EXTRACTION OF METAL IONS FROM SOLUTIONS AFTER LEACHING OF SPENT NiMH BATTERIES

Bernadeta GAJDA

Czestochowa University of Technology, Institute of Metallurgy and Metal Technology, Poland, EU, gajda@wip.pcz.pl

https://doi.org/10.37904/metal.2019.944

Abstract

In the recent years, the amount of waste has been drastically increasing, affected on the environment. On the other hand, there is observed a shortage of metals associated with the increase in their use and depletion of their natural resources. NiMH batteries. NiMH batteries contain, among nickel, cobalt, lanthanum, neodymium and other important metals. One of the possible and effective methods used for the metals recovery are hydrometallurgical processes, i.e. leaching and solvent extraction for metal separation. This work presents the results of the Zn(II), Co(II), Ni(II), La(III), Ce(IV) separation by solvent extraction. The source of metals was the solution from leaching of NiMH batteries. In the extraction process, chosen organic acids like, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 302) and di(2-ethylhexyl)phosphoric acid (D2EHPA) were used as the extractant.

Keywords: Solvent extraction, rare earth elements, nickel-metal hydride batteries

1. INTRODUCTION

In recent years, an increase in the amount of waste is observed, and this is a tremendous problem for the environment. Beyond that natural resources of many valuable natural elements are shrinking, which generates the need to search for other solutions, namely for such as those, which will employ secondary sources. Such waste as used batteries, for example NiMH batteries, are a valuable source containing many metals, such as: nickel, cobalt, manganese, copper and - what is the most precious - rare earth elements (REEs). The critical metals are defined as metals which natural resources do not cover their wider use, for example for the production of solar panels, permanent magnets, catalysts, fuel cells, plasma screens or touch screens, etc. Critical metals - among which are, in particular, REEs and cobalt - are metals whose natural resources do not meet the demand, which causes the necessity of importing them or searching for secondary sources. Used NiMH batteries contain - inter alia - such metals as: nickel, cobalt, manganese and lanthanides, namely: lanthanum, neodymium, promethium, yttrium and cerium. Larsson et al. [1] indicated that the anode in this type of batteries is a metal alloy (Mischmetall - “mixed metal”) described by the formula: Ni_{0.15}Co_{0.25}Mn_{0.44}Al_{0.12}La_{0.05}Ce_{0.24}Nd_{0.08}Pr_{0.03} with additions Y_2O_3. The following metals are contained in the cathode: 82.9 wt% of nickel, 12.4 wt% of cobalt, 1.1 wt% of zinc, 0.7 wt% of magnesium, 0.4 wt% of manganese and 1.9 wt% of yttrium.

Recovering metals that belong to the REEs is of particular importance, due to the fact that they are more and more widely used (for example in mobiles, drones, TV sets, etc.) and - at the same time - there is a lack of their natural deposits in Poland. Furthermore, waste batteries are classified as hazardous waste that is subject to special treatment. Application of hydrometallurgical processes, such as the leaching process [2-5], solvent extraction [6-9], membrane processes or ion exchange [10] in order to recover metals from this type of secondary raw material is a very efficient and future-oriented task. In the processes used for recovery and separation of metals, it is of crucial importance to select proper extractant. Among rare earth metal extractants that are used in extraction processes are such organophosphorus acids as: 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA), di-(2-ethylhexyl) phosphoric acid (D2EHPA), tributyl phosphate (TBP), and others.
The objective of this research study was to determine the applicability of extractant from the organophosphoric acid group for the process of selective extracting such metals as: Zn, Fe, Ni, Co, La, Ce, Mn and Al from acidic chloride solutions obtained after leaching from used NiMH batteries. The impact of pH increase in the feed phase on the efficiency of selective separation of metals was also subject of the research tests.

2. MATERIALS

Waste solution collected after the hydrochloric acid leaching process of used NiMH batteries from various producers served as the test material (Figure 1). The batteries were cut into small pieces and crushed without removing their steel case. Various concentrations of HCl were used as a leaching agent in the leaching process. The solution obtained after tests performed on the battery during the leaching process was used for solvent extraction. The initial solution was diluted 10 times and afterwards divided into two parts. In the first part, the measured level of pH was 1.6; and in the second part, the pH was being increased by using the KOH solution to receive the value of 3.0. Consequent increase of the pH level caused precipitation of iron hydroxides. Table 1 presents concentrations of metal ions observed in the solution used for the extraction process.

![Figure 1 Examples of used NiMH batteries from various manufactures](image)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Zn(II)</th>
<th>Fe(III)</th>
<th>Ni(II)</th>
<th>Co(II)</th>
<th>La(III)</th>
<th>Ce(III)</th>
<th>Mn(II)</th>
<th>Al(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of metal (mg/dm³)×10⁻³</td>
<td>0.1</td>
<td>3.5</td>
<td>10</td>
<td>0.9</td>
<td>0.8</td>
<td>0.02</td>
<td>0.4</td>
<td>0.37</td>
</tr>
</tbody>
</table>

3. EXTRACTION PROCESS

The aqueous phase in the process was a chloride solution with a pH of 1.6 and 3.0, respectively. The organic phase consisted of extractant solutions, namely the Di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl)thio-phosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) with 0.05 M concentration of refined petroleum (Aldrich). The ratio of both phases was 10 ml/10ml. Both phases were shaken in a conical flask by a shaker
for a period of 15 min, and then allowed to stand for 12 hours. After this period of time, both phases were separated and a sample for analysis was taken from the aqueous phase. The concentration of metal ions in the leach aqueous solutions was determined by atomic emission spectrometry method (spectrometer MP-AES 4200, made by Agilent).

The extraction percentage was determined is equal to:

$$\%E = \frac{D}{(D+1)} \times 100 \%$$

Where the distribution coefficient, D, was taken as the ratio of the concentration of metal in organic and aqueous phases:

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}}$$

4. RESULTS AND DISCUSSION

Results of the extraction process from chloride solution with pH = 1.6 by using extractants from the group of organophosphorus acids are shown in Figures 2-5. The initial composition of the aqueous phase is presented in Table 1. Figures 2-5 indicate on the dependence of extraction efficiency of the separated metal ions depending on the extractant used.

**Figure 2** The efficiency of extraction of metals ions from the chloride solution. The aqueous phase: chloride solution, pH-1.6. The organic phase: 0.05 M solution of D2EHPA in kerosene

**Figure 3** The efficiency of extraction of metals ions from the chloride solution. The aqueous phase: chloride solution, pH-1.6. The organic phase: 0.05 M solution of Cyanex 272 in kerosene
Figure 4 The efficiency of extraction of metals ions from the chloride solution. The aqueous phase: chloride solution, pH-1.6. The organic phase: 0.05 M solution of Cyanex 302 in kerosene

Figure 5 The efficiency of extraction of metals ions from the chloride solution. The aqueous phase: chloride solution, pH-1.6. The organic phase: 0.05 M solution of Cyanex 301 in kerosene

Application of D2EHPA as an extractant allowed for separation of Fe and Zn with almost 100 % efficiency. The efficiency of Ni, Co, Mn and Al extraction did not exceed 25 % of the total efficiency level, whereas, the lanthanum and cerium ions under such conditions remained in the aqueous phase. This process allowed to separate iron and zinc from the mixture. From a solution with the initial pH of 1.6, Cyanex 272 effectively extracted iron, while the remaining metal ions stayed in the aqueous phase. The extraction efficiency of Zn, Fe, Ni, Co, La, Ce, Mn and Al metals by using Cyanex 302 received the level of approx. 49, 100, 25, 8, 94, 100, 15 and 81 %, respectively. The results demonstrate that some of the metals can be efficiently separated, and therefore, the second stage of extraction can be applied for separation of the remained metals. By applying the Cyanex 301, Ni, Co, Al and Zn can be almost completely removed, however La, Ce, Mn and Fe are left in the feed solution. In this case, as well, application of the second stage of extraction would allow to increase selectivity of the process.

Due to the fact that acidity of the initial solution can affect the efficiency level of metal extraction and selectivity of the process, as well, there was also performed extraction from a solution with raised level of pH up to 3.0. Table 2 presents results of these research tests.
Table 2 The extraction efficiency of metals extracted from chloride solution at pH = 3 using 0.05M extractant solutions in kerosene

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Zn</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>La</th>
<th>Ce</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2EHPA</td>
<td>95.5</td>
<td>100</td>
<td>31</td>
<td>40</td>
<td>100</td>
<td>100</td>
<td>64.6</td>
<td>100</td>
</tr>
<tr>
<td>Cyanex 272</td>
<td>70.5</td>
<td>100</td>
<td>3</td>
<td>43</td>
<td>11</td>
<td>91.2</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cyanex 302</td>
<td>95.6</td>
<td>99.1</td>
<td>28.4</td>
<td>46.8</td>
<td>30.6</td>
<td>96.2</td>
<td>95.5</td>
<td>97</td>
</tr>
<tr>
<td>Cyanex 301</td>
<td>89.4</td>
<td>99.9</td>
<td>99.4</td>
<td>99.7</td>
<td>99.1</td>
<td>97.6</td>
<td>22.8</td>
<td>100</td>
</tr>
</tbody>
</table>

By raising the pH level in the initial solution, extraction efficiency of metal ions in the solution was significantly improved. Many of them have reached 100 % efficiency of extraction. Unfortunately, selectivity of the process has significantly deteriorated. The results call for introduction of a multi-stage extraction, which would probably lead to efficient and selective separation of metals from the solution. It also seems likely that by removing the steel casting from the material used in the leaching process, the presence of iron ions in the solution could be eliminated. This, in turn, would allow to raise the pH level in the initial solution, and this could further increase the extraction efficiency.

5. CONCLUSIONS

Results presented in the study have demonstrated that all of the used extractant can be applied in the extraction process of metals, namely: Zn, Fe, Ni, Co, La, Ce, Mn and Al from solutions obtained by leaching used NiMH batteries by using hydrochloric acid. Due to the fact that in the solution were present as many as eight metals, the extraction process should be followed in several stages. Results indicated on the need to carry out further research study in this area. At the same time, it can be concluded that the presence of ion in the solution could be eliminated by removing the steel casing prior to the leaching process, and this could contribute to improving the selectivity of the process, being subject to the research study.

REFERENCES


