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Estimating perfluorocarbon emission factors for industrial rare earth metal electrolysis

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ABSTRACT

Rare earth (RE) metals have been widely applied in new materials, leading to their drastic production increase in the last three decades. In the production process featured by the molten-fluoride electrolysis technology, perfluorocarbon (PFC) emissions are significant and therefore deserve full accounting in greenhouse gas (GHG) emission inventories. Yet, in the '*2006 IPCC Guidelines for National Greenhouse Gas Inventories*', no method currently exists to account for PFC emissions from rare earth metal production. This research aims to determine emission factors for industrial rare earth metals production through on-site monitoring and lab analysis of PFC concentrations in the exhaust gases from rare earth metal electrolysis. Continuous FTIR measurements and time-integrated samples (analysed off-site by high-precision Medusa GC–MS) were conducted over 24–60 h periods from three rare earth companies in China, covering production of multiple rare earth metals/alloys including Pr-Nd, La and Dy-Fe. The study confirmed that PFC emissions are generated during electrolysis, typically in the form of CF_4 (~90% wt of detected PFCs), C_2F_6 (~10%) and C_3F_8 (< 1%); trace levels of c-C_4F_8 and C_4F_{10} were also detected. In general, PFC emission factors vary with rare earth metal produced and from one facility to another, ranging from 26.66 to 109.43 g/t-RE for CF_4 emissions, 0.26 to 10.95 g/t-RE for C_2F_6, and 0.03 to 0.27 g/t-RE for C_3F_8. Converted to 211.60 to 847.41 kg CO_2-e/t-RE for total PFCs, this emissions intensity for rare earths electrolysis is of lower (for most RE production) or similar (Dy-Fe production) level of magnitude to industrial aluminium electrolysis.

1. Introduction

1.1. Rare earth metals production & PFC greenhouse gas emissions

'Rare earth metals' typically refer to a set of chemical elements in the periodic table, i.e. the fifteen lanthanides as well as scandium and yttrium. Rare earth (RE) metals have significant applications in new materials which are in wide demand in emerging and advanced industries such as permanent magnets and high-performance electronic devices. Therefore, in the last three decades, production of rare earth metals has soared dramatically. For instance, the global annual production of $Nd_2Fe_{14}B$ permanent magnets have increased from around 1 t in the 1980s to more than 50,000 t in around 2000 (Liu, 2008).

Since the 1990s, rare earth electrolysis using the molten *fluoride*-salt

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system has become the dominant production technology for rare earth metals. This replaced the molten *chloride*-salt system that was prevalent prior to the 1990s but suffered from several limitations, including: low current efficiency, generation of chlorine gas as an environmental pollutant, poor metal quality / purity and other reasons.

The fluoride-based molten salts electrolysis process used today for rare earths production shares many similarities to the process used by the primary aluminium industry. As with aluminium electrolysis, the fluoride electrolysis route for rare earths production has the potential to form perfluorocarbon (PFC) gases, including tetrafluoromethane (CF_4, PFC-14) and hexafluoroethane (C_2F_6, PFC-116), both of which are potent greenhouse gases; octafluoropropane (C_3F_8, PFC-218) is also occasionally reported in aluminium. According to the *Intergovernmental Panel for Climate Change* (IPCC)'s *Fifth Assessment Report* (2013), CF_4 has an extremely long atmospheric lifetime of 50,000 years and a global warming potential (GWP100) of 6630 compared to CO_2 over 100 years, C_2F_6 has a lifetime of 10,000 years and a GWP100 of 11,100, and C_3F_8 has a lifetime of 2600 years and a GWP100 of 8900.

While global production of rare earth metals by molten electrolysis technology is still very low compared to global aluminium production (roughly 0.1% of aluminium in 2013, based on global output of rare-earth oxides versus metallurgical-grade aluminium oxide (U.S. Geological Survey, 2014; International Aluminium Institute (IAI), 2014), it is possible that the resulting volume of greenhouse gas emissions can be comparatively large. Taking neodymium (Nd) metal production by Nd oxide electrolysis for example, it has been estimated by Vogel et al. (2017a) that in a *worst-case scenario*, the off-gases from the process could contain as much as 7% CF_4 and 0.7% C_2F_6. When considering the extremely large GWPs of these PFC gases and global production of roughly 30,000 t/year Nd metal, the rare earths industry could produce as much as 20 million t CO_2-e/year (Vogel et al., 2017a).

If a significant volume of PFC generation from the rare earths industry was confirmed, this would go towards explaining the large discrepancy or 'gap' that has been found between (i) global atmospheric measurements of PFC emissions (a 'top-down' approach for accounting PFCs) and (ii) global 'bottom-up' accounting of PFC emissions from aluminium and semi-conductor industries. Both these industries are currently considered the only major anthropogenic sources of PFCs, with both employing methodologies from the IPCC to account for PFC emissions. Using atmospheric data, Kim et al. (2014) showed that as much as 50% of CF_4 and 48% of C_2F_6 emissions over the 2002–2010 period (5200 t/year CF_4 and 300 t/year C_2F_6, equivalent to 42 million t CO_2-e/year) is being under-estimated or unaccounted for from global industrial sectors.

The potential for large volumes of PFC gas emissions (combined with extremely high GWPs) from the rare earth metal industry implies that it should not be overlooked in terms of mitigating global warming. Therefore, evaluation and calculation of the global warming contribution from the rare earth metal industry is urgently needed. However, in the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (henceforth abbreviated to 2006 IPCC Guidelines) (IPCC, 2006), no guideline exists for the rare earth metal industry. One factor might have been the low proportion of Chinese contributors to the 2006 IPCC Guidelines (only 3.6% of authors and review editors for the entire 2006 IPCC Guidelines and only 1.1% for Volume 3 of the 2006 IPCC Guidelines: 'Industrial Processes & Product Use' (IPPU), where metal industry emissions are described) despite the fact that about 90% of rare earth metals globally are produced in China. Another more likely reason is that the global metal production of rare earths prior to 2006 was too small to consider as a significant contributor to GHG emissions, as already discussed above.

A further critical factor is the fact that to date there is a lack of quality academic research to support a robust guideline for rare earth metal industry, if such a guideline were to be proposed. By contrast, there are numerous academic works and industrial studies on PFC emissions from primary aluminium production (Tabereaux, 1994; Rhoderick et al., 2001; Chase et al., 2005; Zhao et al., 2008; Wong et al., 2015). These have built up a robust foundation for the description of a detailed method for estimating PFC emissions from aluminium production in the 2006 IPCC Guidelines.

As a response to the above, recently a few studies on PFC emissions from the rare earth metals industry have been published. An example is the research conducted by Vogel et al. (2017a) who studied the electrochemistry of the neodymium oxide electrolytic system and the resulting anodic gas emissions. As the goal was to reduce PFC emissions, the paper focused on the interaction mechanism between CO/CO_2 and CF_4 emission concentrations and voltage across the electrochemical cell. With this groundwork, Vogel and Friedrich (2017b) continued the research and concluded that poor control of oxide concentrations of the electrolyte can cause higher PFC emissions. Therefore, a process control strategy similar to that in aluminium electrolysis was proposed to reduce PFCs, with continuous and precise oxide feeding being essential elements.

Vogel and his colleagues' research was conducted under laboratory conditions but mimicked industrial production. Given the variation of production engineering and gas scrubbing, this approach is effective in exploring the fundamental mechanisms of PFC emission but cannot be applied to estimating actual PFC emissions from the rare earth metal production industry. Therefore, Zhang et al. (2018) conducted research which measured continuous PFC emissions in an actual rare earth metal production facility. Zhang's work only focused on the PFC emission from production of Nd metal and Dy-Fe alloy at one rare earth production company. However, there are currently more than ten types of rare earth metals and alloys being produced by electrolysis every year. These include (in order of production output, from greatest to smallest): Pr-Nd, Nd, La, Dy-Fe, Ga-Fe, Ho-Fe, Pr, Ce, La-Ce and Y-Mg (ranking based on production data from major producers, covering 95% of the market). Furthermore, Zhang's data is limited in that it focused only on CF_4 emissions and did not measure other important PFC gases such as C_2F_6 and C_3F_8. Uncertainty analyses were also not provided from the study. Since the time of Zhang's measurements in 2014, there have also been significant improvements made in rare earth electrolysis technologies and in the operations of the process, which are expected to help reduce PFC emissions. Recently, for cleaner production, gas-collection hoods for each electrolytic cell have been applied in some newly established production shops. There was no estimation of gas collection efficiencies of the hooding systems (i.e. emission factors did not take into account any fugitive emissions) in Zhang et al.'s (2018) study, which is a further significant uncertainty in this previous work.

1.2. Aims of this work

In light of the limitations of prior studies and the new developments in rare earth metal production, this paper goes further to measure PFC emissions from the production of Pr-Nd alloy, Dy-Fe alloy and La metal from different electrolytic cell sizes and gas exhaust systems. It aims to provide greater coverage of PFC emissions in the rare earth metal industry so that PFC emission factors for different rare earth metals produced with different technologies can be proposed. The measurement of the PFC emissions was conducted in three typical rare earth companies in Ganzhou, Jiangxi province. These three companies consist of diversified technologies including old and new production shop settings, small and large electrolytic cells, and low and high cell current technologies.

1.3. The fluoride electrolysis process for rare earth metal production

The dominant technology worldwide for primary production of RE metals and alloys is using molten fluoride-salt electrolytic reduction, similar to primary aluminium's Hall-Héroult process. The raw materials for rare earths metal production are in the form of rare earth oxides (REO). In general, REOs are dissolved and electrolytically reduced in a