Sustainable recovery of rare earths elements from spent magnets using pyrometallurgical methods

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Abstract

Due to a high import dependency on raw materials for the rare earth metal production, as well as a constantly increasing demand for rare earth metals, there is a call for an alternative sourcing. From large amounts of available spent NdFeB magnets, recovering the rare earths from within via recycling process deemed to be a convincing alternative. In this context, a recycling process consisting of three main steps is developed and investigated for the extraction of rare earth metals from spent magnets. The three main steps are oxidation of magnets under air to produce oxidised magnets, carbothermic reduction to remove iron and molten salt electrolysis to deposit rare earth alloy. Experimental trials were planned and targeted at recovering a rare earth metal alloy that consists mainly of Nd. Accordingly, spent magnets provided by the research partner Miknatis from Turkey were demagnetised and grinded. The magnet powders were then oxidised under air atmosphere for 3 hours at 1000 °C. Results shown an 18.72 wt.% mass change with the oxidised magnets having up to 76 wt.% of Fe_2O_3 and 8 wt.% of $NdFeO_3$. These oxidised magnets were then smelted under Argon gas at 50-60 mbar in a vacuum induction furnace at temperatures between 1150 to1200 °C. The smelted product was metallic phase with Fe content up to 88 wt.% and mixed rare earth oxide (MREO) enriched phase with total rare earth content up to 43 wt.%. From the 15 experiments, average yield for the slag was 19.5% and 45 % for the metal. The slag was then grinded into powder, mixed with fused salt of NdF_3-PrF_3-LiF, and electrolyzed in a molten bath at 1110 °C. The products were a metallic alloy with up to 72 wt.% Nd and 23 wt.% Pr. The target of developing a recycling process and raw materials for re-manufacturing of similar magnets had been achieved.

1 Introduction

In order to achieve a greener environment by means of efficient energies and manufacturing technologies that underpin climate transition, the demand for rare earth assets has since skyrocketed for the past two decades. According to Trading Economics, the prices of key rare earth elements such as Nd, Pr, and Dy had almost tripled from 2019 – 2022 [1,2]. A widely used component is neodymium iron boron magnets ($Nd_2Fe_{14}B$, further referred to as NdFeB). The role of neodymium- and dysprosium-made magnets, for instance, are crucial due to their outstanding magnetic properties that demonstrate a rich energy density compared to Alnico or ferrite magnets of the same dimension [3]. The increasing amount of available spent NdFeB magnets in the market strongly motivates the recovery of these elements, as the presence of Dy, Nd and Pr in such materials normally sums up to 20 % [4], serving as a valuable secondary source. Albeit, the high recycling potential, secondary production of rare earth elements is not well established and not conducted on an industrial scale. Rare earths recycling efforts is heavily hindered by the absence of recycling technology, infrastructure, and strategies.

This current study aims to investigate and verify the possibility of producing metallic rare earth alloys from spent NdFeB magnets by combining selected pyro metallurgical methods. Depending on the purity, both of which could be fed directly back to the vacuum alloying step in the production of the new NdFeB magnets [5]. The success and reproducibility of this process ensures the circulation of already scarce rare earth elements in economical areas where access to rare earth metals are highly hindered.

The first step of the process aims to increase the oxygen potential of the system by converting the main Φ-Phase i.e. $Nd_2Fe_{14}B$ (up to 80 wt.%) and other rare earth interphases (up to 12 wt.%) into oxides [6], [7]. Based on thermodynamic calculation software FactSage8.0 (GTT-Technologies, Aachen, Germany), main phases of Nd_2O_3, $NdFeO_3$ and Fe_xO_y are highly expected [6-8] when the magnets are oxidised under ambience atmosphere. After this step, the spent magnets are converted into so-called oxidised magnet compounds, containing various oxides.

The next step of the process aims to remove the iron compound from the compound. Here, the principle of carbothermic reduction is utilized. The product after the iron removal is an enriched mixed rare earth oxide (MREO) phase. The chemical reactions for the removal of iron from the compound are listed below: [9,10]

$$3\ Fe_2O_{3\,(l)} + C \rightarrow 2\ Fe_3O_{4\,(l)} + CO_{(g)} \qquad \text{Eq (1)}$$

$$Fe_3O_{4\,(l)} + C \rightarrow 3\ FeO_{(l)} + CO_{(g)} \qquad \text{Eq (2)}$$

$$FeO_{(l)} + C \rightarrow Fe_{(l)} + CO_{(g)} \qquad \text{Eq (3)}$$

$$2NdFeO_3 + C \rightarrow Nd_2O_{3\,(s)} + 2\ Fe + CO_{(g)} \qquad \text{Eq (4)}$$

$$2PrFeO_3 + C \rightarrow Pr_2O_{3\,(s)} + 2\ Fe + CO_{(g)} \qquad \text{Eq (5)}$$

The last step of the process is the metal extraction from the MREO phase. For this purpose, molten salt electrolysis is utilized, an attempt to imitate the primary production of rare earth metal via neodymium electrolysis [11,12]. A salt mixture adapted from [13,14] consisting of NdF_3-PrF_3-LiF_3 is used to dissolve the MREO phase. After that, the system is set for potentiostatic deposition for a duration of 4 hours to allow the reduction of rare earth ions i.e. Nd^{3+} and Pr^{3+} to metallic rare earth i.e. Nd or Pr.

2 Experimental

2.1 Material

The starting materials are provided by the Turkish company Miknatis and pre-treated by firstly de-magnetising under 300ºC for 3 hours and then crushed into powders of particle size < 100µm. The chemical composition of the magnets is listed in Table 1 below:

Table 1: Chemical Composition of magnets used for this study

Sample	**Nd**	**Ni**	**Fe**	**B**	**Pr**	**Dy**
NdFeB	15.9	0.0006	73.8	0.662	5.6	0.201

2.2 Oxidation

1056 g of the crushed materials are placed on a ceramic crucible plate and allow to oxidised at 1000ºC under ambience atmosphere for 3 hours inside an electric heated muffle furnace (compare Figure 1). The weight change before and after oxidation is recorded, this correspond to the oxygen uptake by the NdFeB magnets. In addition to that, the oxidised magnets compound was analysed by XRD to identify the oxide compounds.

Figure 1: Muffle Furnace for the oxidation

2.3 Iron Removal via Carbothermic Reduction

The experimental trials took place in a vacuum induction furnace (Heraeus MiniVIM, Hanau, Germany) according to the following experimental setup (compare Figure 2). The air atmosphere within the chamber is controlled at 80 mbar Ar. A clay graphite crucible is used as a source of contact carbon for the carbothermic reduction. The crucible is heated to 1300 °C and held for 10 minutes for the reduction to take place. The products from this step are metallic Fe and the mentioned MREO phase.

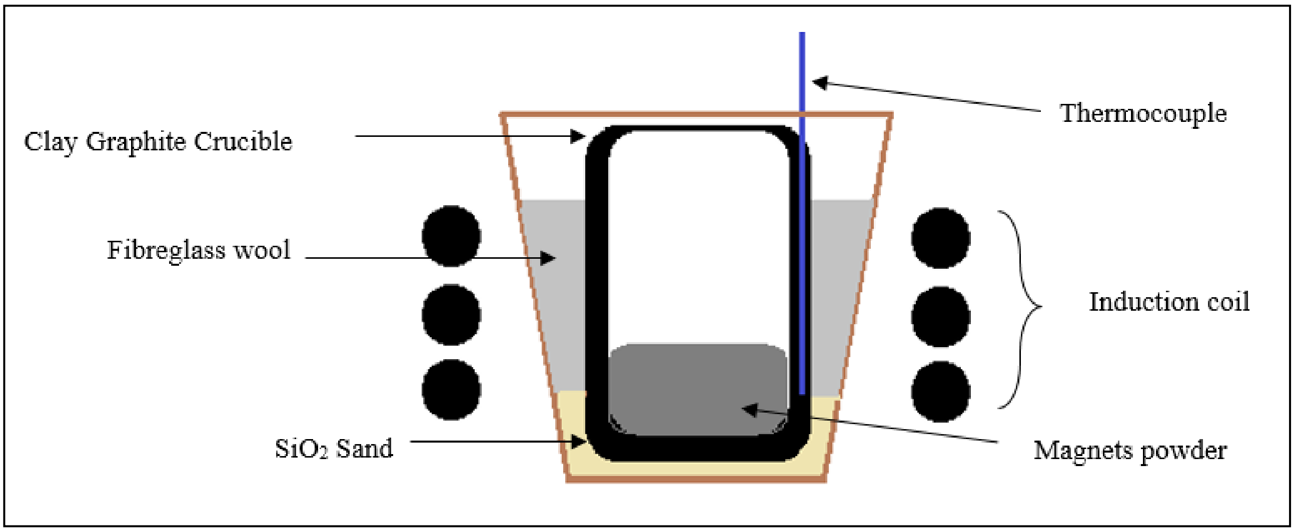

Figure 2: Experiment setup of graphite crucible in induction furnace

2.4 Molten Salt Electrolysis

A salt mixture containing 61.11 wt.% NdF_3, 26.3 wt.% PrF_3 and 12.6 wt.% if firstly fused at 800 °C and then casted at 1100 °C at an overpressure of 1800 mbar. The casted salt is then crushed and mixed with the MREO phase, melted at 1150°C and allowed to deposit for 4 hours on a Mo working electrode at -1.0V potential. The setup of the experiment used for this experiment series is adapted from [13, 14]. From the electrolysis, a thin layer of metallic rare earth is deposited onto the molybdenum working electrode.

2.5 Results

2.5.1 Oxidation

From two consecutive oxidation experiments, a total weight change of +18.72 % is recorded (compare Figure 4). Demonstrating the positive outcome of oxidising the phases within the initial magnets. Based on literature suggestions [9], the main products are formed according to the following equations:

$Nd_2Fe_{14}B\ (s) + 3/2\ O_2\ (g) \rightarrow 12\ Fe(s) + Fe_2B\ (s) + Nd_2O_3\ (s)$ Eq (6)

$2\ Fe\ (s) + 3/2\ O_2\ (g) \rightarrow Fe_2O_3\ (s)$ Eq (7)

$2/3\ Nd_2O_3\ (s) + 4/3\ Fe\ (s) + O_2\ (g) \rightarrow 4/3\ NdFeO_3$ Eq (8)

Formation of Dy_2O_3 and Pr_2O_3 are assume to follow Eq (17), $DyFeO_3$ and $PrFeO_3$ are assumed to follow Eq (19). Similarly, it is expected that the boron content in the magnets were oxidised to B_2O_3 first and eventually formed $NdBO_3$ according to Eq (19). Qualitative analysis by XRD (Bruker D8 Advance, Karlsruhe, Germany) shows the expected phases of Fe_2O_3, $NdFeO_3$ and Nd_2O_3 phases along with other phases such as $NdBO_3$ and Fe_2B. The results are shown in Figure 5.

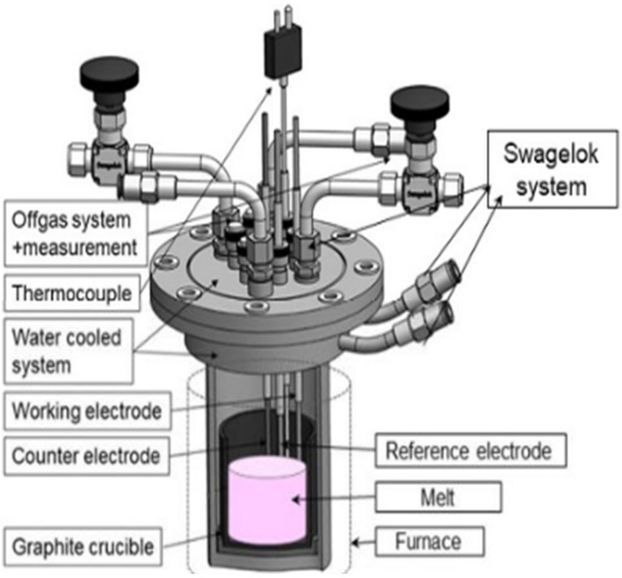

Figure 3: Illustration of experimental setup for molten electrolysis

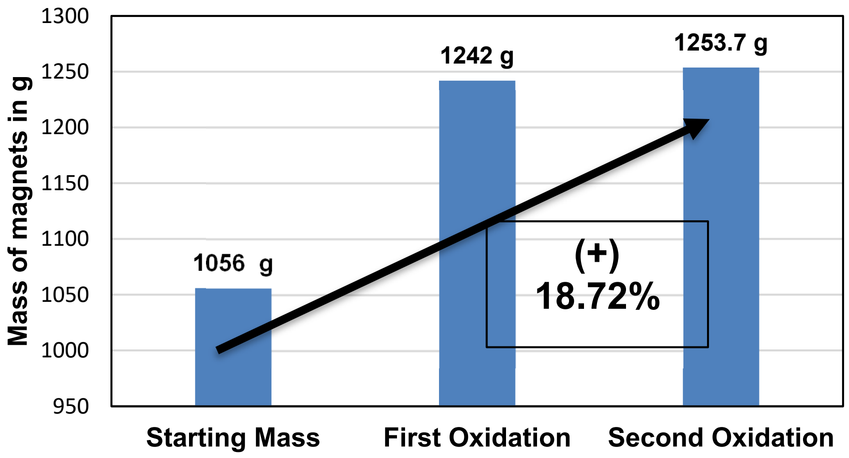

Figure 4: Oxygen uptake by the NdFeB Magnets from two consecutive experiments

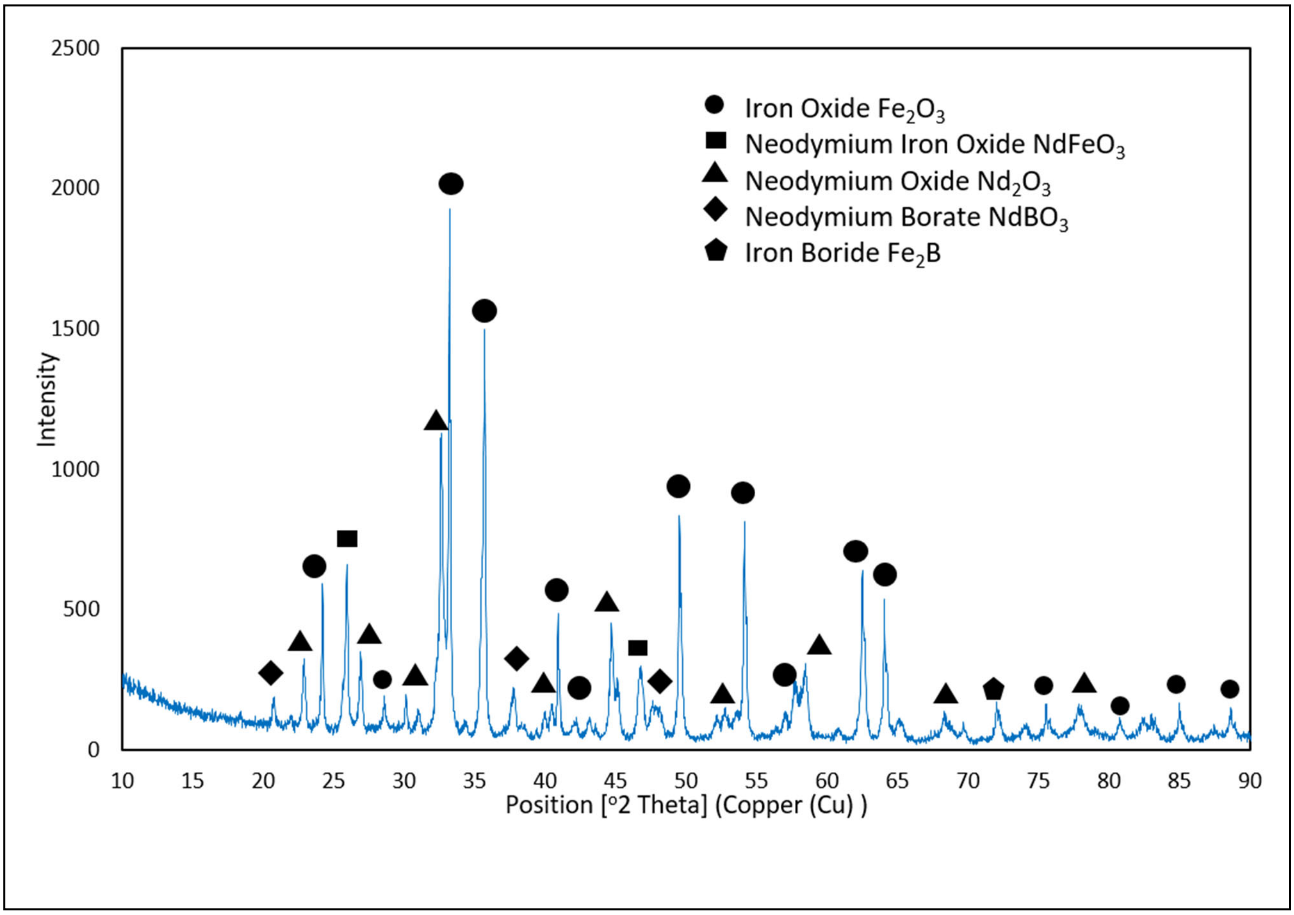

Figure 5: XRD analysis of oxidised NdFeB magnets

2.5.2 Iron Removal by Carbothermic Reduction

The product of the iron removal step consists of two main phase as seen in Figure 6. Both the silver colored metallic Fe phase and the brownish-green colored MREO phase were analysed with ICP-OES (Spectro Arcos, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The results shown nearly a two-fold increase of Nd and Pr content from 15.9 wt.% to 33.2 wt.% Nd and 5.6 wt.% to 10.2 wt.% Pr in the MREO phase. The metallic phase on the other hand consists of 89 wt.% with the rest assuming to be carbon due to the intense interaction with the carbon crucible. The full results are listed in Table 2.

Table 2: Chemical composition of reduction products by ICP-OES in wt.%

Samples/Elements	Nd	Pr	Dy	Fe	B
Metallic Phase	1.7	0.05	0	88.70	0.08
MREO Phase	33.2	10.2	0.31	2.42	1.93

Figure 6: Phases form from carbothermic reduction, silver-grey: metallic phase; brownish-green: MREO phase

2.5.3 Molten Salt Electrolysis

The tip of the working electrode submerged into the molten bath, where the deposition is expected to take place is analysed for its chemical composition by ICP-OES. The electrode is first etched to remove the leftover salt using HNO_3 and then HCl both under ultrasound, to make sure that the chemical composition is not influenced by the composition of the salt. Since the whole electrode was analysed, a large portion of the sample contains the metal from the electrode. The chemical result is shown in the Figure 7 below, excluding the electrode material while considering only the deposited metal.

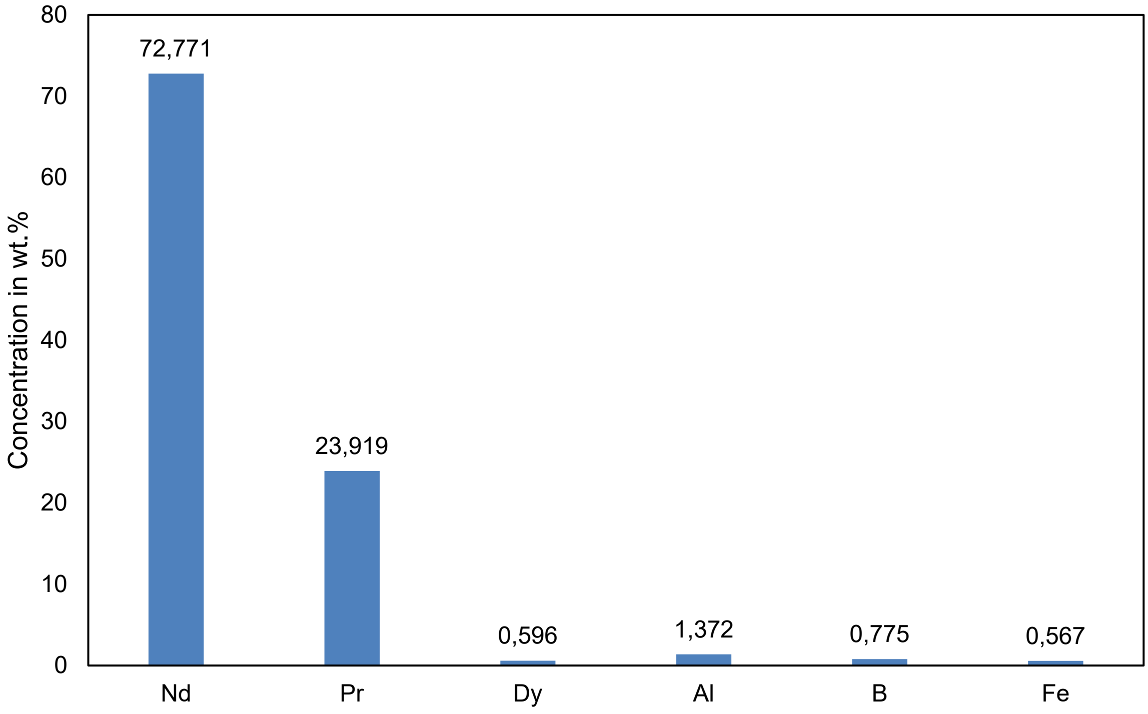

Figure 7: Chemical composition of deposited metal

3 Conclusion

The recycling of rare earth metals from spent NdFeB magnets were successfully performed by a three step recycling process, starting with two consecutive oxidations under air atmosphere for 3 hours at 1000 ºC, following by iron removal by carbothermic reduction at 1300 ºC and 80 mbar Ar, with carbon crucible as contact material for the carbon supply, finishing off by molten salt electrolysis at –1.0 V at 1150 ºC with a Nd-Pr-Li-F salt system. From the initial spent NdFeB magnets of roughly 22wt.% total rare earth element, a metallic alloy of 72.77 wt.% Nd and 23.92 wt.% Pr is successfully produced. The viability of combining three pyro metallurgical methods for the recycling of NdFeB magnets has hence been proved.

References

[1] Trading Economics, Neodymium - 2023 Data - 2012-2022 Historical - 2024 Forecast - Price - Quote - Chart (tradingeconomics.com), Last visited on 15.02.2023

[2] International Energy Agency, The role of critical minerals in clean energy transitions, World Energy Outlook Special Report, Revised in March 2022. https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions , last visited on 15.02.2023

[3] Adamas Intelligence, Rare Earth Magnet Market Outlook to 2035, Published April 2022

[4] E.Kaya, O. Kaya, B.Friedrich & S. Gürmen,(2021) : NdFeB magnets recycling process: An alternative method to produce mixed rare earth oxide from scrap NdFeB magnets, in Metals (Basel), vol. 11, no. 5, pp. 1–13, 2021, doi: 10.3390/met11050716.

[5] Production of NdFeB Magnets. https://www.stanfordmagnets.com/the-production-of-ndfeb-magnets.html, Last visited on 15.02.2023

[6] S. Kruse, K. Raulf, T. Pretz, & B. Friedrich (2017): Influencing Factors on the Melting Characteristics of NdFeB-Based Production Wastes for the Recovery of Rare Earth Compounds, Journal of Sustainable Metallurgy, vol. 3, no. 1, pp. 168–178, 2017, doi: 10.1007/s40831-016-0093-1.

[7] S. Kruse, K. Raulf, A. Trentmann, T. Pretz, & B. Friedrich (2015): Processing of Grinding Slurries Arising from NdFeB Magnet Production, Chem Ing Tech, vol. 87, no. 11, pp. 1589–1598, 2015, doi: 10.1002/cite.201500070.

[8] S. Stopic, H. Chung, B. Polat, E.E. Kaya, S. Smiljanic, S. Gürmen & B.Friedrich (2022) : Recovery of Rare Earth Elements through Spent NdFeB Magnet Oxidation (First Part), Metals (Basel), vol. 12, no. 9, p. 1464, Aug. 2022, doi: 10.3390/met12091464.

[9] H. Tanvar & N. Dhawan (2021): Microwave-Assisted Carbothermic Reduction of Discarded Rare Earth Magnets for Recovery of Neodymium and Iron Values, *JOM*, vol. 73, no. 1, pp. 54–62, Jan. 2021, doi: 10.1007/s11837-020-04409-9

[10] T. Mendiara, A. Jensen, and P. Glarborg (2010): Chemical Looping Reforming of Generator Gas. CHEC Report No. R1001, Department of Chemical and Biochemical Engineering, Technical University of Denmark.

[11] P. S. Ananthanarayanan et al. (2014) Treatise on Process Metallurgy, Volume 3: Industrial Processes, in *Treatise on Process Metallurgy*, S. Seetharaman, Ed. Boston: Elsevier, 2014, pp. xxvii–xxx. doi: https://doi.org/10.1016/B978-0-08-096988-6.09987-9

[12] C. K. Gupta and N. Krishnamurthy (2013): Oxide reduction processes in the preparation of rare-earth metals, Mining, Metallurgy & Exploration 30, 38–44 (2013). https://doi.org/10.1007/BF03402339

[13] V. S. Cvetković, D. Feldhaus, N. M. Vukićević, T. S. Barudžija, B. Friedrich, and J. N. Jovićević (2021): Electrochemical study of Nd and Pr co-deposition onto Mo and W from molten oxyfluorides, *Metals (Basel)*, vol. 11, no. 9, Sep. 2021, doi: 10.3390/met11091494.

[14] V. S. Cvetković, D. Feldhaus, N. M. Vukićević, T. S. Barudžija, B. Friedrich, and J. N. Jovićević, & K. Milicevic Neumann, (2022). Influence of Rare Earth Oxide Concentration on Electrochemical Co-Deposition of Nd and Pr from NdF3-PrF3-LiF Based Melts. Metals - Open Access Metallurgy Journal. 12. 10.3390/met12071204.