

Supplementary information

A facile method for the simultaneous recovery of the rare-earth elements and transition metals from Nd–Fe–B magnets

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Experimental

Reagents: Iron(II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, > 99%), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$, > 99%), sodium citrate dihydrate ($\text{Na}_3\text{cit} \cdot 2\text{H}_2\text{O}$, > 99%), sodium sulphate (Na_2SO_4 , > 99%), boric acid (H_3BO_3 , > 99%) and sulphuric acid (H_2SO_4 , 98%) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. The sintered Nd–Fe–B magnets were supplied by Magneti Ljubljana d.d., Slovenia and were used as model materials of EoL PMs. These magnets were demagnetized and mechanically polished to remove the protective coating on the surface ($\text{Al}/\text{Al}_2\text{O}_3$). The chemical compositions of the magnets were measured with inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300 DV), with the results listed in Table S1. Although the magnets contain Dy and Pr in addition to the Nd, we refer to them as “Nd–Fe–B magnets” for simplicity.

Table S1 Elemental composition of the sintered Nd–Fe–B magnets in wt.%.

Element	Content (wt.%)	Element	Content (wt.%)
Dy	6.55	Ga	0.25
Nd	23.71	Al	0.06
Fe	64.23	Cu	0.12
Pr	0.78	Co	2.13
B	1.12	Total	98.95

Electrochemical test: A 100-mL glass beaker was used as the electrochemical cell for leaching the Nd–Fe–B magnet and depositing the Fe at room temperature. A three-electrode cell (Figure S1) with a potentiostat (Gamry, Reference 600, USA) was used for all the electrochemical measurements.

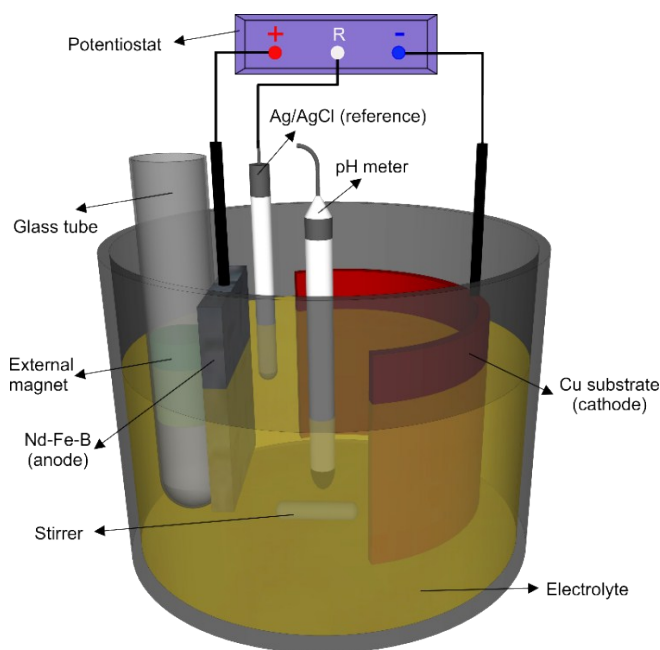


Fig. S1 Schematic of the electrochemical cell for leaching Nd–Fe–B magnets and the deposition of the Fe metal at room temperature.

Linear sweep voltammetry (LSV): The electrochemical behaviours of the magnets in 70 mL of an aqueous bath containing $0.6 \text{ mol L}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$, $0.4 \text{ mol L}^{-1} (\text{NH}_4)_2\text{SO}_4$, $0.175 \text{ mol L}^{-1} \text{ Na}_3\text{cit} \cdot 2\text{H}_2\text{O}$ and $0.4 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$ with a pH of 4.0 were evaluated using LSV at room temperature. A polished magnet ($30 \text{ mm} \times 15 \text{ mm} \times 5 \text{ mm}$) connected with a Pt wire as the conductor and a Pt wire ($\phi = 0.5 \text{ mm}$) were used as the working electrodes. An external magnet was put inside a glass tube to hold the anode to the side wall of the glass tube. It was observed that pulverization of the magnet led to loose magnetic particles that were no longer in electrical contact. However, the external magnet kept the loose magnetic particles attached to the anode for continuous leaching. The magnet and the Pt-wire working electrode had effective areas of 0.05 and 0.047 cm^2 , respectively. A Pt plate ($30 \text{ mm} \times 10 \text{ mm}$) was selected as the counter electrode, with an effective area of 2 cm^2 . A Ag/AgCl ($3 \text{ mol L}^{-1} \text{ KCl}$) electrode was used as the reference electrode.

Electrochemical leaching of the Nd–Fe–B magnets and Fe metal deposition (electrolysis step): The electrolyte bath contained $0.6 \text{ mol L}^{-1} \text{ FeSO}_4 \cdot 7\text{H}_2\text{O}$, $0.4 \text{ mol L}^{-1} (\text{NH}_4)_2\text{SO}_4$, $0.175 \text{ mol L}^{-1} \text{ Na}_3\text{cit} \cdot 2\text{H}_2\text{O}$ and $0.4 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$. The electrolysis experiment was performed for 8 hours as a single batch. A polished magnet connected with a Pt wire as the conductor was used as the anode with an effective area of 2.0 cm^2 . A copper foil ($40 \text{ mm} \times 60 \text{ mm}$) with an effective area of 8–16

cm² was dipped into the electrolyte as the cathode and the back of the foil was masked with insulating tape. A Ag/AgCl (3 mol L⁻¹ KCl) electrode was used as the reference electrode. Currents of 50, 100, 150 and 200 mA were applied (initial current density of 25, 50, 75 and 100 mA cm⁻² on the anode, respectively and 12.5 mA cm⁻² on the cathode) to investigate the leaching efficiency of the Nd-Fe-B magnet and the corresponding energy consumption. The electrolyte baths containing 0.6 mol L⁻¹ FeSO₄, 0.4 mol L⁻¹ (NH₄)₂SO₄ and 0.4 mol L⁻¹ H₃BO₃ with the Na₃cit concentration varied from 0.05 to 0.175 mol L⁻¹. were used to investigate the influence of sodium citrate concentration on Fe deposition. Four pieces of the polished magnet (30 mm × 15 mm × 5 mm) connected with a Pt wire as the conductor were used as the anode with an effective area of 8.0 cm². The copper foil with an effective area of 16 cm² was used as the cathode. It should be noted that in the practical application, Fe plate would be the best choice of cathode material. In this study, Cu was considered in order to get the EDS signals and information from the deposit clearly distinguished from the substrate material. A current of 200 mA was applied with an initial current density of 25 mA cm⁻² on the anode and 12.5 mA cm⁻² on the cathode. The electrolyte was agitated magnetically via a magnetic PTFE-coated stirring bar at a constant rotating speed of 500 rpm. Some 4 mol L⁻¹ H₂SO₄ was added to the electrolyte dropwise every 10 min to keep the pH between 3.5 and 4.5, measured with a pH meter immersed in the electrolyte throughout the experiment. Every 1 hour, 0.2 mL solution was sampled for a concentration measurement of the total dissolved Fe and the weight of deposited Fe was measured for a current efficiency calculation.

Selective precipitation of the REEs: After the electrolysis step, 0.57 grams of Na₂SO₄ was added to the electrolyte solution, followed by heating at 70 °C for 2 hours to selectively precipitate the REEs based on a description in the literature¹. While the solution was warm, the precipitates were filtered and washed thoroughly with water, followed by drying at 105 °C for 12 hours. The filtrate was recycled back to the electrolysis cell for the next electrolysis batch.

Characterization: Characterization involved a scanning electron microscope (SEM, JSM-7600F and 5800, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). An accelerating voltage of 18 kV was used for the imaging and the EDS analysis in the JSM-7600F. In order to achieve good accuracy for the quantitative elemental analyses, the efficiency of the EDS detector was calibrated at 18 kV using a pure Co-standard. For the JSM-5800, an accelerating voltage of 20 kV was used for the imaging and the EDS analysis. The pH was measured with a pH

meter (Mettler-Toledo, S210). The concentration of the REEs, i.e., Nd, Dy and Pr as a whole, was analysed by mass spectrometry with inductively coupled plasma (ICP-MS, Agilent 7700, Agilent Technologies, Tokyo, Japan). The concentration of the total dissolved Fe was determined using the 1,10-phenanthroline method² and an ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer (LAMBDA 950, PerkinElmer, USA) at $\lambda = 510$ nm for the Fe-phen complexes. The precipitates obtained by filtration were analysed with an X-ray diffractometer (XRD, PANalytical, Netherlands) using Cu-K $_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å).

Calculation

The leaching efficiency (η_L) for the dissolution of the Nd–Fe–B magnets was calculated as follows:

$$\eta_L = \frac{m_0}{m_t} \times 100 \text{ (\%)} \quad (1)$$

where m_0 and m_t are the observed and theoretical mass loss of the Nd–Fe–B magnets, respectively. The observed mass loss was calculated as the mass change of the Nd–Fe–B magnets before and after the electrolysis. The theoretical mass loss for the magnet was calculated as³

$$m_t = \frac{I * t}{F * N_{EQ}} \quad (2)$$

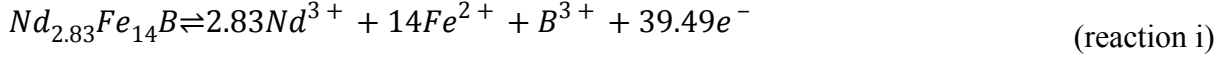
where I is the applied current, A; F is the Faraday constant, 96485.33 C mol⁻¹; t is the time of the electrolysis, s; and N_{EQ} is the total number of equivalents obtained from dissolving a unit mass of the alloy:⁴

$$N_{EQ} = \sum \frac{f_i * n_i}{a_i} \quad (3)$$

where f_i , n_i , and a_i are the mass fraction, the number of electrons exchanged, and the atomic weight, respectively, of the i th alloying element.

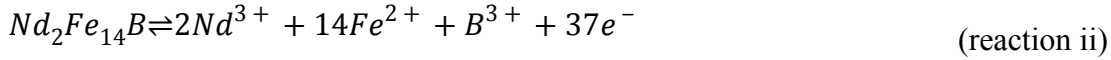
The Fe leaching efficiency (η_{Fe-L}) from the Nd–Fe–B magnets is estimated based on the leaching efficiency of the magnets under a constant current. We assumed that the Nd₂Fe₁₄B phase accounts for 90% by weight, while the grain boundary accounts for 10%⁵. There are two extreme

cases: the grain boundary contains only i) metallic Nd or ii) Nd₂O₃ (without considering other phases, e.g., NdFe₄B₄, due to their negligible content). In the case of i), the formula for the magnets can be written as Nd_{2.83}Fe₁₄B, under a constant leaching without selectivity (reaction i), the Fe leaching efficiency is calculated as



$$\eta_{Fe-L} = \eta_L * \frac{14 * 2}{2.83 * 3 + 14 * 2 + 1 * 3} \times 100 (\%) = 70.9\% * \eta_L$$

In the case of ii), the formula of the magnets can be written as Nd₂Fe₁₄B, because the Nd₂O₃ is electrochemically inert and thus does not consume charge (current). Under a constant leaching without selectivity (reaction ii), the Fe leaching efficiency is calculated as



$$\eta_{Fe-L} = \eta_L * \frac{14 * 2}{2 * 3 + 14 * 2 + 1 * 3} \times 100 (\%) = 75.7\% * \eta_L$$

Generally, both metallic Nd and Nd₂O₃ are present in the grain boundary; therefore, the Fe leaching efficiency (η_{Fe-L}) under a constant current should be in the range of (70.9–75.7%)* η_L . Specifically, when the magnet is leached with a η_L of 100%, η_{Fe-L} is in the range 70.9–75.7%.

The current efficiency (η_D) of the Fe deposition on the cathode is calculated as

$$\eta_D = \frac{m_{Fe}/M_{Fe}}{I * t/2F} \times 100 (\%) \quad (4)$$

where m_{Fe} is the mass of the deposited Fe on the cathode, g; M_{Fe} is the molar mass of Fe, 55.85 g mol⁻¹; I is the applied current, A; t is the duration of the electrolysis, s; and F is the Faraday constant, 96485.33 C mol⁻¹.

The recovery (%) of REEs from the Nd–Fe–B magnets is calculated as

$$\%R = \frac{\text{REEs in REE sulphate double salts (\%)} \times \text{Recovered REE sulphate double salts (\%)}}{\text{REEs in magnet (\%)} \times \text{Amount of leached magnet (g)}} \times 100 (\%)$$

(5)

The energy consumption, E (kWh kg⁻¹) is calculated as

$$E = \frac{U * I * t}{3600 * m}$$

(6)

where U is the voltage measured between the magnet anode and the copper cathode, V; I is the applied current, A; t is the duration of the electrolysis, s; and m is the amount of magnet dissolved, kg. Thus the reported values are kilowatt hours per kilogram of the magnet.

Notes and References

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