BRIEFING NOTE

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RECOVERY OF RARE EARTH ELEMENTS FROM WASTE PERMANENT MAGNETS

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KEY FINDINGS

The REEs recovery study from waste permanent magnets was conducted to optimize the method of hydrometallurgical processing required for this class of e-waste. The process is composed of three separate steps: leaching, extraction and precipitation. According to the obtained data, the optimal leaching conditions were 12.3M nitric acid at the temperature of 60°C performed using 100-150 µm size waste permanent magnet powder particles over 24 hours. The 1M concentration HDEHP was deemed a good extractant, allowing for recovery of above 90% of REEs from the leachate with the minimal extraction of iron and boron. The oxalic acid precipitation was the most successful from the experiments performed using oxalic acid to organic phase ratios above 5:1, allowing for recovery of more than 95% REEs in the form of oxalates. Scalability studies have shown that the extraction aspect of this process can be scaled to pilot plant scale using a continuous extraction column, however additional work should be performed to optimize the column performance.

INTRODUCTION

The implementation of commercial processes for Rare Earth Elements (REEs) is limited to date. With the increasing demand for REEs and the monopolisation of the REE mining industry by China, new sources of critical metals are required. Besides the exploration of the earth's crust in search of new deposits, the additional measure which can be undertaken is so-called urban mining – the process of recovery of critical materials from waste electronic and electrical equipment (WEEE).

This project focuses on the processing of waste permanent magnets (WPMs) as a source of REE-rich WEEE. With the increasing interest in electromobility and wind turbines, the global demand for permanent magnets has risen. This opens an opportunity for scientists to develop novel methods of dealing with this kind of WEEE before it becomes a significant issue.

The hydrometallurgical processing utilized in this project stands as an attractive alternative to the commonly used pyrometallurgical methods. Hydrometallurgy uses acidic solutions to dissolve metals present in WEEE and separate desired, more valuable elements through chemical processes, such as liquid-liquid extraction and precipitation. Contrary to the pyrometallurgical methods, hydrometallurgical processing can be performed at relatively low-temperature conditions, which minimizes energy consumption and decreases the carbon footprint.

METHODOLOGY

In the course of the project, samples of magnets obtained from spent hard disk drives (HDDs) were demagnetized, comminuted and treated with HNO_3 in the leaching process to obtain solutions containing REE ions. Parameters of leaching such as temperature (45°C and 60°C), acid concentration (6.7M and 12.3M), WPM powder particle size (100-150 µm and ≥600 µm) and contact time (0.5, 1, 6 and 24 hours) were varied, while each experiment utilized a solid-to-liquid ratio of 1:50. Additionally, some WPM powders were treated using a temperature of 950°C to establish the influence of the iron oxidation on the overall process.

Solutions of ions were then contacted with bis(2-ethylhexyl) phosphate (HDEHP) in n-dodecane, which served as an extractant in the liquid-liquid extraction process, varying extractant concentration (0.5M and 1M of HDEHP in n-dodecane) and extraction scale (10 ml and 100 ml). The final step of the process was the precipitation of the REE oxalates from the extractant using a saturated aqueous solution of oxalic acid in varying ratios to the extract (organic phase). Additionally, a study of the scalability of the liquid-liquid extraction process utilizing HDEHP in n-dodecane was performed using Nd_2O_3. Three scales were studied: laboratory scale (10 ml), increased laboratory scale (200 ml) and pilot plant scale using a vibrating plate column. The laboratory scale study allowed for the determination of partitioning coefficients D_{Nd} as a function of the initial acid concentration. The increased laboratory scale experiments were performed utilizing approximately 140g of aqueous phase containing 8303 ppm of Nd^{3+} ions and contacting it with approximately 50g of a solution of 1M HDEHP in n-dodecane. The raffinate from the previous step was then contacted with a fresh organic phase. This allowed the establishment of a number of steps required for the extraction of Nd^{3+} ions from the aqueous phase to the organic phase. The pilot scale column allowed the full assessment of the scalability of the process. The experiment was performed at ambient conditions using a vibration frequency of 10 Hz.

RESULTS

The leaching experiments showed that the best results in terms of metal ions concentration were obtained for the samples contacted with 12.3M nitric acid at the temperature of 60°C performed using 100-150 µm size WPM powder particles over 24 hours. This statement is true for all six components of the studied magnets, namely neodymium, dysprosium, praseodymium, samarium, iron and boron. Iron is the most abundant in the magnetic alloy used to create HDDs magnets. Its presence is not desired in the further hydrometallurgical processing. To prevent iron from being leached, an additional countermeasure in the form of roasting was implemented. Waste permanent magnet powder samples were treated using the temperature of 950°C to create chemically inert Fe$_2$O$_3$. This helped to decrease the wt % of the iron in the leachate from approximately 60-65 wt% to 15-18 wt%.

Leachate samples (aqueous phase) obtained in the previous step were contacted with the organic phase in the form of HDEHP diluted with n-dodecane. According to the findings, HDEHP can be considered a good extractant for this application. A 1M of HDEHP in n-dodecane allowed for the recovery of 90.0% - 99.9 % of REE ions in a smaller scale (10 ml) and 85.0% - 95.0% in a larger scale (100 ml). Interestingly, only a small fraction of the iron and boron was transferred from the aqueous to the organic phase (between 0.8% and 7.7%, and 0.1% and 9.0%, respectively). Results showed that a 1M concentration of HDEHP in n-dodecane increases the extraction of REEs, while the extraction of iron and boron is decreased, contrary to 0.5M HDEHP concentration (see Figure 1).
Samples of the organic phase were then contacted with oxalic acid to precipitate the insoluble salts of REEs. According to the obtained results, ratios of oxalic acid to organic phase above 5:1 allow for the recoveries of REEs above 95%.

The laboratory scale extraction study using Nd$_2$O$_3$ showed that the lower acidity increases the value of the partitioning coefficient D_{Nd}, which achieved values of approximately 75.0 at [H$^+$] of 0.257M and approximately 45.0 at [H$^+$] of 0.452M HNO$_3$. This indicates that the pH of leachate should be adjusted to increase REE transport from the aqueous to the organic phase.

Increased laboratory scale experiments (see Figure 2) showed that after the first extraction step, the amount of the Nd^{3+} ions decreased from 8303 ppm to 688 and 638 for runs 1 and 2, respectively. The following steps allowed for a decrease of neodymium ions concentrations even further, to approximately 70 ppm in both runs, while the third extraction step allowed for a decrease of ions concentration only to approximately 30 ppm in both runs. This means that after the first step, the recovery of neodymium from the aqueous phase was approximately 92% for both runs. After the second extraction step, the recovery of Nd^{3+} ions via extraction was above 99% for both runs.

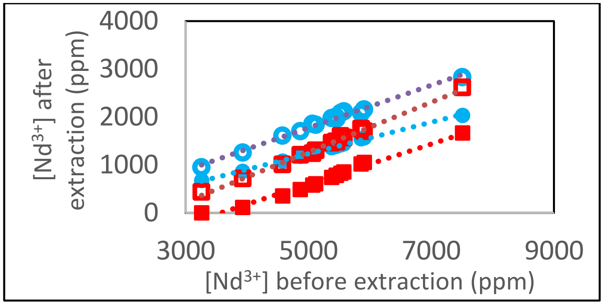

Figure 1. Concentrations of Nd^{3+} ions in extraction experiments using HDEHP in n-dodecane; ● – 0.5M HDEHP (10 ml), ■ – 1M HDEHP (10 ml), ○ - 0.5M HDEHP (100 ml), □ – 1M HDEHP (100 ml).

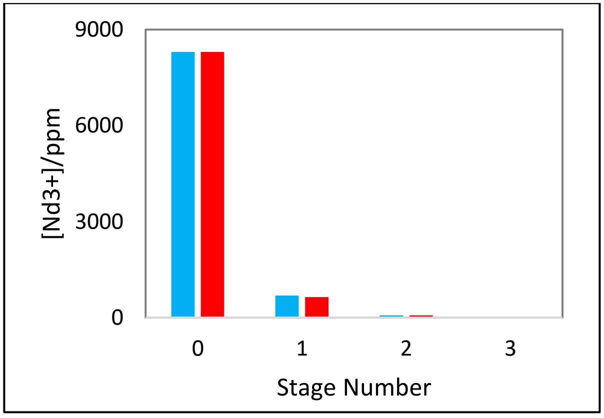

Figure 2. The concentration of Nd3+ ions (ppm) in raffinate after each stage of extraction study in 200 ml scale experiments at T = 298.15K and P = 101.3 kPa; 🟦 – run 1, 🟥 – run 2.

In the last experiment, the vibrating plate column was utilized. The initial feed concentration was 8352 ppm of Nd3+ in 0.5 M HNO3 for experimental run 1 and 8304 ppm of Nd3+ in 0.1 M of HNO3 for experimental runs 2 and 3 (see Figure 3). Samples withdrawn after 30 minutes showed a 53% Nd^{3+} concentration decrease for run 1 and 83.3% and 81.7% decrease for runs 2 and 3, respectively. This shows that lower acid concentration is beneficial in the extraction process. However, additional experiments should be performed to establish the column working conditions to match the increased experimental scale recoveries.

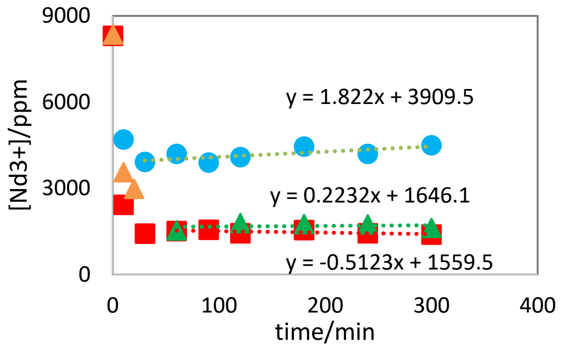

Figure 3. Change in Nd3+ concentration (ppm) over column operation time at T = 298.15K and P = 101.3 kPa; ● – run 1 , ■ – run 2, ▲ – run 3.

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