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Preparation of rare-earths oxalates from double sulfate salts obtained by selective precipitation of Ni-MH battery leachates

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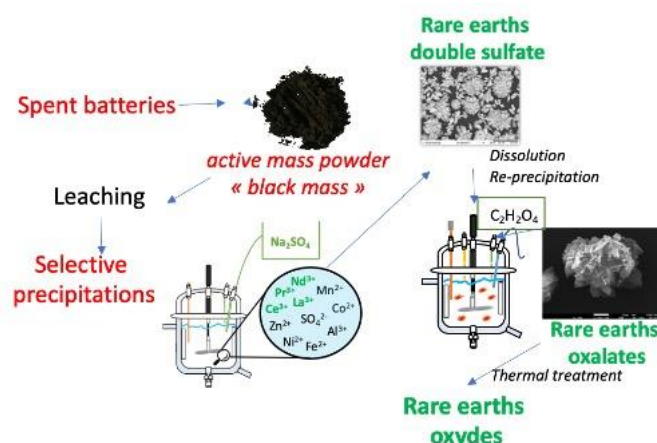
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ABSTRACT

Spent nickel-metal hydride (Ni-MH) batteries can serve as an attractive secondary source of rare earths elements (REEs). The valuable powder, called black mass (BM), extracted after crushing these batteries can contain up to 15 wt % REEs. Recycling by hydrometallurgical processes at an industrial scale is a key issue. It involves two main steps: dissolution of the BM in an acid solution and recovery of these metals by selective precipitations [Porvali et al., 2018; Zielinski et al., 2021]. The quality of the recovered products, and in particular of the REEs, depends on the control of the operating conditions of the precipitation stage and the washing of the filtered precipitates. Due to an initial material of complex composition and structure, the number of constituents likely to precipitate from the battery leachates is significant.

This work implements the precipitation of REEs, at a pilot scale, from an industrial leachate containing about 15 g/L of REEs. The product of this first step is a solid solution of sodium-potassium lanthanide double sulfate, identified as $(\text{Na}_{0.9}\text{K}_{0.1})(\text{La}_{0.65}\text{Ce}_{0.24}\text{Nd}_{0.07}\text{Pr}_{0.04})(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ by complementary characterization techniques (X-Ray Diffraction, elemental analyses and thermo-gravimetric analyses). In order to remove Na, K and S elements from this intermediate compound, the powder was then dissolved and re-precipitated as a hydrated rare earth oxalate $\text{REEs}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ using oxalic acid. The resulting oxalates were then characterized and valorized in the oxide form through calcination at 800°C. The precipitation experiments were conducted in a semi-continuous jacketed stirred reactor (0.6 L), temperature-regulated and equipped with a pH probe. During a standard experiment, the reagent was introduced by simple jet, at a constant flow rate. The filtration of the precipitates was carried out on a Buchner filter (pore diameters 16-40 μm) using a vacuum pump. The influence of several operating parameters on the efficiency and kinetics of precipitation was studied: temperature, pH, reagent concentration and addition rate.

The results show that, depending on the operating conditions, the process yield can be higher than 95% and that it can be easily implemented at industrial scale.



References

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