric acid) and CYANEX 272 (di-(2, 4, 4 trimethyl pentyl ) phosphinic acid) in kerosene were investigated aiming to maximize metal separation for recycling purposes. The developed process for the recovery and separation of nickel (II), cobalt (II), and rare earth from spent NiMH batteries is tested and the obtained sulfate salts CoSO$_4$ and NiSO$_4$ have a high purity, suggesting that these recovered products could be used as chemical materials without further purification.

Key-words: Nickel-Metal-Hydride batteries; rare earth elements; solvent extraction; cobalt-nickel recovery

1-INTRODUCTION

The secondary battery Nickel-Metal Hydride (NiMH) is commonly used as power source in electronic devices like mobile phones, computers and Hybrid Electric Vehicles (HEV). Recycling of spent nickel-metal hydride batteries is considered a public service responsibility. Recovery of spent N-MH batteries provides multipurpose targets; control the hazardous materials’ protect the environment against pollution; conserve the mineral resources and recover pure valuable nickel, cobalt and chemical compounds needed in the market. The applied method may be environmentally friendly with no hazardous by-products. The cost of recovered products is competitive with the market price for the same chemicals prepared from primary resources. The main parts of a NiMH battery are the cathode, anode, electrolyte, separator and the steel case. The cathode is made of nickel coated with nickel hydroxide whereas the anode consists of a hydrogen storage alloy based on mischmetal (mainly cerium, lanthanum, praseodymium and neodymium) and nickel including substituent ($^1$). Hydrometallurgy is a well-established process for the separation and recovery of metal ions, with such benefit as: complete recovery of metals with high purity, low energy requirements, minimization of wastewater and avoidance of air emissions. Recently, some hydrometallurgical processes for the treatment of spent batteries have been developed ($^2$, $^3$, $^5$, $^6$). A number of papers reported that the separation factors of Co/Ni from sulfate solutions increase in the order phosphoric < phosphonic < phosphinic acid due to the increasing stability of tetrahedral coordination compounds of Co with these extractants in the organic phase because the tetrahedral compound is more lipophilic than the octahedral one ($^7$, $^8$, $^9$, $^{10}$). As the need for electronic devices grows worldwide, the consumption of batteries is expected to increase in the coming years. Therefore the continuous development of recycling battery technologies may contribute to economical and environmental aspects ($^{11}$, $^{12}$, $^{13}$).
this context, the present paper aims to investigate the main operating variables affecting the extraction of nickel (II) and cobalt (II) using HDEHP (di-2-ethylhexyl phosphoric acid) and CYANEX 272 (di-(2, 4, 4 trimethyl pentyl) phosphinic acid) were used as extractants, The results are used to assess the optimum conditions for maximum extraction and separation of these metals. A process for the recovery and separation of nickel (II), cobalt (II), and rare earth from spent NiMH batteries is proposed and tested in order to contribute to the protection of the environment from hazardous waste and to the conservation of natural resource.

2-EXPRIMENTAL

Apparatus

Atomic Absorption Spectrometer (AAS), Model (S4) thermo Electron Corporation was used for the measurement of the metal concentration in the aqueous phase and the rare earth composition was determined by Energy Disperse X-ray (EDX) Spectrometer. An analytical balance of Precisa 205 type having maximum sensitivity of 10-3 g and an accuracy ± 0.01 mg was used for weighing all samples used in this work. The hydrogen ion concentration for the solutions was measured using a digital pH meter of Hanna Instruments type at the ambient laboratory temperature degree 25 ± 1 ºC. A thermostated mechanical shaker of the type Julabo SW-20 C, Germany, was used in the extraction experiments for mixing the organic and aqueous phases. Complete separation of the two phases was attained by using a centrifuge of the type Z 230 obtained from Hermle, Germany.

Reagents

NiMH batteries (50% cylindrical and 50% prismatic batteries) from different manufacturers (Nokia, Motorola, Siemens, Ericsson, etc.) were used in this study. Plastic and metallic cases were firstly removed according to the manual procedure depicted elsewhere.

The internal content of batteries (including the grids that support the active material) was weighed, dried in a drying oven for 24 hours at 60 ºC, and weighed again to measure the content of volatile substances. One battery was randomly chosen and was submitted to qualitative metal characterization using Energy Dispersive Spectrometer in order to identify the main metal species present in the NiMH batteries as well as its morphology and qualitative metal composition. In order to get homogeneous samples for the leaching tests, the dried material was submitted to a knife mill for defragmentation by a ball mill for almost 1 hour and sieved. The extractants HDEHP (di-2-ethylhexyl phosphoric acid) and CYANEX 272 (di-(2, 4, 4 trimethyl pentyl) phosphinic acid) were used as extractants for the separation of Ni$^{2+}$ and Co$^{2+}$. Kerosene was used as diluent both for both extractants. All reagents were used as received without further purification.

Solvent extraction procedure

Equal volumes of aqueous (leach liquor) and organic phases were contacted for 5 min as preliminary experiments had showed that equilibrium was reached within 1 min. The phases were separated and the metal concentration in the aqueous phase (raffinate) was estimated directly by AAS. The loaded organic (LO) phases were stripped three times with 1 M HCl, and the combined strip solutions were analyzed for metal values by AAS. All the experiments were carried out at room temperature (25 ± 1 ºC). 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 &DISCUSSION

Leaching

Sulfuric acid has been chosen, after comparison with other leaching agents, considering, beside the metal yields, the economic aspects and, in particular, the low iron dissolution rate of the electrode grids. This requirement is necessary because considering the whole batteries treatment process,
iron can produce many problems during the successive selective separation steps for Ni, Co and Zn, performed by ion exchange and solvent extraction \(^{(15)}\). The cathode is completely dissolved (Ni (OH)\(_2\) or NiOOH species) Figure.1. While leaching of the anode depends on the charge/discharge status of the electrodes, probably due to the Ni metal form \(^{(3)}\) Fig.2.

**Precipitation tests**

The aqueous solution used in the subsequent tests was obtained by leaching the NiMH powder in the following conditions: \([\text{H}_2\text{SO}_4] = 3\text{M}, [\text{H}_2\text{O}_2] = 3\% \text{ wt.} \) \(T = 70 \pm 1 ^\circ\text{C}, \) S/L ratio = 1/10 g.mL\(^{-1}\) and \(t = 5\) h. The solutions were mixed and filtered to remove solids in suspension. As the pH of the leach solution was near zero, NaOH was added to raise the pH to 1.0. Consequently, the formation of a dense and white precipitate was verified. The solution was filtered again and the solid phase was dried and stored. The precipitation still lasted for some days but at a very slow rate; then, the solution was filtered for the third time. Samples of the final solution were analyzed by AAS for Co and Ni while samples of the precipitate were submitted to EDX analysis (Fig.3). The leaching yields of spent batteries is shown in table 1.
Table 1: Leaching yields of spent batteries

<table>
<thead>
<tr>
<th>Element</th>
<th>Anode (yields),%</th>
<th>Cathode (yields),%</th>
<th>Anode + cathode (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>76.6</td>
<td>100</td>
<td>14.0</td>
</tr>
<tr>
<td>Co</td>
<td>97.6</td>
<td>100</td>
<td>2.00</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0</td>
<td>1</td>
<td>0.13</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>100</td>
<td>0.28</td>
</tr>
<tr>
<td>La</td>
<td>92.5</td>
<td>-</td>
<td>RE =2.25</td>
</tr>
<tr>
<td>Nd</td>
<td>95.6</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Solvent extraction tests

After the separation of RE from the leaching solution, the removal of iron and some impurities at pH 3.5, Co\(^{2+}\) and Ni\(^{2+}\) were left. HDEHP and Cyanex 272 in kerosene solution were tested for extracting Co\(^{2+}\) and Ni\(^{2+}\) under different pH values to obtain the optimum conditions for separating Co\(^{2+}\) and Ni\(^{2+}\) with these two extractants. Several extraction factors, including extractant concentration, reaction temperature and time, pH value and O/A phase ratio were investigated. A solution mixture of (6.5 wt. % NaOH+3.5 wt. % Na\(_2\)CO\(_3\)) was used to adjust the pH value.

Effect of extractant concentration

The effect of extractant concentration on the extraction of Co\(^{2+}\) and Ni\(^{2+}\) at pH=5.8 was investigated, Fig.4. The figure shows that the extraction of Co\(^{2+}\) by HDEHP increases in the range (0.05 M -0.4M) from 25% to 96.8% then remains constant with further increase up to 0.7M, whereas increasing the concentration of HDEHP from 0.05M to 0.4M increases the extraction of Ni (II) from 0 to 50% and remains slightly constant in the concentration range (0.4-0.7) M. On the other hand, the increase in CYANEX272 in the concentration range (0.05-0.6) M increases the extraction of Co\(^{2+}\) from 30% to 98.9 and remains constant above 0.6M. The obtained results indicate also that CYANEX272 hardly extract Ni\(^{2+}\) in the same concentration range.

![Fig.4. Effect of the concentration of HDEHP and CYANEX 272 on the selective extraction of 2.0 g/l cobalt over 14 g / L nickel at pH=5.8, T = 25±1 °C, O: A = 1:1, and t = 5 min.](image-url)
Effect of contact time

The effect of contact time on the extraction of cobalt and nickel with HDEHP and CYANEX 272 extractants was investigated. The extraction equilibrium was reached after 1 minute when CYANEX272 in kerosene was used with both metals, while it was reached after 5 and 1 minutes in case of using HDEHP in kerosene with nickel and cobalt, respectively.

Effect of pH

The effect of pH on the extraction of cobalt and nickel with HDEHP and CYANEX272 extractants is shown in Fig. 5. As expected, metal extraction increases with the increase of pH because such metals exist in the aqueous phase as cation species. According to the curves shown in Figure 5, it can be seen that Cyanex 272 generally needs higher pH values than HDEHP to extract the same amount of metal ions amount because phosphinic acids derivatives are weaker acids than phosphoric ones\(^{(16)}\). Fig.5. also shows that HDEHP is an efficient reagent to separate cobalt from nickel at pH = 1.0 whereas CYANEX272, is an efficient reagent for the separation of cobalt from nickel at pH = 6.

![Graph showing the effect of pH on the extraction of 2.0 g/l cobalt over 14 g/L nickel by HDEHP and CYANEX 272 on the selective extraction of 2.0 g/l cobalt over 14 g/L nickel at [Extractant] = 0.5M, T = 25±1 °C, O: A = 1:1, and t = 5 min.]

Fig. 5. Effect of pH on the extraction of 2.0 g/l cobalt over 14 g/L nickel by HDEHP and CYANEX 272 on the selective extraction of 2.0 g/l cobalt over 14 g/L nickel at [Extractant] = 0.5M, T = 25±1 °C, O: A = 1:1, and t = 5 min.

Separation Feasibility

The separation factor (SF) is the ratio of the distribution ratio of both solutes measured under the same conditions. Mathematically it can be written as:

\[
SF = \frac{D_I}{D_{II}}
\]

where the subscripts I and II refer to two distinct metal ions. The separation feasibility of recovering of Ni\(^{2+}\) and Co\(^{2+}\) from the sulfate leachate solution obtained from NiMH spent batteries has been demonstrated by means of real solution. The obtained results show that pH and concentration of extractant are key variables on the extraction of metals with cationic extractants CYANEX272 and HDEHP. The selectivity factor \(\beta = \frac{D_{Co}/D_{Ni}}{}\) calculated based on the curves in figure 5. Table .2. measures the efficiency of the extractant in the separation of cobalt over nickel.
The higher is the concentration of extractant the higher is the metal extraction; such effect was not significant for nickel extraction because conditions were chosen to minimize its extraction. In terms of selectivity factors, calculated \( \beta_{\text{Co/Ni}} \) was found to be higher than 1,000 for concentrations of CYANEX 272 higher than 0.6 M. Therefore, the optimum conditions for the separation of cobalt from nickel may occur at pH = 5.7 with [CYANEX 272] = 0.6-0.7 M. According to the isotherm shown in Fig. 6, at least two theoretical stages operated in counter-current extraction are necessary for the removal of cobalt from the NiMH leach liquor ([Ni] = 24.1 g/L, [Co] = 3.3 g/l.

**Table 2: The selectivity factor \( \beta = \frac{D_{\text{Co}}}{D_{\text{Ni}}} \)**

<table>
<thead>
<tr>
<th>pH</th>
<th>( D_{\text{Co(III)}} )</th>
<th>( D_{\text{Ni(II)}} )</th>
<th>( D_{\text{Co(III)}} )</th>
<th>( D_{\text{Ni(II)}} )</th>
<th>( \beta_{\text{Co/Ni}} )</th>
<th>CYANEX272</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
<td>0.18</td>
<td>0.00</td>
<td>0.02</td>
<td>16.7</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
<td>1.63</td>
<td>0.05</td>
<td>0.03</td>
<td>1.96</td>
<td>1.67</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>2.53</td>
<td>0.43</td>
<td>0.03</td>
<td>1.30</td>
<td>14.3</td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>2.75</td>
<td>1.00</td>
<td>0.05</td>
<td>1.27</td>
<td>20.0</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>2.63</td>
<td>98.0</td>
<td>0.07</td>
<td>1.37</td>
<td>1400</td>
</tr>
<tr>
<td>6</td>
<td>4.4</td>
<td>2.88</td>
<td>99.0</td>
<td>0.06</td>
<td>1.53</td>
<td>1650</td>
</tr>
<tr>
<td>7</td>
<td>7.3</td>
<td>2.57</td>
<td>99.0</td>
<td>49.0</td>
<td>2.84</td>
<td>20.0</td>
</tr>
<tr>
<td>8</td>
<td>9.0</td>
<td>2.85</td>
<td>100.0</td>
<td>49.0</td>
<td>3.16</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Extraction isotherm

The stripping of cobalt form the loaded CYANEX272 in kerosene solution was studied using different concentrations of HCl, HNO\(_3\), H\(_2\)SO\(_4\), oxalic acid, KOH, Na\(_2\)CO\(_3\), and NaOH solution in the range 0.1-1M in addition to distilled water to choose the suitable stripping agent that can successfully strip cobalt from the loaded organic solution. The obtained results show that more than 99.9% of cobalt is stripped out from the loaded organic phase Fig .7. ([CYANEX 272] = 0.6, A/O ratio = 2, pH = 5.8, 2 stages, [Co] = 2 g.L\(^{-1}\)) at 2M of H\(_2\)SO\(_4\) (T = 25\(\pm\) 1 °C and A/O ratio = 1). The concentration of cobalt in the stripping solution was 4 g /L. Once purified, the aqueous solutions could be directly submitted to crystallization or electrowinning operations for metal recovery.
Fig. 6. Extraction isotherm of cobalt with Cyanex 272 ([Ni] = 24.1 g/L, [Co] = 3.3 g/L, [CYANEX 272] = 0.6 M, T = 25°C, pH = 5.7).

Fig. 7. Stripping of cobalt with different H\textsubscript{2}SO\textsubscript{4} concentrations (A/O ratio = 1, T = 25±1).

Conceptual flow sheet for Ni and Co recovery from spent Ni-MH batteries

Based on the above results, the detailed steps of the developed process for recovery and separation of nickel and cobalt from spent Ni-MH batteries are given in Fig. 8
Fig. 8. Overall flowsheet for recovery of Ni, Co and RE and preparation of spherical Ni (OH)₂ from spent Ni–MH batteries.

4. CONCLUSIONS

Leaching with sulfuric acid was considered efficient for the dissolution of metal content of NiMH battery powder. Cobalt and nickel were easily leached from the powder; around 80-85% of nickel and 95-100% of cobalt was leached from the NiMH powder in one single stage. No significant effect has been identified for the operating variables concentration of H₂O₂ and temperature. The full...
extraction of nickel and rare earth elements will require staged operation (nearly 87% of rare earth elements (La + Nd) was leached in two stage operation.

- The technical feasibility of recovering rare earths from the sulfate leachate solution obtained from NiMH spent batteries has been demonstrated by means of real solution.

- CYANEX 272 was found to be effective in separation of cobalt and nickel from the of spent Ni-MH batteries. Cobalt/nickel separation factors higher than 1.000 were obtained at [CYANEX 272] > 0.5 M, so the best condition for the separation of cobalt from nickel may occur at pH = 5.7 with [CYANEX272] = 0.5 M.

5-REFERENCES

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