

# RECYCLING OF NEODYMIUM, DYSPROSIUM, AND PRASEODYMIUM FROM END-OF-LIFE NdFeB MAGNETS

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## Abstract

*Around the world, there is growing wave towards recycling of waste electrical and electronic equipment (WEEE) to enable the circular economy. The performance many WEEE relies on the unique physiochemical properties of their building block critical metals such as rare earth elements (REEs)<sup>1</sup>. Neodymium-iron-boron (NdFeB) magnets that are widely utilized in hybrid and electric vehicles and wind turbines contain more than 20% critical REEs which is more than 10 times of the minimum industrial grade of primary ores (1.5-2.0%)<sup>2</sup>. Considering the increasing utilization of wind energy and hybrid and electric vehicles, the use of these magnets is rapidly increasing. Managing end-of-life NdFeB magnets through recycling not only reduces the amount of landfilled wastes, but also provides a secondary resource for valuable materials they contain.*

*State-of-the-art recycling processes are based on pyrometallurgy or hydrometallurgy. Among the two, pyrometallurgy is based on calcination using a mixture of reducing and fluxing agents. This process is energy intensive and generates large volumes of greenhouse gas (GHG) emissions. Moreover, in many cases during calcination REEs partition into slag phases, which requires a hydrometallurgical step to recover<sup>3</sup>. Hydrometallurgy is the preferred technique because of relatively low energy consumption and adaptability to resources scale; however, it faces challenges like high reagent consumption, often requiring the consumption of strong acids and organic solvents, and large volumes of hazardous waste generation<sup>3</sup>. Considering the drawbacks of these two processes, a recycling process with high REE recovery rate but low energy and reagent consumption and low waste generation is highly desirable.*

*Here, a novel recycling process called aerio-metallurgy was developed to recycle critical rare earth elements from postconsumer NdFeB magnets utilized in wind turbines. This new process uses supercritical CO<sub>2</sub> as the solvent, which is abundant, safe, and inert, along with tributyl-phosphate-nitric acid (TBP-HNO<sub>3</sub>) adduct as the chelating agent and methanol as the co-solvent. Aerio-metallurgy is our proposed*

terminology to differentiate supercritical fluid extraction from hydrometallurgy, pyrometallurgy, and solvometallurgy. The “aerio” prefix is from the Greek word for “air or gas”. This term is selected because in this process a gas-like solvent, which is a part of the air we breathe is utilized.

Supercritical fluid extraction (SCFE) is an emerging green separation technology that has gained significant attention for lanthanides recovery in recent years. This process has been developed in late 1970s to extract or produce high value products, and then expanded to less specialized applications. Major commercial SCFE processes have been focused on energy industry as well as chemical industry, including food and pharmaceuticals. Examples include coffee decaffeination <sup>4</sup>, wood and vegetable oil production <sup>5</sup>, and extraction of organics like alcohols from aqueous solutions<sup>6</sup>.

In this work, a fractional factorial design of experiment methodology was used to design the experimental matrix to investigate the effect of seven operating parameters including temperature, pressure, chelating agent ration, and agitation on the extraction efficiencies. An empirical model was developed, and the process was optimized. Using the optimum operating conditions resulted in 94% Nd, 94-100% Dy, and 87-94% Pr extraction with only 57-67% Fe co-extraction and minimal waste generation.

Moreover, a fundamental investigation was performed to elucidate the complexation chemistry and to propose the process mechanism. In our previous study on SCFE of REEs from NiMH battery, a mechanism for the extraction process was proposed, in which bidentate nitrate anions from the TBP–HNO<sub>3</sub> extractant chelate to the REE<sup>3+</sup> cation, forming neutral REE nitrates REE(NO<sub>3</sub>)<sub>3</sub><sup>1</sup>. Two types of interactions result in the formation of reverse micelles. These interactions include hydrophobic interactions between aliphatic tails and dipole-dipole interactions between phosphate groups of TBP. When TBP chelating agent comes into contact with hydrophilic REE salts, they are attached to the polar cores. If we consider Nd as an example, the cation is centered in a coordinate environment consisting three bidentate nitrate anions and *n* TBP molecules, consistent with the mechanism suggested by Shimizu et al. <sup>7</sup> (Reaction 1 and 2).



For determining *n*, synthetic solutions containing Nd(NO<sub>3</sub>)<sub>3</sub> with varying composition of TBP from 0 to 6.5 in hexane were made. These solutions served as a model solution for sc-CO<sub>2</sub>, and they were characterized using UV-Visible spectroscopy. Based on the

point at which absorbance peak reaches a plateau, it was observed that the stoichiometric ratio at which  $\text{Nd}(\text{NO}_3)_3$  complexes with TBP is 1 Nd: 3 TBP, confirming that,  $n$  is equal to 3, which is in agreement with Braatz et al.<sup>8</sup> and Healy and McKay<sup>9,10</sup> proposed TBP–trisolvate complexes of Ln(III) ions. Based on our results, we propose the complex has a formula of  $\text{Nd}(\text{NO}_3)_3(\text{TBP})_3$ .

The results of this study assure the feasibility of supercritical fluid extraction as a cleaner and more sustainable technique for WEEE recycling to enable the circular economy.

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