

Rare-Earth Elements Recovery from Nd-Fe-B Hard Magnets by Hydrometallurgical Processes



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Abstract In this study, a hydrometallurgical process was evaluated for the recovery of Nd from a Nd-Fe-B magnet. Each leaching test was performed at the solid (weight) to liquid (volume) ratio of 1:50 and was mixed at 400 rpm at ambient temperature. The effects of 3 different acids (HCl, HNO₃, and H₂SO₄) on the extraction of Nd were investigated and H₂SO₄ was found to be more effective than other acid solutions. Under the optimal conditions, pregnant leach solution was produced with H₂SO₄ for subsequent Nd precipitation testing. Each precipitation test was carried out using 100 mL of feed solution mixed at 600 rpm at 25°C. NaOH and H₂C₂O₄ were used for Nd precipitation. The highest Nd was precipitated as Nd₂(C₂O₄)₃ · 10H₂O with C₂H₂O₄ at 20 min.

Keywords Leaching · Rare earths · Magnet recycling

Introduction

The Rare Earth Elements (REEs) are described as a group of elements containing lanthanides with Sc and Y. The lanthanides are generally separated into two groups, light rare earth elements (LREEs—lanthanum through europium) and the heavier rare earth elements (HREEs—gadolinium through lutetium) [1]. The growing popularity and usage of wind turbines, electric and hybrid cars, HDDs, etc. has

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increased the demand of REEs. According to the medium-term criticality matrix from the U.S. Department of Energy (DoE), the five most critical REEs are neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy), and yttrium (Y) [2]. The European Commission considers the LREEs and HREEs as the most critical raw materials groups, with the highest supply risk. China has 95% of mine production of all REEs [3]. Current predictions indicate that the current production of Nd and Dy will not be sufficient for the projected demand in near future. The demand of Nd and Dy in 2020 is expected to increase and the shortage of Nd and Dy is projected to be 30 and 49% when the base year is 2015 [4]. Recycling of Nd containing scraps could be one of the potential options to minimize this risk. For Nd, there are two main sources for recycling: magnet manufacturing wastes and magnet scraps. Up to 25% of REEs (mostly Nd) can be lost during permanent magnet manufacturing process (sintering, cutting/polishing, magnetizing, etc.) as waste [5]. NdFeB magnets are composed of 30–40% REEs (15–30% of which is Nd), 50–70% Fe and 1% B. The composition can be changed due to required operating conditions [2].

Hydrometallurgical methods for NdFeB recycling typically starts with a leaching step. The leaching efficiency can be increased by grinding with NaOH followed by roasting at 500 °C. The grinding and roasting also provide selective leaching of REEs, however they increase the costs of the total process [6]. The consumption of acid solution is decreased with the roasting step, but total process duration can be reached up to 15 h. Solvent extraction (SX) is used for both removal of transition metals and production of high purity REE solution. REEs can be precipitated from their solutions with oxalic acid. The usage of oxalic acid depends on the amount of Nd in the solutions [7] and the impurity levels. In a direct leaching study, 3 M HCl solution was used at 110 °C for 6 h. The concentration of oxalic acid used for precipitation was 0.2 mol/L. After filtration, high purity neodymium oxalate hydrate was obtained as final product [8].

In this study, a cheap and fast process was evaluated. Stoichiometric amounts of three different acids (HCl, HNO₃, and H₂SO₄) were used for the leaching of Nd-Fe-B hard magnetic material. Tests were carried out by varying the leaching time and acid concentrations to determine the optimum conditions. Sodium hydroxide and oxalic acid were used as precipitation agents.

Experimental

Materials

The raw materials used as the Nd-source were obtained from hard magnets that were demounted from end-of-life hard disk drives. The chemicals used in this study were; NaOH (97 wt%), H₂C₂O₄ (99 wt%), HCl solution (37% wt%), HNO₃ solution (55% wt%), and H₂SO₄ solution (97% wt%) obtained from Merck.

Leaching Procedure

The magnet scraps were demagnetized at 300 °C, then ground in a ball mill and sieved under 100 microns. In the first series of leaching experiments, the effects of three different acids (HCl, HNO₃, and H₂SO₄) on the leachability of raw materials were investigated. Each leaching test was conducted at the solid (weight) to liquid (volume) ratio of 1:50 with 2 g of sample and 100 mL of 0.147 M acid solution mixed at 400 rpm at ambient temperature. In the second test series, after determining the better acid type, the effects of acid concentration and leaching time were studied. The acid concentrations were selected where chosen to target solutions pH's of about 0.00, 0.15, and 0.45 and the leaching durations were selected as 15, 30, and 60 min; all other operating conditions were unchanged. The effects of the controlled parameters were investigated by the 3-level, 2-factor Taguchi experimental design method. Minitab 17 software was used to optimize the leaching parameters.

Precipitation

The precipitation experiments were carried on pregnant leach liquor, which was produced under the optimal leaching conditions. The experiments were performed at room temperature, for a 100 mL of solution with a stirring rate of 600 rpm. The amount of the reagents used was 0.5 g. The effectiveness of NaOH and C₂H₂O₄ and the precipitation duration (10, 20 min, and 18 h) were investigated. Vacuum filtration was applied for solid-liquid separation and filter papers with precipitates were dried in an oven at 105 °C for 24 h.

Characterization

Particle size analysis was carried out with a Malvern, Master Sizer Hydro 3300. The phase analysis of the feed samples and solid products were carried out by X-ray diffractometer (Rigaku D/Max 2200/PC). Elemental analysis of samples was carried out by inductively coupled plasma—mass spectrometry (ICP–MS Agilent Tech. 7700 Series) for Nd and inductively coupled plasma—optical emission spectrometry (ICP–OES PerkinElmer Optima 2100DV) for Fe and B. Elemental analysis for solutions was carried out by only ICP–MS.

Results and Discussion

From the XRD analysis of the raw material, the main phase was detected as Nd₂Fe₁₄B. The chemical composition of the raw materials was 65.2% Fe, 25.1% Nd, and 1.0% B. In the first leaching series, where the leaching duration was

selected as 3 h, the amount of Nd dissolved in the solutions (Nd-mass) are shown in Fig. 1. The highest Nd-mass was obtained in H_2SO_4 solution as 162.35 mg. During leaching of head material with H_2SO_4 , the temperature of the solution was increased due to exothermic behavior of the reaction; this is thought to be the reason H_2SO_4 gave the highest dissolution of Nd. During the leaching with H_2SO_4 , in the first 60 min, almost all the solid was dissolved. Due to this observation, one more test was carried out under the same conditions.

In the second series of leaching experiments, diluted H_2SO_4 solutions were used. Results are shown in Fig. 2, which suggests that the extraction of Nd is slightly increased with increasing the leaching time. While no significant differences were observed in the Nd-mass by changing in the acid concentrations.

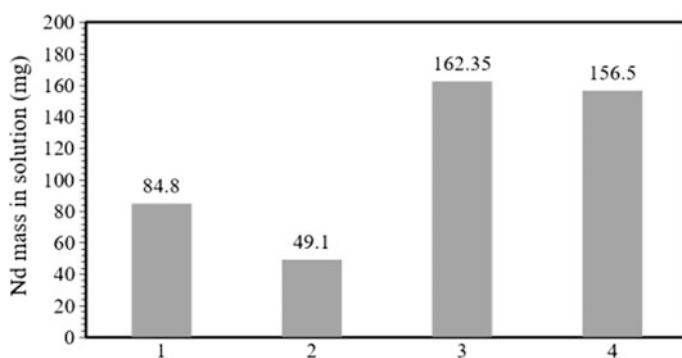


Fig. 1 Nd mass in solution dependence on the acid type (1—HCl, 2—HNO₃, 3—H₂SO₄, 4—1 h leaching duration with H₂SO₄)

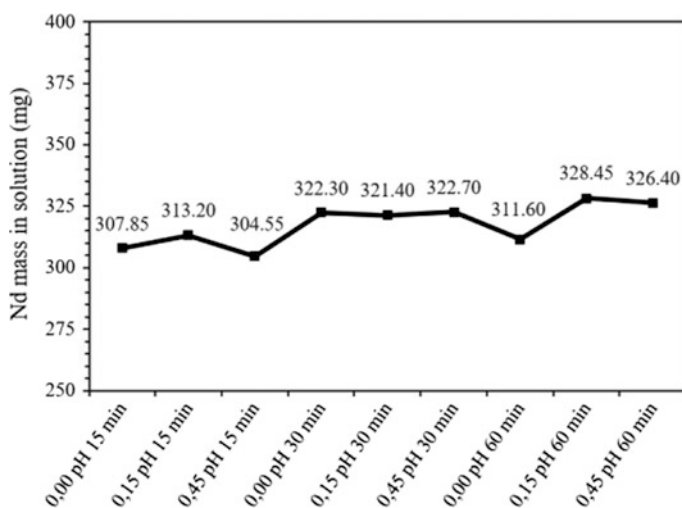


Fig. 2 Nd mass in solution dependence on the pH and leaching duration

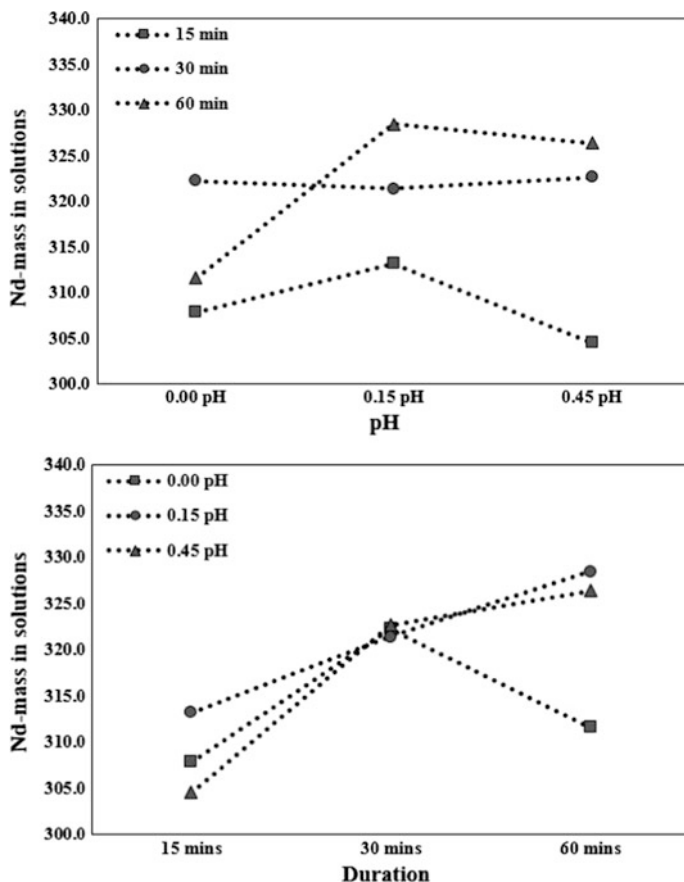


Fig. 3 Interaction plot for factors. Nd-mass in solution versus pH for differing leach durations (Up) and Nd-mass in solution versus leach duration for differing pH values (Down)

The interaction between the factors is given in Fig. 3. The experiments with 30 min of leaching duration has similar Nd concentration for each pH values. The highest Nd-mass in 30 min leaching duration was obtained at 0.45 pH. The solution with less acid concentration is feasible from an economic and environmental perspective.

In the precipitation experiments with NaOH, the amount of precipitate was not enough for XRD. The amount of precipitated Nd at different durations is given in Fig. 4. The XRD result of particulate obtained by $C_2H_2O_4$ is shown in Fig. 5. The raw data was analyzed by HighScore X'pert Plus and the highest peaks were belonged to $Nd_2(C_2O_4)_3 \cdot 10H_2O$.

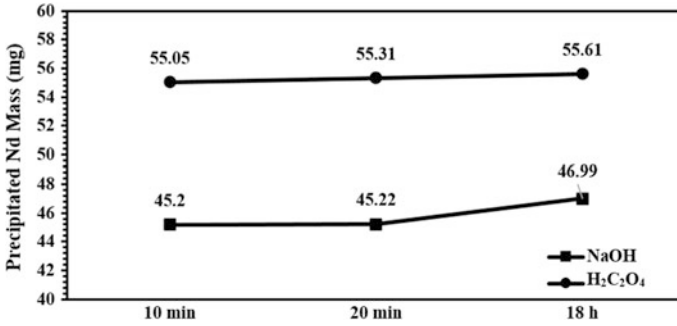


Fig. 4 Precipitated Nd mass dependence on precipitation time with sodium hydroxide (NaOH) and oxalic acid (H₂C₂O₄)

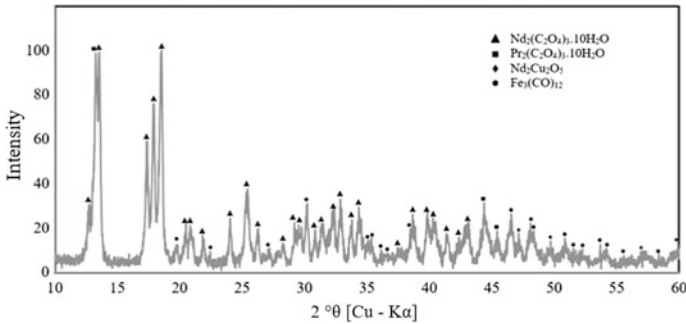


Fig. 5 XRD pattern of precipitate

Conclusion

The H₂SO₄ solution was determined as the most suitable acid for leaching of NdFeB scrap magnets. The optimum leaching conditions were determined as 30 min of leaching duration and 34.1 g/L 98% w/w H₂SO₄. The highest amount of Nd precipitated from 100 mL of leach solution was with 0.5 g C₂H₂O₄ at 20 min. Further study is required to evaluate the calcination time and temperature for the production of neodymium oxide (Nd₂O₃) from neodymium oxalate hydrate (Nd₂(C₂O₄)₃ · 10H₂O).

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