

Sulphuric Acid Leaching of Spent Nickel Metal Hydride Car Batteries [†]

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Abstract: The treatment of spent nickel metal hydride batteries (NiMHs) of Lexus vehicles to recover nickel (Ni) and cobalt (Co) as well as rare earth elements (REEs) including La, Ce, Nd and Y was investigated. Co-extraction of Al, Fe, Cr and Cu has also been examined. Following batteries' manual dismantling to remove metallic cases, outer plastics and current collectors, the remaining parts including cathodes of black coloured nickel (oxy)hydroxides, anodes consisting of a nickel-containing alloy (AB5 mischmetal type), and separators were simultaneously ground down to –5 mm using a hammer mill equipped with sieves. The fine (–1 mm) fraction of this product was further subjected to sulphuric acid leaching to recover the high-value elements contained. Acid consumption of 14 mol H₂SO₄ per kg of this fraction was found to be sufficient to decrease pH to less than 1. Leaching experiments were performed using 0.5, 1 and 2 M sulphuric acid solution at 5% pulp density and temperature 50, 75 or 95 °C. The optimum conditions for the extraction of all elements were 2M H₂SO₄ concentration and temperature of 75 °C with the exception of Ni extraction, which reached its highest value at 95 °C and 2M H₂SO₄ concentration. Extractions of 93.34% of Ni, 99.03% of Co and 100% of REEs were achieved at these conditions.

Keywords: NiMHs batteries; recycling; leaching; nickel; cobalt; REEs



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1. Introduction

NiMH batteries represent the evolution of the nickel–hydrogen (Ni–H₂) battery, as hydrides have replaced hydrogen to avoid the danger of working with gases at high pressures. They have replaced, along with lithium-ion batteries (LIBs), NiCd batteries, due to the presence of toxic cadmium. NiMHs entered the market in 1991, introduced by the Japanese company Sanyo [1].

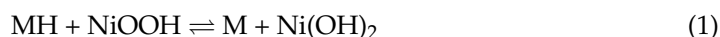
NiMH batteries are widely used in many energy storage applications. They are mostly used in all electric plug-in vehicles, hybrid vehicles, robots [2]. Moreover, some typical applications are the power tools, cell phones, hand tools, emergency lighting, laptop computers, calculators, GPS systems [3].

The nickel-metal hydride battery is a type of secondary battery and can be fully recharged. NiMH batteries contain significant amounts of critical metals that include Ni, Co and rare earth elements (REEs) such as Ce, Pr, Nd, the recycling of which is very important as it contributes to the Circular Economy model. In addition, Co and REEs are classified by the European Union as extremely critical components due to the high risk of their supply [4,5]. Ni-MH batteries have many advantages over other types of secondary batteries, especially concerning energy density and life cycle. They are capable of being recharged hundreds of times with battery life age restricted to five years or less. NiMH batteries are characterized by their energy density being translated in to either long working times, or reduction in the battery space needed. They are safe and can be manufactured in

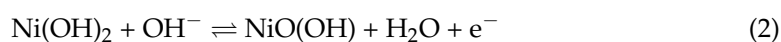
virtually many sizes (10 mAh–5 Ah). They also have some disadvantages, such as lower charging efficiency and issues with automatic charging which become worse when the batteries are in high temperature environments [4].

The main parts of a Ni-MH battery are the anode, cathode, electrolyte, separator and the steel case [6]. The anode is made of hydrogen storage alloy powder based on mischmetal- and nickel-containing substituents. Nowadays, all the NiMH cells are made of AB5 metals due to their better performance. The cathode consists of nickel coated with nickel hydroxide. The approved electrolyte in such batteries is KOH.

The electrochemistry of the nickel-metal hydride battery is generally represented by the following charge and discharge reactions. The overall reaction taking place in Ni-MH batteries is [2]:



At the positive electrode, the charge reaction is based on the oxidation of nickel hydroxide just as it is in the nickel–cadmium couple.



European industry demand for nickel, cobalt and REE is increasing and, since Europe is not self-sufficient, recovery from secondary sources such as NiMH batteries is of great importance for the coming years.

2. Materials and Methods

The experimental process followed includes several different stages. Each battery consists of eight individual cell batteries, metallic cases, outer plastics and current collectors. Manual dismantling was used to remove metallic cases, outer plastics and current collectors, while the remaining parts including cathodes of black coloured nickel (oxy)hydroxides, anodes consisting of a nickel-containing alloy (AB5 mischmetal type), and separators were ground down to –5 mm using a hammer mill equipped with sieves. The finer (–1 mm) fraction of this product was chemically analysed by X-ray Fluorescence Spectroscopy (XRF) and fusion and its mineralogical analysis was determined by X-ray Diffraction analysis (XRD) and scanning microscopy (SEM).

The sample was then subjected to sulphuric acid leaching, in order to recover the metals of interest. All experiments were conducted in a 500-mL five-necked, round-bottomed glass split reactor, which was fitted with a glass stirrer, a vapour condenser and a thermometer. In all the experiments, a constant stirring speed was applied to ensure suspension of the particles. Heating was provided by an electrical mantle and the temperature of the liquid was controlled by a Pt-100 sensor. Acid consumption of 14.16 moles H_2SO_4 /kg of a battery fine sample was determined to be sufficient to achieve the desired final pH value of 1. Nine leaching experiments were performed using 0.5, 1 and 2 M sulphuric acid solution at 5% pulp density, under stirring (450 rpm) and temperatures of 50, 75 or 95 °C. Each run lasted 90 min. The solid residues were filtered under a vacuum and analysed with SEM and XRD. All leach solutions were analysed by Atomic Absorption Spectrometry (Flame-AAS) and ICP-OES.

3. Results

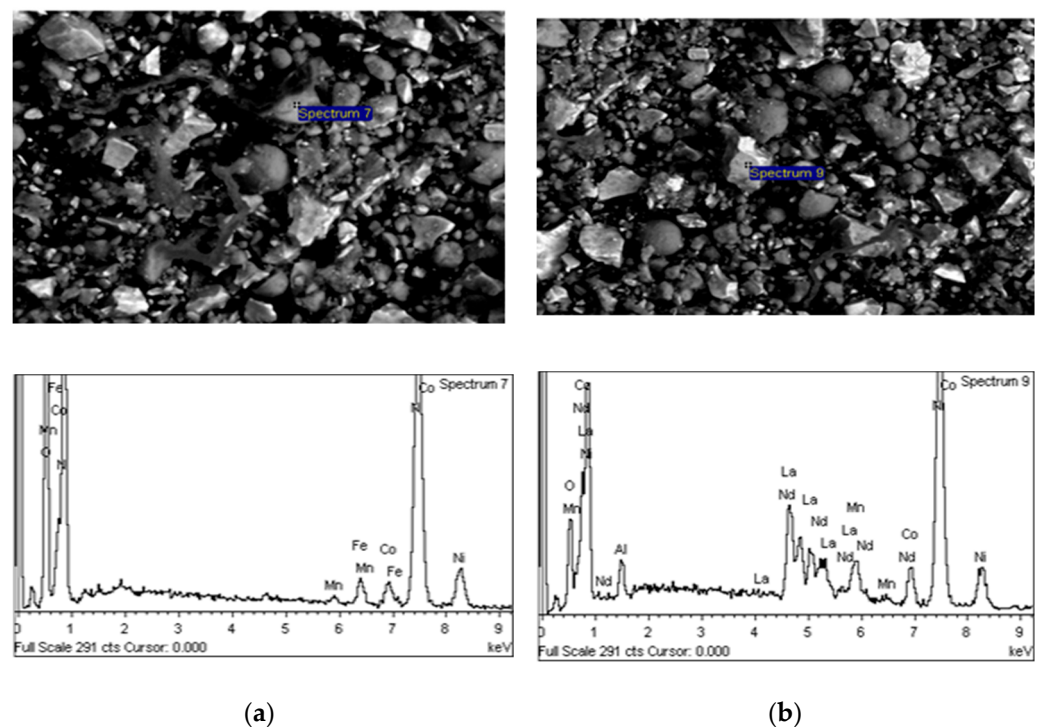
The chemical analysis of the fine solid was conducted by XRF analysis as well as by fusion and analysis by AAS and ICP-OES. The results are presented in Table 1. No copper or chromium were detected.

Table 1. Analysis of the fine solid sample.

Element	Sample 1	Sample 2	Content (% w/w)		XRF
			Sample 3	Average	
Al	1.22	1.26	1.22	1.23	0.54
Co	4.86	4.97	4.59	4.81	5.76
Fe	2.26	2.76	2.29	2.44	1.21
Mn	2.40	2.15	2.33	2.29	2.26
Ni	49.05	48.8	46.45	47.43	50.7
La	9.53	9.48	8.18	9.06	7.79
Ce	5.08	4.82	4.87	4.92	4.56
Nd	1.53	1.47	1.53	1.51	1.52
Y	0.74	0.76	0.73	0.74	1.02

The sample consists mainly of nickel (Ni), lanthanum (La), cobalt (Co) and caesium (Ce), with a significant amount of neodymium (Nd) and yttrium (Y) and the basic metals Al, Fe and Mn. No copper (Cu) or chromium (Cr) were detected.

Figure 1 presents SEM images of the sample. Figure 1a shows cathode material, consisting mainly of nickel and cobalt. Figure 1b shows anode material of AB5 type. The main mineralogical phases in the sample are LaNi_5 , Ce_2Ni_7 , $\text{Ce}_5\text{Co}_{19}$, Ni, $\text{Ni}(\text{OH})_2$, NiH and SiO_2 , as they can be seen in the XRD pattern of the sample given in Figure 2.

**Figure 1.** SEM images of the solid sample: (a) nickel, cobalt particle; (b) AB5 type.

The results of the leaching experiments are given in Table 2. Figure 3 presents a comparison to the initial X-ray diffraction diagram of some of the solid leach residues to the initial sample pattern (blue colour), where it is obvious that the mineralogical phases of LaNi_5 , Ce_2Ni_7 , $\text{Ce}_5\text{Co}_{19}$ and NiH do not appear, whereas Ni, $\text{Ni}(\text{OH})_2$ and SiO_2 can still be determined.

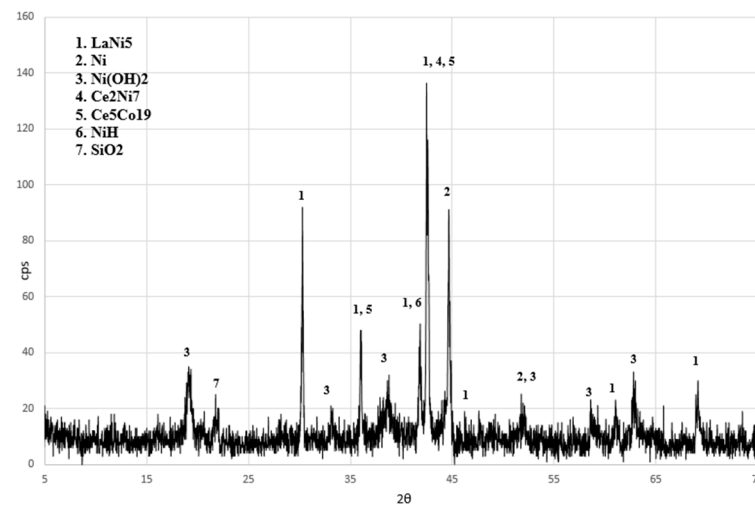


Figure 2. XRD of the battery solid sample.

Table 2. Results of leaching experiments.

Experiment	H ₂ SO ₄ (M)	T (°C)	Extraction (%)								
			Al	Co	Fe	Ni	Mn	La	Ce	Nd	Y
4	0.5	50	52.09	92.36	41.37	73.94	100.00	87.80	93.44	94.02	92.21
5	0.5	75	19.34	92.32	53.60	74.50	97.81	85.11	90.96	94.16	94.47
6	0.5	95	24.08	84.87	52.08	65.93	83.16	73.68	77.83	80.80	87.85
1	1	50	94.39	97.36	94.53	84.57	100.00	90.46	95.88	100.00	96.73
2	1	75	93.21	99.00	95.35	86.74	100.00	93.09	99.11	100.00	98.32
3	1	95	90.76	95.69	95.28	84.23	100.00	87.37	92.63	100.00	98.50
7	2	50	87.27	98.16	96.52	83.53	100.00	92.64	98.29	100.00	97.83
8	2	75	91.52	98.96	99.03	87.30	100.00	95.25	100.00	100.00	98.87
9	2	95	93.39	99.03	84.49	99.34	100.00	91.34	97.51	100.00	98.61

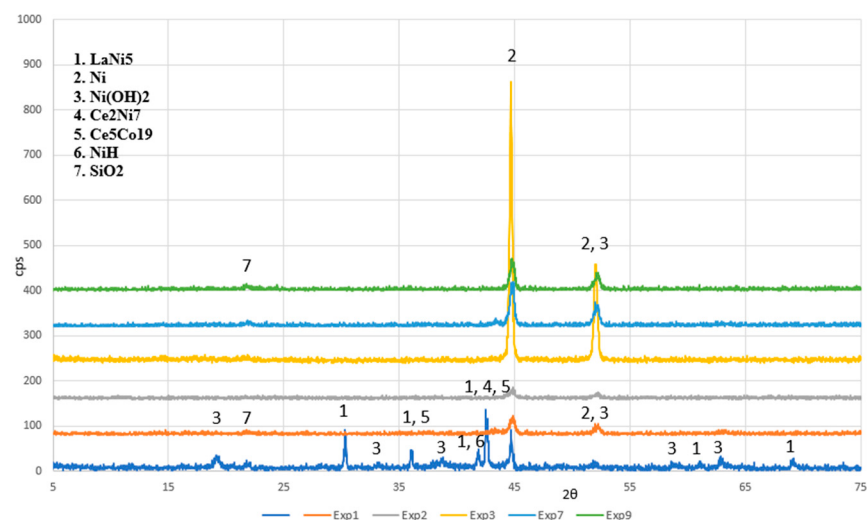


Figure 3. XRD patterns of the solid residues compared to the initial sample (blue line).

The results of the leaching experiments are given in Table 2. % extraction is the ratio of the element mass recovered in the leach solution compared to the initial content in the sample. Figure 3 presents a comparative to the initial X-ray diffraction diagram of some of the solid leach residues to the initial sample pattern (blue colour), where it is obvious that the mineralogical phases of LaNi₅, CeNi₇, Ce₅Co₁₉ and NiH do not appear, whereas Ni, Ni(OH)₂ and SiO₂ can still be determined.

4. Conclusions

The recycling of NiMH batteries is of great importance in order to recover economically, technologically important metals (Ni, Co, REEs). The purpose of this work was to find the optimal conditions in order to achieve maximum leaching from NiMH batteries of Lexus vehicles. Based on the experimental results, the following conclusions can be drawn:

- The present work showed that metal recoveries of almost 100% can be achieved, during leaching, for Co, Ce, Y, Nd and La. The extraction of Ni did not follow this pattern and reached about 85% with leaching agents of 1 or 2M H₂SO₄. Maximum Ni recovery was obtained with a 2M sulphuric acid solution at a temperature of 95 °C, reaching 93%.
- The optimum conditions for the extraction of other than Ni elements were 2M H₂SO₄ concentration and temperature of 75 °C.
- A concentration of 0.5 M sulfuric acid for the tested liquid to solid ratio (20 L/kg) is not sufficient to achieve high metal recoveries.
- Increasing the sulphuric acid concentration favours the metals extraction.
- Increase in temperature does not seem to have a significant effect in the metal extraction.

Author Contributions: A.X. and P.O. contributed to the study conception and design. Material preparation, data collection and analysis were performed by E.P., P.O., K.B. and P.T. All authors contributed equally to the interpretation of the results and provided critical feedback. The first draft of the manuscript was written by E.P. and revised by all authors. All authors have read and agreed to the published version of the manuscript.

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