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CF₄/C₂F₆ Gases Emissions During Rare Earth Electrolysis

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Rare earth elements (REE) have become vital in our daily life because they are used as a key component in a variety of the advanced technology applications [1]. Large scale REE exploitation is a waste-generating process that causes serious environmental problems and forces industrialised countries to turn to alternative resources for RE, such as recycling of the elements from end-of-life (EOL) products [1]. Fluoride-based molten salts are widely used in the RE molten salt electrolysis (MSE) because of their distinct advantages such as continuous production and short process flow [2]. However, this electrolyte media is associated with the consumption of anode, and emission of greenhouse gases (GHGs), CO/CO₂ and perfluorocarbon gases (PFCs), mainly CF₄ and C₂F₆. Our work in this area has led to the development of a new process for the recovery of REE from EOL magnets. Pyrometallurgical treatment of spent NdFeB magnets was used to produce the magnet recycling derived oxides (MRDO), a REE containing product. The subsequent fluoride-based MSE of the produced MRDO was carried out to recover REE from EOL magnets [2,3]. Continuous monitoring of PFC emissions by in-situ FTIR-spectrometry during the RE recovery from NdFeB EOL magnets by MSE was the main objective of this study. The RE electrolysis from fluoride-based molten salts composed of NdF₃+PrF₃+LiF with MRDO was carried out using molybdenum (Mo) as a cathode, tungsten (W) as a reference electrode, and a glassy carbon (GC) electrode as an anode. The FTIR results show that the anode gas products were composed mainly of CO and CO₂, while CF₄ has been detected before the full anode effect and C₂F₆ at and after this phenomenon. The anode reactions in the fluoride-based melts after the dissolution of RE oxides are most likely the result of the oxide or fluoride complexes formed in the electrolyte, on whose very formation the subsequent reactions at the GC anode depend. The generated oxygen reacts with GC to produce CO and CO₂. Upon fluoride salt dissolution produced F⁻ ions, can also react with GC anode and generate PFC compounds such as CF₄ and C₂F₆. The content of CF₄ during constant potentiostatic electrolysis was on average 0.3 ppm except for spikes that were detected periodically, and then the highest concentration was around 1 ppm, while C₂F₆ was not detected.

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