

Off-gases emission during the rare earth electrolysis from magnet recycling derived oxides

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In the progressive energy transition process, rare earth elements (REE) became key components in crucial products that play a central role in the development of renewable energy and low-carbon technologies. With China currently producing more than 90 % of the world's REE output, many of the world's economies are facing REE supply risk [1]. To address this problem, many countries need to look for alternative resources of rare earths, e.g. recycling of these elements from REE-containing end-of-life products. A new route for recovery of REE from NdFeB magnet scrap, using a combination of pyrometallurgical treatment of spent NdFeB magnets, and a subsequent molten salt electrolysis process, has been investigated in the authors' laboratory [2]. The magnet recycling derived oxides (MRDO), were produced from spent NdFeB magnets by oxidation in air and subsequent carbothermal reduction under an 80 mbar Ar gas atmosphere. High-temperature molten salt electrolysis was introduced as an option that enables the separation of rare earth elements from fluoride-based molten salts using produced MRDO [3]. One of the challenges in this electrochemical approach for REE electrowinning is effective control of the anode effects to make the electrolytic production of rare earths more environmentally friendly [3,4]. Minimizing the perfluorocarbon compounds emission (PFC), in rare earth electrolysis, should be the primary goal, owing to their high global warming potential [4,5].

In the present work, we investigated the off-gases emissions during the REE electrolysis from NdFeB magnet scrap using in-situ FTIR-spectrometry, in order to understand the formation pathways of CO, CO₂, and perfluorocarbon gases (CF₄ and C₂F₆) made at the anode. The electrolytic extraction of rare earths from fluoride-based molten salts with different contents of MRDO present was performed using molybdenum (Mo) as a cathode, tungsten (W) as a reference electrode, and a glassy carbon (GC) electrode as an anode. It was found that depending on the content of the starting material, the dissolution of MRDO in their corresponding fluoride molten salts most probably induces the formation of different oxyfluoride complexes and their subsequent reactions on the GC anode. The anode reactions in the fluoride-based melts are, most likely, results of either oxide or fluoride formation by exchange with the fluoride or oxide complexes present in the electrolyte. The produced oxygen subsequently reacts with carbon to generate CO and CO₂. With F⁻ present, PFC compounds such as CF₄ and C₂F₆ can also be formed from a GC anode. The anode gas products are composed mainly of CO and CO₂. The average CO₂ concentration was approximately 450 ppm, while CO concentration was around 40 ppm. CF₄ emissions in off-gas products were detected periodically, except for some spikes, and even then, the concentration was below 4 ppm. C₂F₆ was not detected. The results indicate that the electrodeposition of REE within the applied potential range occurs at the expense of their corresponding oxides, provided by MRDO. To develop a more efficient RE recovery process, we opted for a low deposition overpotential to suppress the emission of greenhouse gases and further enhance the control of their emission in rare earth electrolysis.

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References

1. S. Riaño, K. Binnemans, *Green Chem.* **17** (2015) 2931-2942 <https://doi.org/10.1039/C5GC00230C>
2. H. Chung, L. Prasakti, S.R. Stopic, D. Feldhaus, V.S. Cvetković, B. Friedrich, *Metals* **13** (2023) 559 <https://doi.org/10.3390/met13030559>
3. J. Thakare, J. Masud, *J. Electrochem. Soc.* **169** (2022) 023503 <https://doi.org/10.1149/1945-7111/ac4f77>
4. H. Vogel, B. Flerus, F. Stoffner, B. Friedrich, *J. Sustain. Metall.* **3** (2017) 99-107 <https://doi.org/10.1007/s40831-016-0086-0>
5. V.S. Cvetković, D. Feldhaus, N.M. Vukičević, T.S. Barudžija, B. Friedrich, J.N. Jovičević, *Metals* **10** (2020) 57 <https://doi.org/10.3390/met10050576>