

# **Electrochemical Leaching of Rare-Earth Elements from Spent NdFeB Magnets**

Makarava Iryna

Scientific supervisors:  
Eveliina Repo,  
Markku Laatikainen

# • Ores

- **Monazite**, thorium rare-earth phosphate  $(\text{Th, Ln}) \text{PO}_4$ 
  - India, Brazil, Australia, South Africa, U.S.A.
- **Bastnaesite**, rare-earth fluorocarbonate,  $\text{LnFCO}_3$  (70-80%  $\text{Ln}_2\text{O}_3$ )
  - It has been found in a number areas in Europe and Africa, but the only commercially important deposit is in California, U.S.A.
- **Gadolinite**,  $(\text{Be, Fe})\text{Ln}_2\text{Si}_2\text{O}_{10}$ 
  - The mineral is found in Scandinavia and U.S.A.
- **Xenotime**, A rare-earth phosphate,  $\text{LnPO}_4$  (55-70%  $\text{Ln}_2\text{O}_3$ )
  - Malaya and Nigeria
- **Euxenite and polycrase**  $(\text{Ln, U, Th})(\text{Nb, Ta, Ti})_2\text{O}_6$  (20-30%  $\text{Ln}_2\text{O}_3$ )

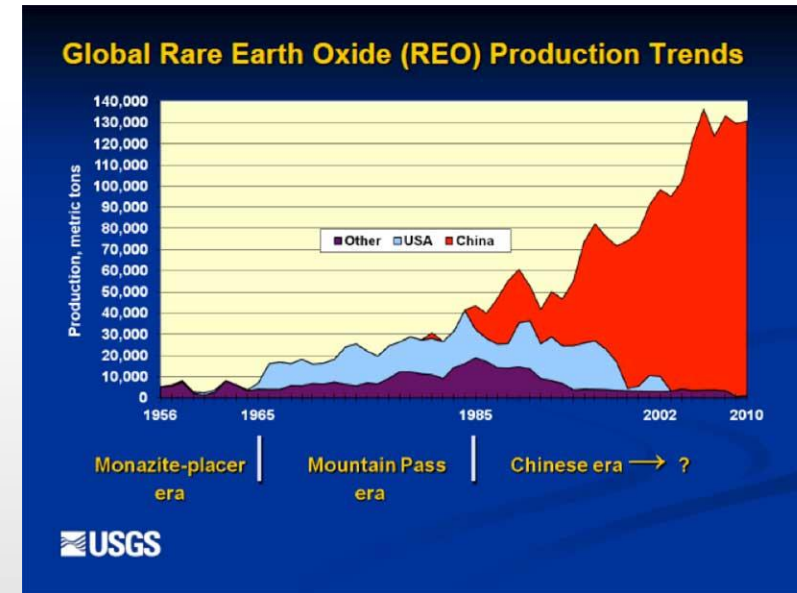


# Rare earth elements (REE)

Light Rare Earths	Last Price	31.12.2017	Units
Cerium >99%	6,365.83	5,774.40	USD/tn
Cerium Oxide >99.5%	2,025.49	2,731.14	USD/tn
Lanthanum >99%	5,570.10	5,774.40	USD/tn
Lanthanum Oxide >99.5%	2,061.66	2,497.04	USD/tn
Neodymium >99.5%	58,956.29	77,252.17	USD/tn
Neodymium Oxide >99.5%	45,573.57	46,296.96	USD/tn
Praseodymium >99%	95,487.48	88,202.71	USD/tn
Praseodymium Oxide >99.5%	58,232.89	59,317.98	USD/tn
Samarium >99.9%	15.5	15	USD/kg
Samarium Oxide >99.9%	1,953.15	2,200.00	USD/mt
Heavy Rare Earths			
Dysprosium >99%	235.1	235.1	USD/kg
Dysprosium Oxide >99.5%	184.2	226.8	USD/kg
Erbium >99.5%	110.47	110.43	USD/gm
Erbium Oxide >99.5%	23,510.17	27,327.12	USD/tn
Europium Oxide >99.5%	42.68	99	USD/kg
Gadolinium >99.9%	203.98	200	USD/gm
Gadolinium Oxide >99.5%	19,025.16	20,300.15	USD/tn
Mischmetal >99%	6	5.9	USD/kg
Scandium >99.9%	3,617.00	3,458.00	USD/kg
Scandium Oxide >99.95%	1,747.50	1,079.00	USD/kg
Terbium >99.9%	423.18	655	USD/kg
Terbium Oxide >99.9%	560.63	553.6	USD/kg
Yttrium >99.9%	32.55	36.5	USD/kg
Yttrium Oxide >99.99%	2,965.90	3,435.41	USD/tn

<http://mineralprices.com/>

<http://www.rareelementresources.com/rare-earth-elements#.VEpQWfnkcel>



Ferrite magnet



Neodymium  
magnet



Recycling technologies:

- pyrometallurgical
- hydrometallurgical

# The aim

is to find connection between the mechanism of NdFeB alloy dissolution and possibility for direct recovery of REEs due to electrochemical methods.



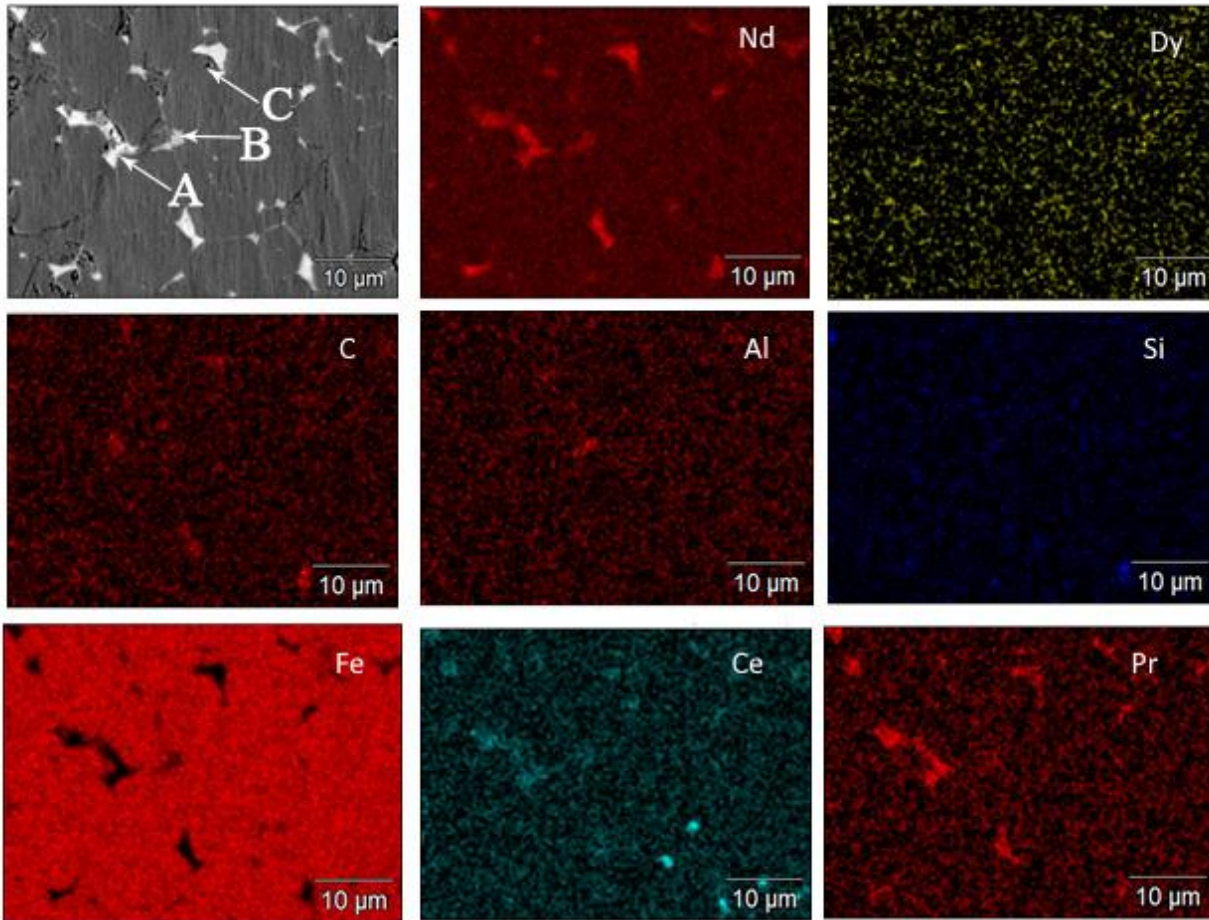


Fig. High-resolution EDX mapping of the main elements on the spent NdFeB magnet surface showing different chemical composition.

Table. Composition of domains A-C in Figure 1 determined by EDX.

Element	A (light grain)		B (bright grain)		C (dark grain)	
	wt-%	mol-%	wt-%	mol-%	wt-%	mol-%
<b>C</b>	7.3		3.9		2.2	
<b>O</b>	0.8		1.3			
<b>Al</b>	0.3		0.5		0.6	
<b>Si</b>	1.4		—		—	
<b>P</b>	0.6		—		—	
<b>Fe</b>	10.2	12.3	10.3	18.1	67.6	74.6
<b>Ce</b>	10.2		14.6		4.8	
<b>Pr</b>	15.6		21.1		5.1	
<b>Nd</b>	53.8	25.3	48.3	33.1	18.7	8.0
<b>Gd</b>	—		—		0.6	
<b>Dy</b>	—		—		0.3	
<b>Fe : Nd</b>		1 : 2		1 : 1.8		9.3 : 1

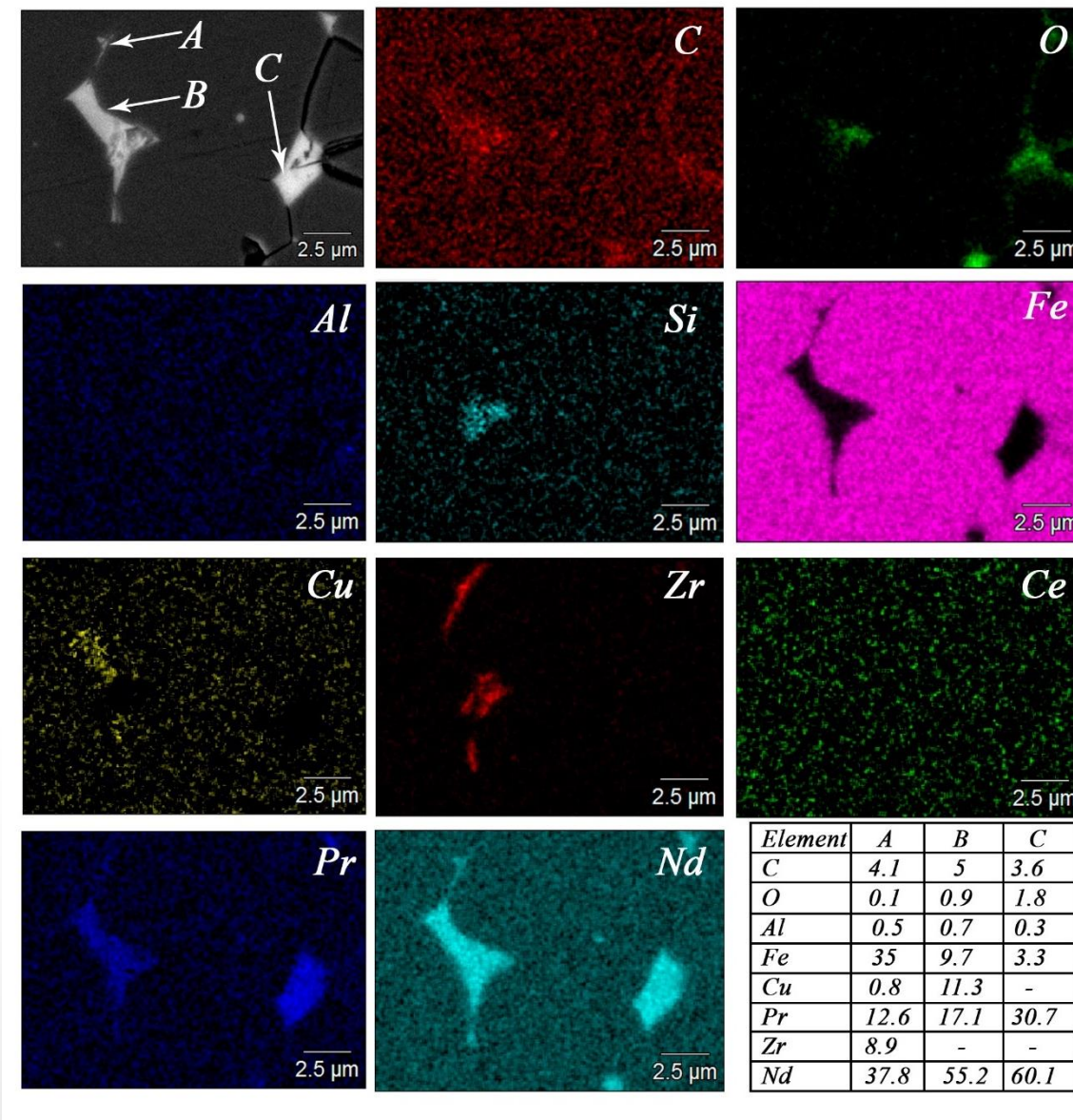


Fig. High-resolution EDX mapping of Nd-rich phases showing different chemical composition.

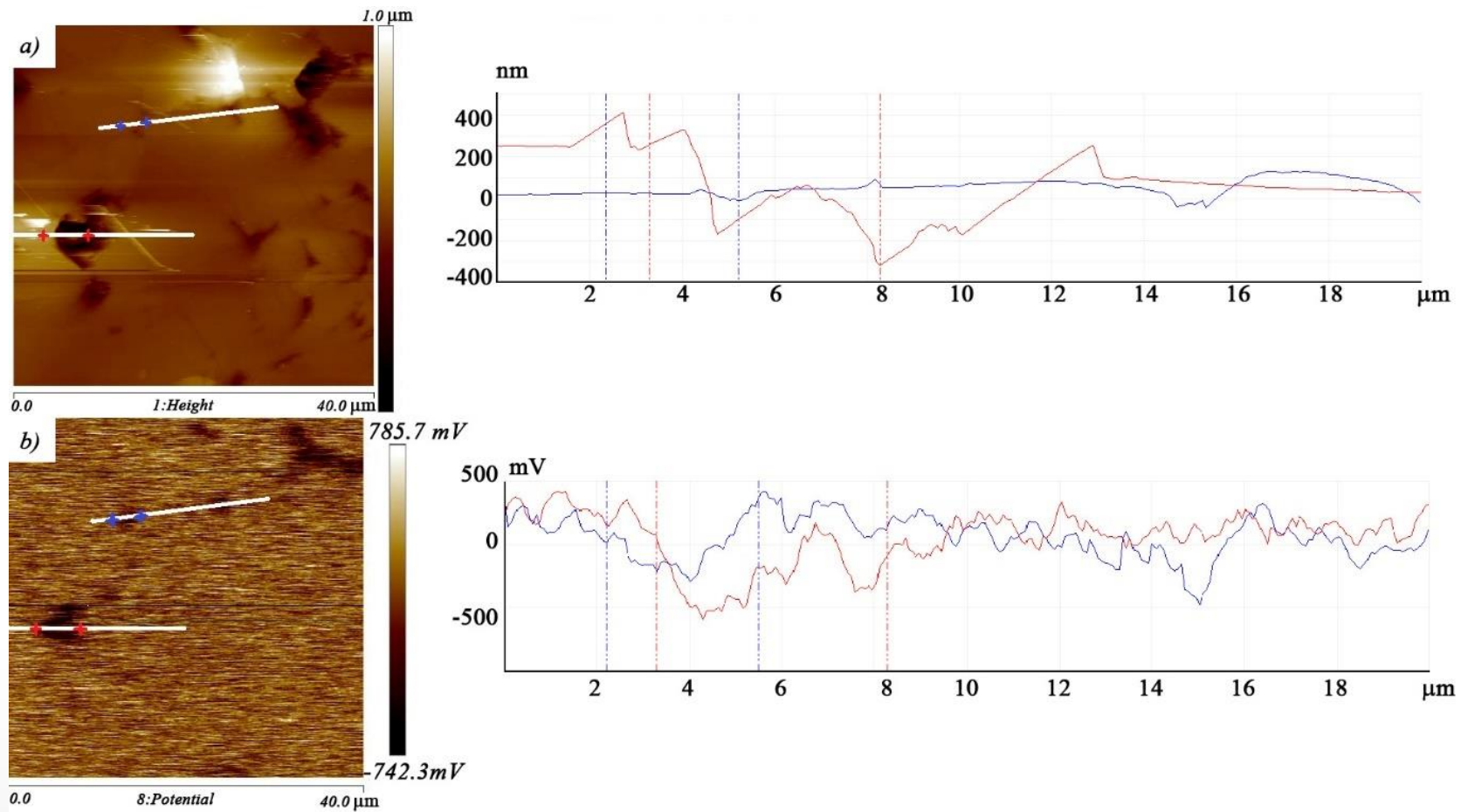


Fig. (a) Topography and (b) Volta-potential map measured using SKPFM in air on the surface of polished NdFeB magnet. Profile analysis in each map is a section along two lines.



Leaching solutions:

0.1 M  $\text{H}_2\text{SO}_4$

0.1 M  $\text{H}_2\text{SO}_4$  + 0.05 M  $\text{H}_2\text{C}_2\text{O}_4$

Current densities: 0, 10, 20 A/dm<sup>2</sup>

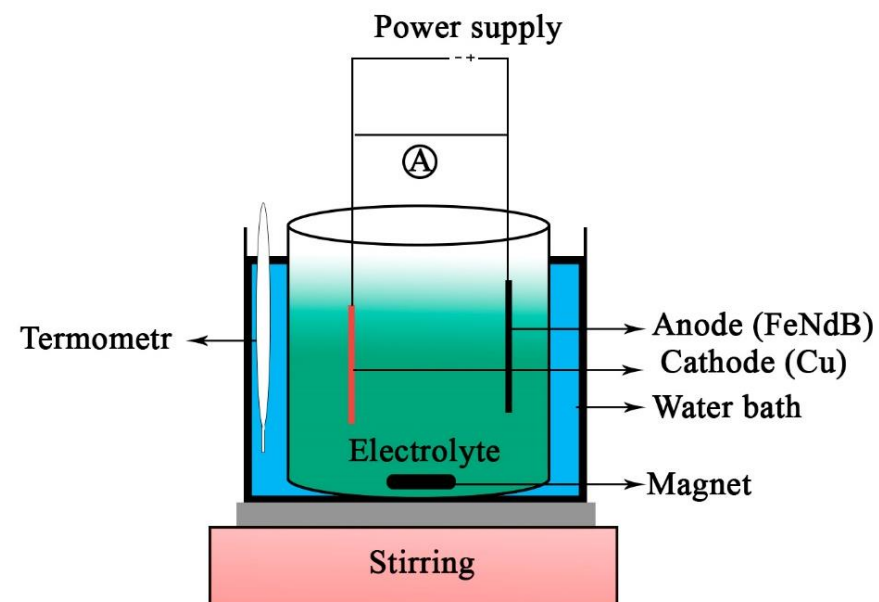


Fig. Schematic picture of electro-leaching of NdFeB plate

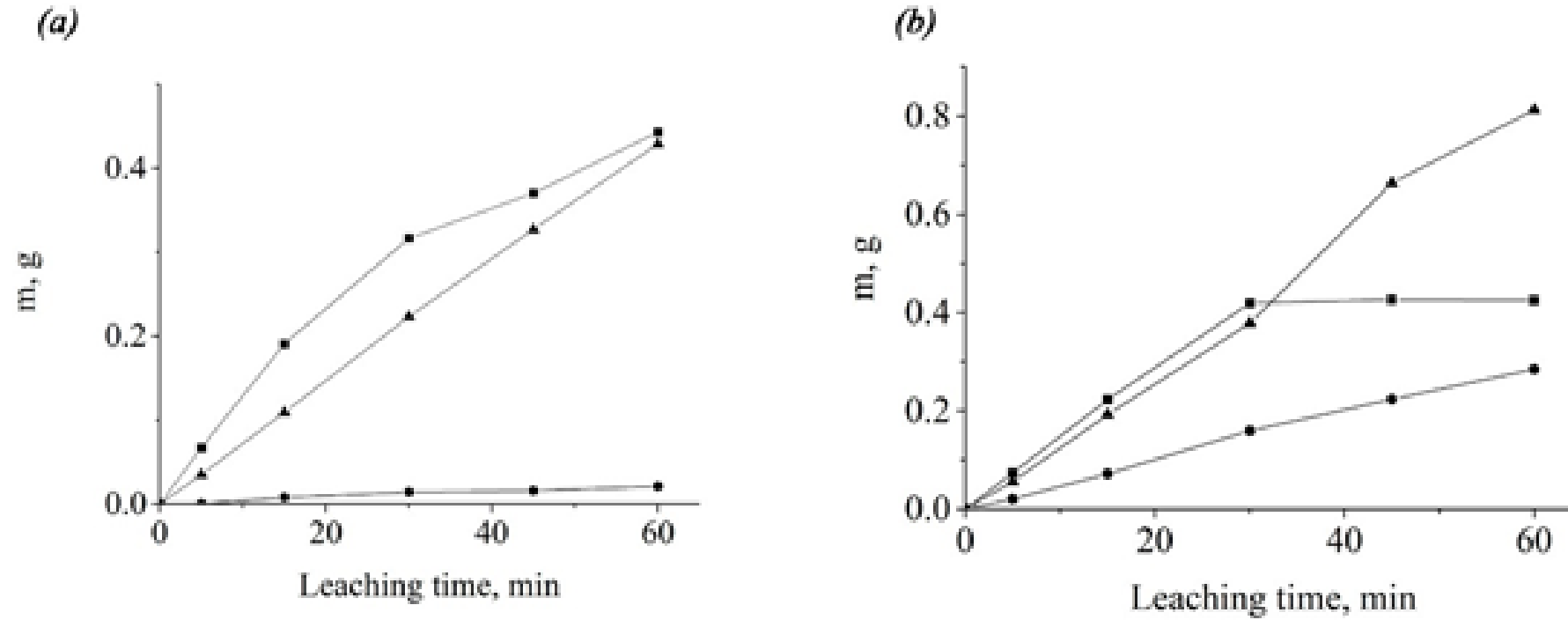


Fig. Effect of current density on iron leaching from NdFeB magnet waste in (a) 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and (b) 0.1 M H<sub>2</sub>SO<sub>4</sub>. Stirring rate 400 rpm,  $T = 23$  °C,  $i = 0$  A/dm<sup>2</sup> (circles), 10 A/dm<sup>2</sup> (triangles), 20 A/dm<sup>2</sup> (squares).

Table. Weight loss of NdFeB magnet during chemical and electrochemical leaching

	0.5 M H <sub>2</sub> SO <sub>4</sub>		0.1 M H <sub>2</sub> SO <sub>4</sub>		0.05 M H <sub>2</sub> SO <sub>4</sub>		Theoretical value*
	—	0.05M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	—	0.05M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	—	0.05M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	
i, A/dm <sup>2</sup>	Δm, g						
Chemical leaching	1.46 ± 0.03	1.11 ± 0.13	0.45 ± 0.04	0.089 ± 0.08	0.029 ± 0.005	0.009 ± 0.002	—
10	1.64 ± 0.11	1.19 ± 0.08	0.74 ± 0.03	0.67 ± 0.07	0.61 ± 0.04	0.67 ± 0.01	0.76
20	1.68 ± 0.07	1.48 ± 0.06	1.32 ± 0.05	0.80 ± 0.07	—	—	1.51
50	2.97 ± 0.14	1.07 ± 0.02	—	—	—	—	3.78

\*  $\Delta m = Iq_{\text{alloy}}t$ , where  $I$  is current (A),  $q_{\text{alloy}}$  is electrochemical equivalent of the alloy, 1.51 (g/Ah) and  $t$  is time, (h).

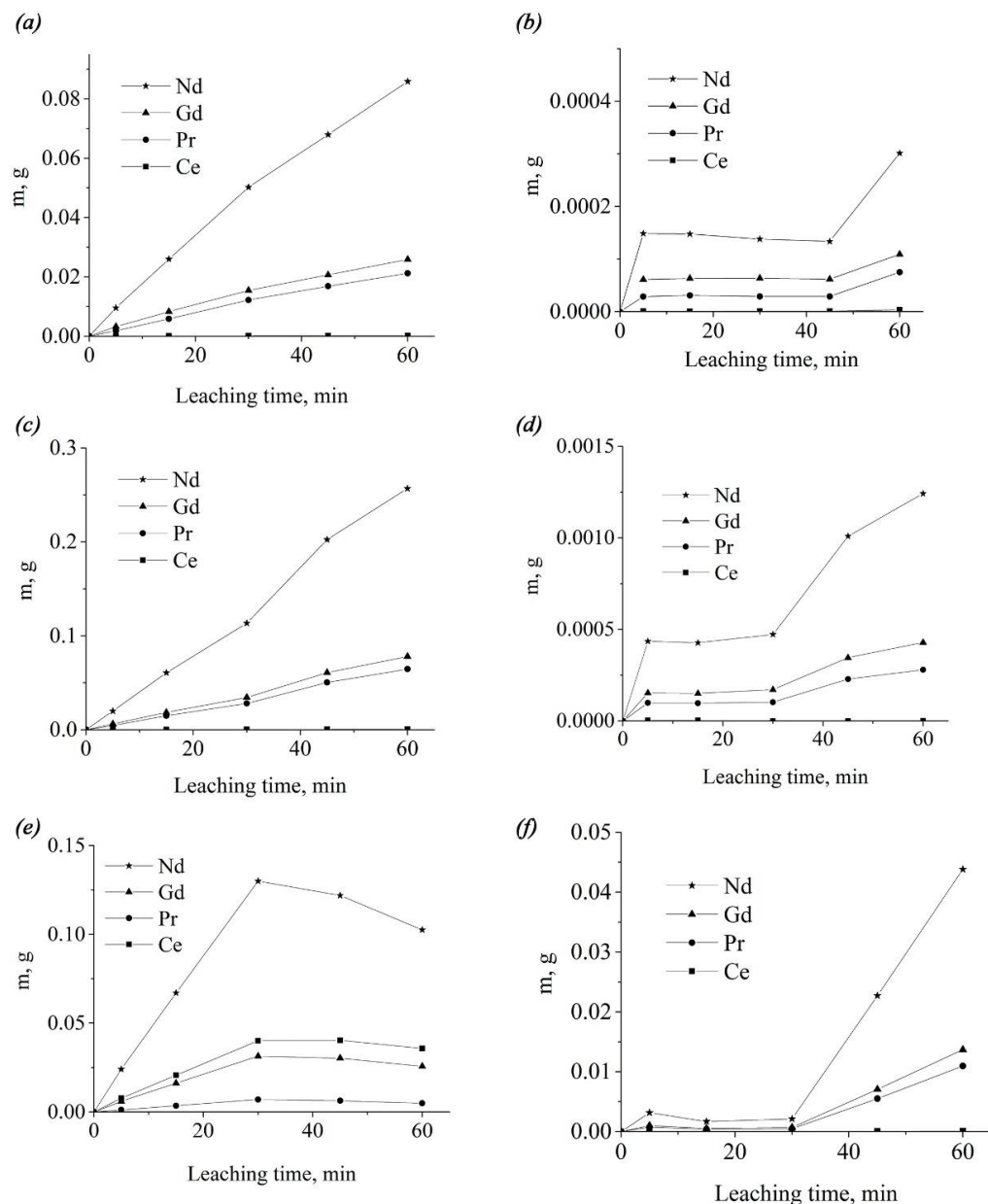


Table. Metal composition of the precipitate after chemical and electrochemical leaching in the mixture of 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

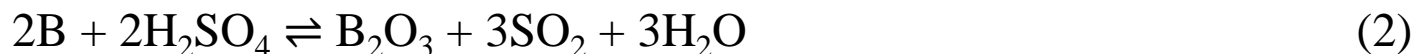
	Fe	Cu	Nd	Ce	Pr	Gd
	g/kg					
<b>chemical leaching</b>	2.8	0.8	295.0	0.7	87.0	75.5
<b>10 A/dm<sup>2</sup></b>	3.1	0.5	291.3	0.7	85.0	75.1
<b>20 A/dm<sup>2</sup></b>	3.1	0.5	289.7	0.7	83.4	75.0

\* amount of Tb, Dy, Ho, Er, Yb, La, Sm was 0.03–0.09 g/kg

Fig. Effect of current density on the leached weight of REEs from NdFeB magnet waste in (a, c, e) 0.1 M H<sub>2</sub>SO<sub>4</sub> and (b, d, f) 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; (a, b) chemical leaching; electrochemical leaching at current density, (c, d) 10 A/dm<sup>2</sup> and (e, f) 20 A/dm<sup>2</sup> (Stirring rate 400 rpm, T = 23 °C).



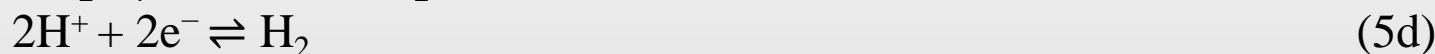
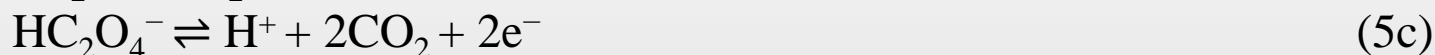
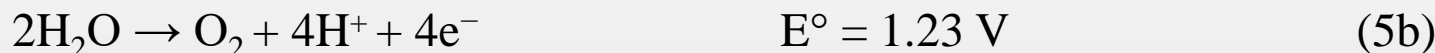
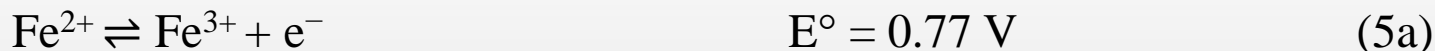
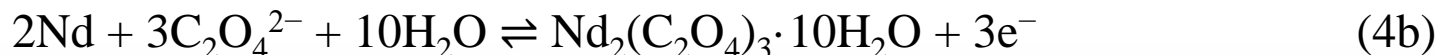
## Chemical leaching



## Dissolution in a mixture of sulfuric and oxalic acid



## Electro-leaching



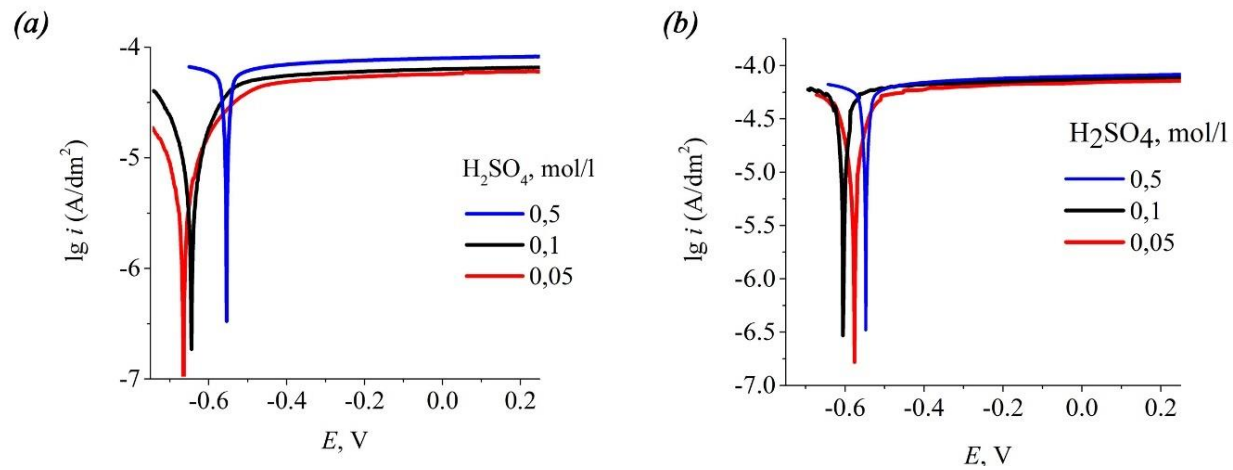


Fig. Linear polarization curves of the polished NdFeB magnet in  $\lg i$ - $E$  coordinates in (a) 0.1 M  $\text{H}_2\text{SO}_4$  and (b) 0.1 M  $\text{H}_2\text{SO}_4$  + 0.05 M  $\text{H}_2\text{C}_2\text{O}_4$ .

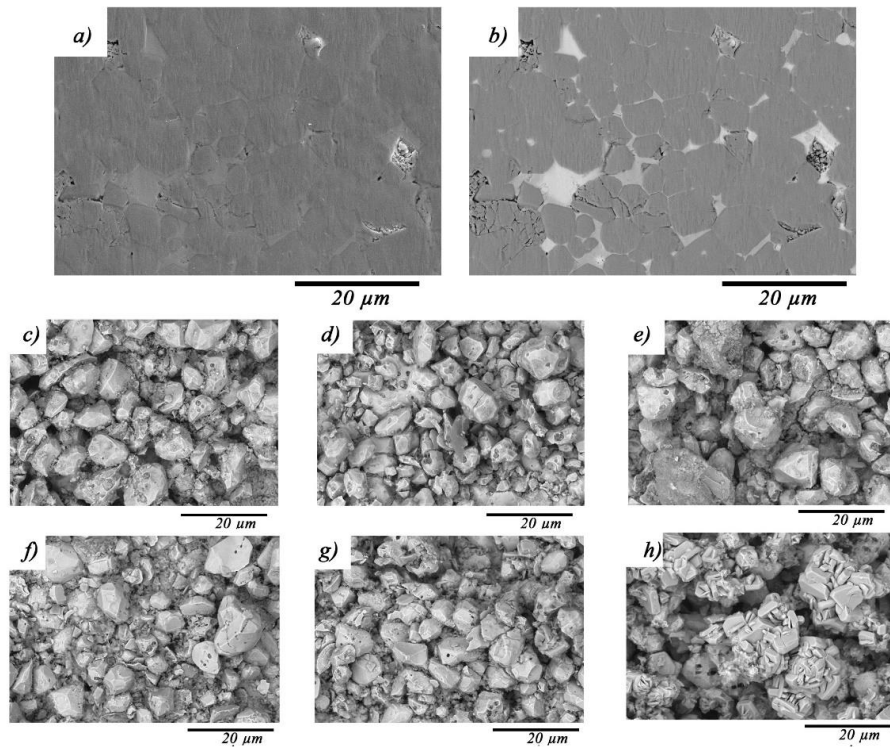


Fig. Microstructure of initial FeNdB magnet SE-SEM (a) and BSE-SEM (b) image of the surface after leaching in mixture 0.1 M  $\text{H}_2\text{SO}_4$  (c-e) and in 0.1 M  $\text{H}_2\text{SO}_4$ +0.05M  $\text{H}_2\text{C}_2\text{O}_4$  (f-h): chemical leaching (a, f), electrochemical at current density,  $\text{A/dm}^2$ : 10 (d, g), 20 (e, h)

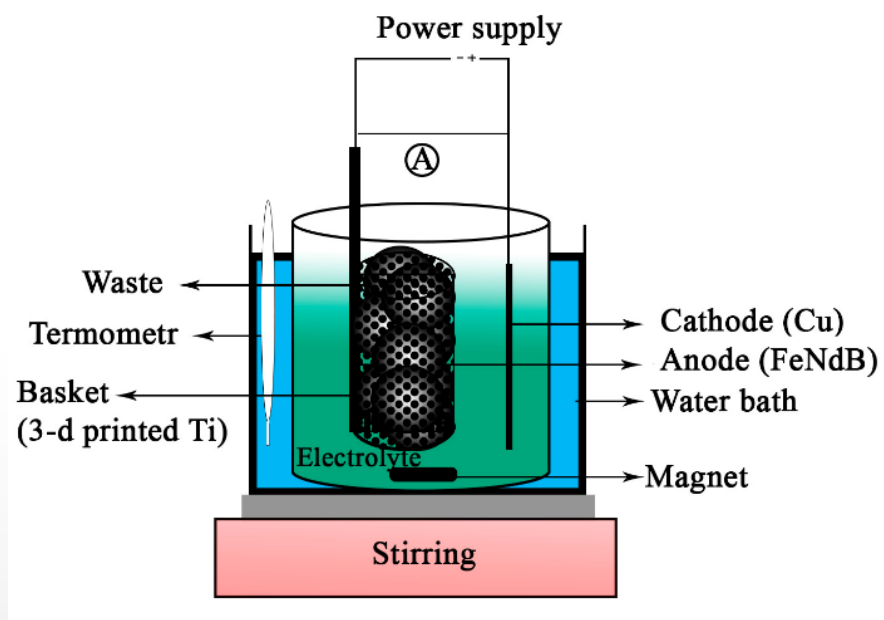


Fig. Schematic picture of electro-leaching in a Ti basket.

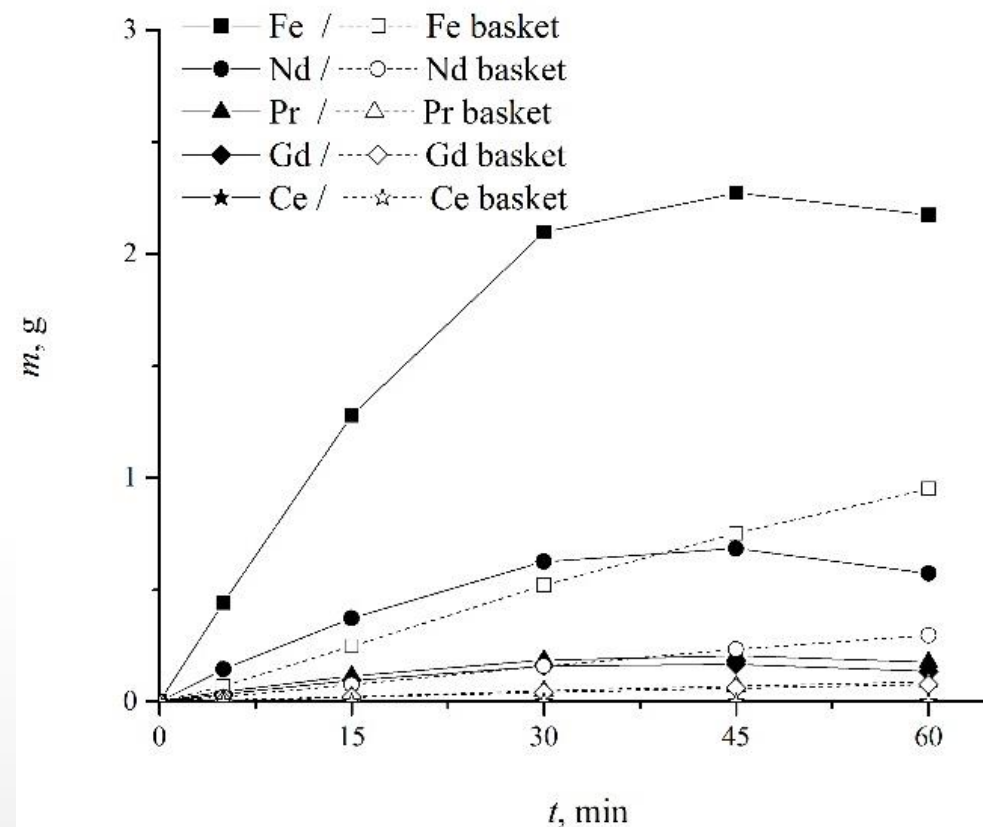


Fig. Comparison of iron and REEs leaching from NdFeB magnet waste powder in a basket and with plate.

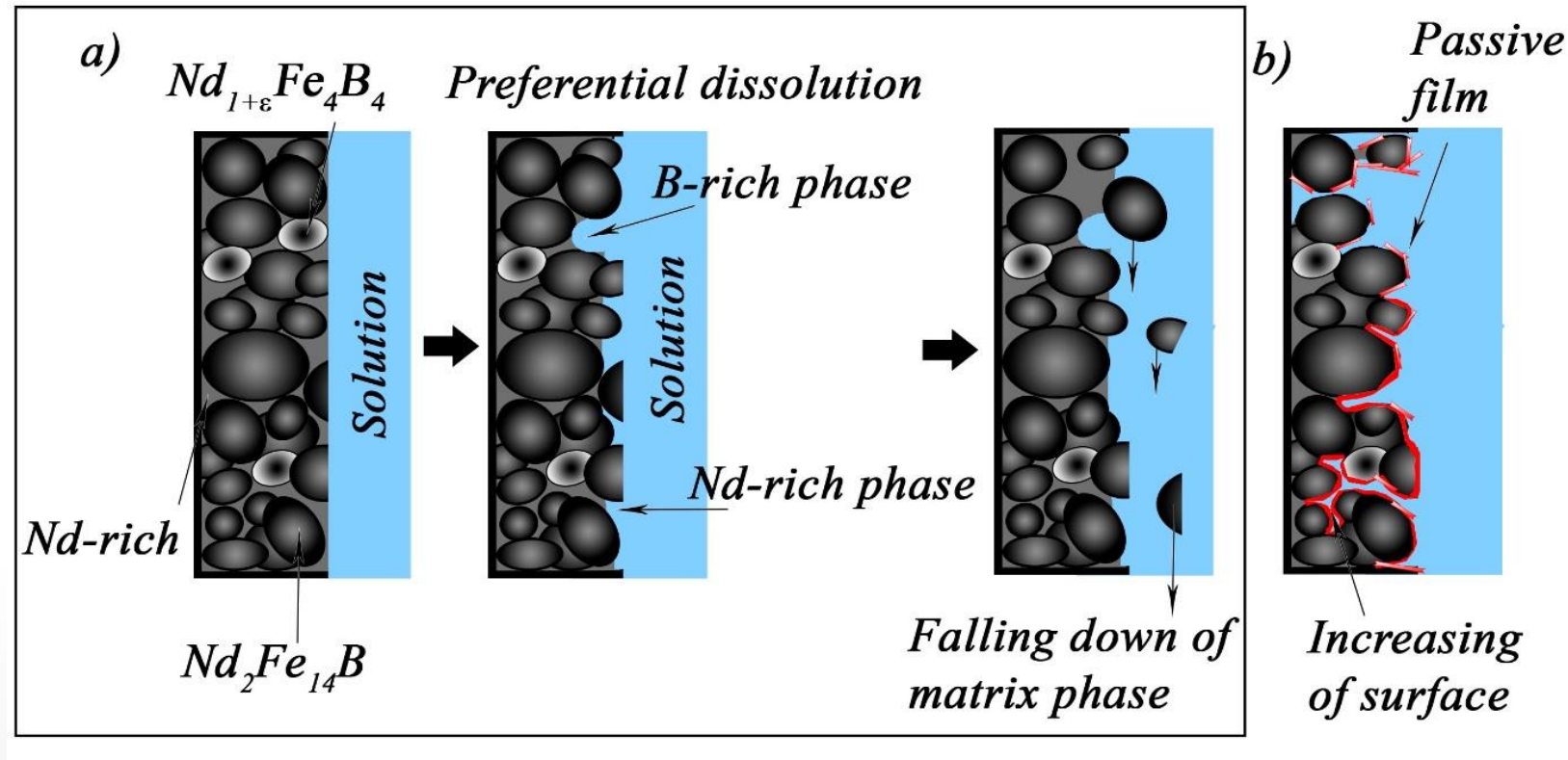


Fig. Schematic illustration of leaching process on the surface of spent NdFeB magnet in a)  $\text{H}_2\text{SO}_4$ , b) mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$



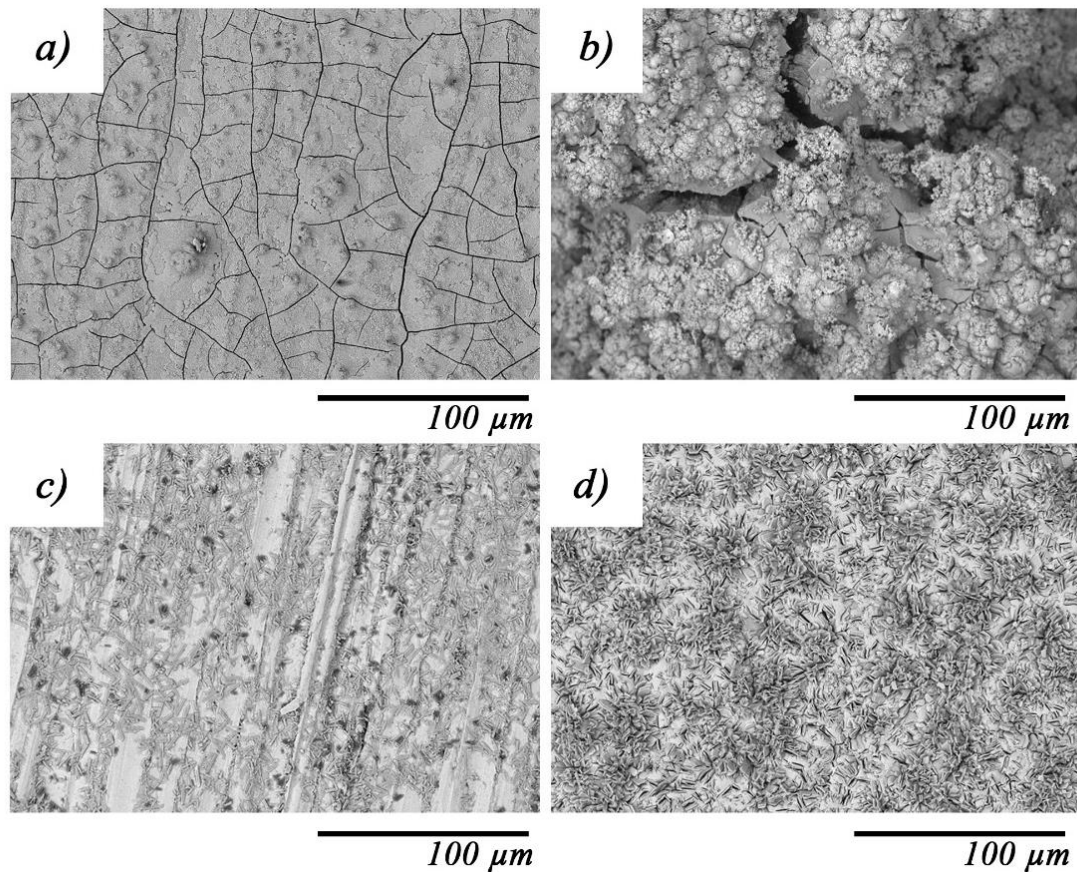


Fig. Micrographs of the cathode surface after 1 hour electrolysis (*a*, *b*) in 0.1 M H<sub>2</sub>SO<sub>4</sub>, (*c*, *d*) in mixture 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at current density (*a*, *c*) 10 A/dm<sup>2</sup> and (*b*, *d*) 20 A/dm<sup>2</sup>.

Table. EDX analysis of the cathodic deposit (the values are in wt-%)

	0.1 M H <sub>2</sub> SO <sub>4</sub>		0.1 M H <sub>2</sub> SO <sub>4</sub> and 0.05 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	
	10 A/dm <sup>2</sup>	20 A/dm <sup>2</sup>	10 A/dm <sup>2</sup>	20 A/dm <sup>2</sup>
<b>C</b>	2.9	3.9	12.8	11.7
<b>O</b>	17	28.3	19	24.1
<b>Al</b>	0.5	0.3	—	—
<b>S</b>	1.4	0.9	—	—
<b>Fe</b>	62	44.7	5.3	30.3
<b>Ce</b>	—	4	—	—
<b>Pr</b>	2.9	3.2	2.7	6.4
<b>Nd</b>	13.2	14.7	10.6	27.4

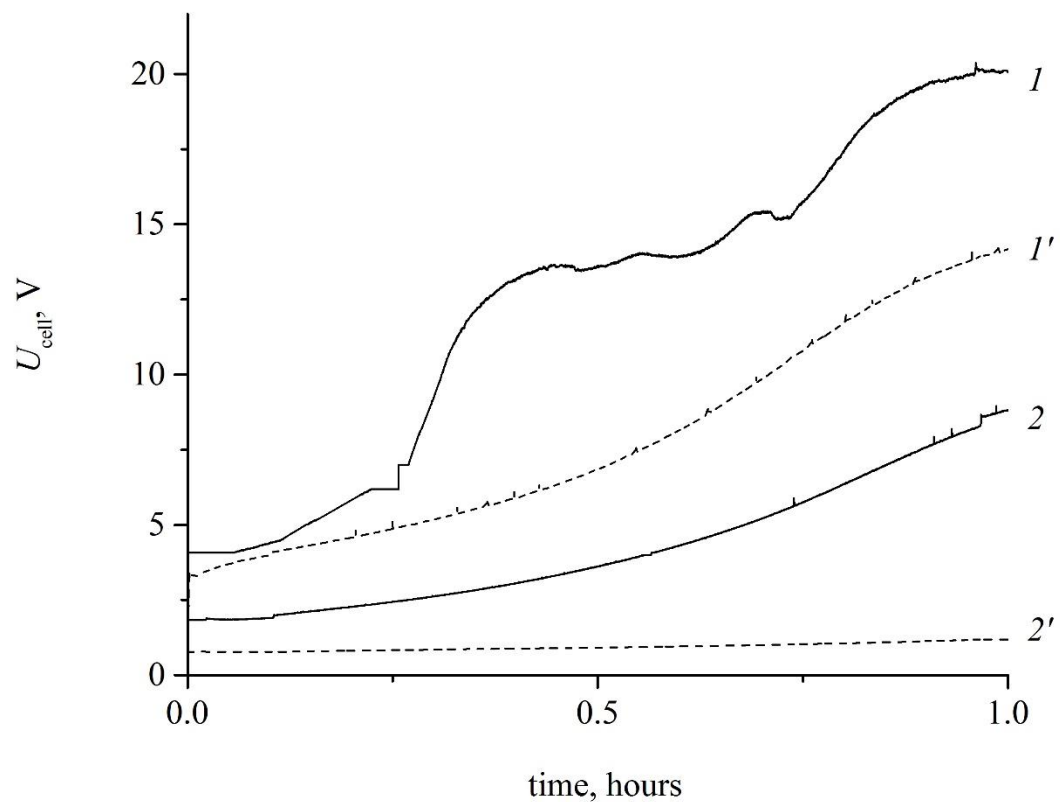


Fig. Cell voltage during electrolysis: (1, 2) 0.1 M H<sub>2</sub>SO<sub>4</sub>, (1', 2') 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; current density (2, 2') 10 A/dm<sup>2</sup> and (1, 1') 20 A/dm<sup>2</sup>.

Table. Energy consumption (kWh/kg magnet) of electro-leaching.

i, A/dm <sup>2</sup>	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.1 M H <sub>2</sub> SO <sub>4</sub> + 0.05 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
<b>10</b>	6.0	0.91
<b>20</b>	15.0	18.0

## Conclusions

1. In this study we investigated the leaching process of spent NdFeB magnet via chemical and electrochemical methods for the recovery of REEs.
2. XRD and SEM/EDX analyses revealed the presence of Nd<sub>2</sub>Fe<sub>14</sub>B micrometer-sized ferromagnetic granules surrounded by Nd-rich phases. Local Volta potential differences as high as 500 mV within the microstructure suggests preferential selective leaching of the Nd-rich phase and this was proven by chemical and electrochemical leaching experiments with 0.05 – 0.5 M H<sub>2</sub>SO<sub>4</sub>.
3. The leaching rate strongly depends on the acid concentration and current density. The positive effect of applied voltage was significant especially at low acid concentrations thus making the leaching process more environmentally friendly.
4. Addition of oxalic acid in the leaching solution further reduces the energy consumption and at the same time improves recovery of REEs as solid oxalates. Some of the REEs were also found in the cathodic deposits.