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SOLVENT EXTRACTION OF La, Ce, AND Nd ELEMENTS FROM THE NiMH BATTERIES LEACH SOLUTION

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ABSTRACT – To separate rare earth elements D2EHPA, Cyanex 272, and DBC extractants used and results showed they couldn't selectively separate them, but in optimized conditions simultaneous extraction of them achieved. A DBC-D2EHPA mix had a synergistic effect, achieving recoveries of 98.76% (cerium), 97.94% (lanthanum), and 100% (neodymium). The McCabe-Thiele diagram indicated 3, 2, and 1 steps with Cyanex 272 for 90% recovery of cerium, lanthanum, and neodymium, respectively. Stripping tests with sulfuric, nitric, and hydrochloric acids were unsatisfactory, requiring further study.

Keywords: Rare Earth Elements, Nickel Metal Hydride, Recycling, Solvent Extraction.

INTRODUCTION

NiMH batteries were developed in Japan in 1989-1990 to replace Ni-Cd batteries due to the toxicity of Cd and their better performance [1]. Before lithium-ion batteries, NiMH batteries were widely used in devices like notebook computers, telephones, mobile phones, and electric cars due to their high energy density, compact size, overcharge resistance, and stable electrolyte during charge-discharge cycles [2][3]. The accumulated waste of nickel metal hydride batteries is increasing every year. The amount of waste from nickel-metal hydride batteries is increasing each year as their usage declines, mainly due to the growing popularity of newer battery technologies like lithium-ion. Based on their components, these resources can serve as a secondary source of valuable metals, including rare elements, nickel, and cobalt [4][5]. The reserves of rare elements in the world are limited and recycling of secondary resources such as NiMH can be used to compensate their limitation [2].

NiMH batteries have five main components: cathode, anode, electrolyte, separator, and steel case. The cathode of these batteries is made of nickel core coated with NaOH and its anode is made of elements such as Ni, Co, and REEs [4].

Rare earth elements (REEs) comprise 17 elements, including 15 lanthanides, Yttrium (Y), and Scandium (Sc), all possessing unique properties. Their separation is challenging due to their similar ionic and atomic radii. In NiMH batteries, REE alloys, such as $LaNi_5$, are used for hydrogen storage, with $LaNi_5$ storing hydrogen as $LaNi_5H_6$ in the anodes.

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Due to the high cost and purity required for lanthanum (La) and nickel (Ni), mischmetal, a mix of rare elements like La, Ce, Nd, Pr, and trace amounts of Tb, Sm, and Y, is commonly used as a substitute for La in steel deoxidation and desulfurization [6].

Failing to extract valuable elements from these secondary sources not only wastes resources but also leads to environmental issues. Therefore, it is essential to develop and study effective processes for recovering valuable elements like rare earths [2].

Various studies have been conducted to recover rare elements from NiMH batteries in the past years. Most of these studies have used two different paths of pyrometallurgy and hydrometallurgy to recover rare elements from this source [3].

Hydrometallurgy is commonly used for metallic element recovery due to its lower energy consumption and reduction of greenhouse gas emissions compared to pyrometallurgy. To minimize environmental pollution from strong mineral acids, research is also focused on using eco-friendly organic acids in this process [5][7]. In the hydrometallurgical process, the black mass a fine powder derived from pre-processed used NiMH batteries (involving fiber and plastic separation, crushing, and sieving) is leached with acid solutions. Research focuses on recovering metals (Ni, Co, Mn) and rare elements. Inorganic acids like H_2SO_4 and HCl are commonly used. For example, Danuza Pereira Mantuano et al. achieved 100% recovery of REE, Ni, Co, Fe, and Mn using 3 M HCl at 95°C with a solid-to-liquid ratio of 1:10 over 2 hours [8]. Also, M.S.

Gasser et al achieved 100% recovery for REEs, 85% for Ni, and 98% for Co using 2 M H_2SO_4 at 25°C, S/L ratio of 1/10 for 2 hours [9]. The next step after obtaining the leach solution of rare elements and others of NiMH batteries is the purification and extraction of rare elements from the solution using different methods such as solvent extraction. For instance, Yun Xia et al. have reported the recovery of 99.98% of rare elements from sulfuric medium under the conditions of A/O = 1.5/1 and pH = 1.5 at 20°C by 5 counter current stages using a N1923 primary amine extractor [10]. Pospiech et al. were able to achieve a high recovery of 95% for rare elements in a sulfuric medium with using Cyanex 272 and Cyphos IL 104 as an extractant and pH = 3.8 [11]. Pingwei Zhang et al., using D2EHPA extractor and kerosene diluent in 2 steps, pH equal to 2, A/O ratio equal to 1/3 in chloride medium, achieved 98% recovery of rare elements [12]. Linyan Li et al. achieved a high recovery of 99% for rare elements from sulfuric medium with the help of 20% P2O4 as an extractant and O/A ratio = 1 and pH = 2.5 [13].

In this article, the extraction of rare earth elements (Ce, La, and Nd) was investigated using D2EHPA, Cyanex 272, and DBC.

EXPERIMENTAL

To explore the extraction of lanthanum, cerium, and neodymium from the pregnant solution derived from the leaching process, as well as the potential for selective separation of these rare elements, experiments were conducted using D2EHPA, Cyanex 272, and DBC extractants. Kerosene was used as a diluent in all solvent extraction experiments, while sodium hydroxide was used to adjust the pH. The leach solution was prepared using sulfuric acid to leach the black mass obtained from spent NiMH batteries.

RESULTS AND DISCUSSION

Nickel-metal hydride batteries were collected from the recycling system at Tarbiat Modares University in Tehran. After separating the fibers and plastics, the internal materials were processed into a 150-micron powder, known as black mass. Leaching experiments were conducted using sulfuric acid to extract rare elements, with conditions set at 3 M sulfuric acid, 85°C, and a 3-hour duration. The recovery rates for cerium, lanthanum, and neodymium were 98.46%, 98.75%, and 98.25%, respectively.

D2EHPA Extractant

Because of separating rare elements from others in the pregnant solution D2EHPA was used.

Table 1 Solvent extraction results and conditions using D2EHPA

Test num.	A/O ratio	Temperature (°C)	Time (min)	Concentration of the extractant (M)	pH	Recovery of neodymium (%)	Recovery of lanthanum (%)	Recovering of cerium (%)
1	1/1	25	30	0.3	2.5	71.25	33.17	33.33

Table 1 shows that D2EHPA did not yield high recoveries for cerium and lanthanum. However, its effectiveness in recovering neodymium suggests it could be used for selective neodymium separation, provided further condition checks and optimizations are performed.

Cyanex 272 Extractant

In order to extract rare elements from the charged solution and the feasibility of separating these elements from each other individually, based on the conditions of the studied articles, experiments were carried out using Cyanex 272. The test conditions and results are given in Table 2.

Table 2 Solvent extraction results and conditions using Cyanex 272

Test num.	A/O ratio	Temperature (°C)	Time (min)	Concentration of the extractant (M)	pH	Recovery of neodymium (%)	Recovery of lanthanum (%)	Recovery of cerium (%)
1	1/1	25	30	0.15	2	75.2	46.54	49
2	1/1	25	30	0.66	3	92	77	85
3	1/1	57	30	0.04	5	99.04	98.4	98.82

The results indicate that Cyanex 272 cannot individually separate lanthanum, cerium, and neodymium from one another; instead, it facilitates their cumulative separation from other impurities. However, under suitable conditions, effective cumulative

extraction of rare elements from the pregnant solution can be achieved with appropriate recoveries.

DBC extractant

The DBC extractant was investigated to verify the feasibility of extracting rare elements from the pregnant solution cumulatively or individually if possible. Table 2 shows the results and conditions of the tests performed by DBC.

The solvent extraction experiments using DBC demonstrated its capability to extract rare elements collectively rather than individually, indicating the need for condition optimization to improve recoveries. To explore the synergistic effect of combining two extractants, D2EHPA and DBC, without a diluent, an experiment was conducted as outlined in Table 4. Results in Table 5 confirm a positive synergistic interaction between DBC and D2EHPA, leading to maximum cumulative recovery of rare elements from the leach solution.

Table 3 Solvent extraction results and conditions using DBC

Test num.	A/O ratio	Temperature (°C)	Time (min)	Extractant percentage (%)	pH	Recovery of neodymium (%)	Recovery of lanthanum (%)	Recovery of cerium (%)
1	1/1	25	30	50	1.3	68.7	40.5	34.4
2	1/1	25	30	20	1.3	61.7	23.9	23.5
3	1/1	25	30	100	5	78.05	52.35	55.5

Table 4 Solvent extraction results and conditions using DBC+ D2EHPA

Test num.	A/O ratio	Temperature (°C)	Time (min)	DBC percentage (%)	D2EHPA percentage (%)	pH	Recovery of neodymium (%)	Recovery of lanthanum (%)	Recovery of cerium (%)
1	1/1	25	30	50	50	3	100	97.94	98.76

Table 5 Points used for drawing operating line in the McCabe diagram of cerium, lanthanum, and neodymium elements

Element	x_n	y_{n+1}	x_0	y_1
Cerium	1.3	0	13	36
Lanthanum	2.8	0	28	73
Neodymium	0.4	0	4	15.2

Based on the results in Tables 1 to 4, Cyanex 272 demonstrated the highest efficiency for the cumulative extraction of rare elements from the leach solution. Using Cyanex 272, the McCabe diagrams for cerium, lanthanum, and neodymium (Figures 1 to 3) were

plotted to achieve 90% extraction under the conditions detailed in Table 6. Additionally, the operating line in the McCabe diagrams was drawn based on the data in Table 5. X_0 is solute concentration in aqueous feed, Y_1 is solute concentration in extract, X_n is solute concentration in raffinate, and Y_{n+1} is solute concentration in fresh organic feed.

Table 6 Solvent extraction test conditions using Cyanex 272 and their results

Test number	A/O ratio	Temperature (°C)	Time (min)	Concentration of the extractant (M)	pH	Recovery of neodymium (%)	Recovery of lanthanum (%)	Recovery of cerium (%)
1	1/1	25	30	0.66	3	92	77	82
2	1/2	25	30	0.66	3	90	75	80
3	1/3	25	30	0.66	3	82.5	61.78	67.92
4	1/4	25	30	0.66	3	77.5	53.57	58.61
5	1/5	25	30	0.66	3	76	52.14	55.38

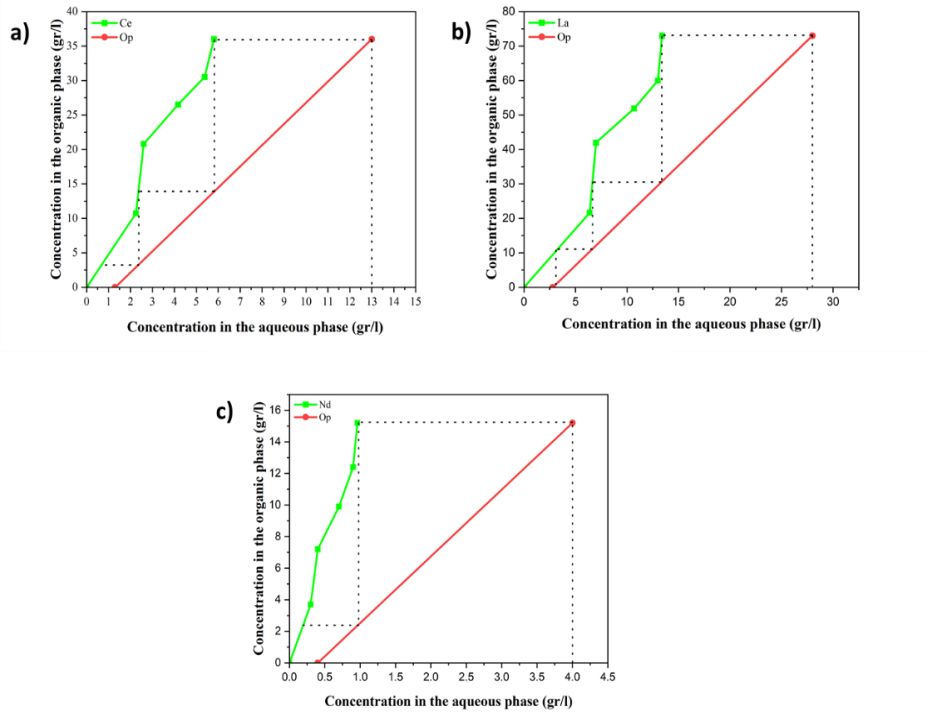

Figure 1 Mc-Cabe diagram a) for the cerium, b) for the lanthanum, c) for the neodymium

Based on McCabe diagrams, achieving 90% recovery requires 2, 3, and 1 extraction steps for cerium, lanthanum, and neodymium, respectively. Stripping tests with sulfuric acid, nitric acid, and hydrochloric acid solutions were conducted on the loaded organic

phase, but element recovery during stripping was insufficient, necessitating further research.

CONCLUSIONS

Attempts to separate rare earth elements from impurities in the leach solution were made using D2EHPA, Cyanex 272, and DBC extractants. While none could selectively separate rare elements, they successfully extracted all three elements under optimized conditions. A mixture of DBC and D2EHPA showed a synergistic effect, achieving recoveries of 98.76% for cerium, 97.94% for lanthanum, and 100% for neodymium. According to the McCabe-Thiele diagram, 3, 2, and 1 extraction steps are required with Cyanex 272 to achieve 90% recovery for cerium, lanthanum, and neodymium, respectively. However, stripping experiments using sulfuric, nitric, and hydrochloric acids yielded unsatisfactory results, highlighting the need for further research.

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