Gaseous emissions during rare earth electrolysis

Ole S. Kjos, Heiko Gaertner, Karen Osen, Arne P. Ratvik, Ana Maria Martinez, Thor A. Aarhaug

SINTEF Industry, Richard Birkelands vei 2B, 7034 Trondheim, NORWAY

ole.kjos@sintef.no

Abstract

Rare earth metals and alloys are currently produced by electrolysis of rare earth oxides in fluoride melts using carbon anodes. This process has emissions both from the electrolysis itself as well as oxide additions and reactions with ambient air. Understanding and quantifying the gases evolved, related to process conditions, are essential to obtain optimal operation and maintain correct mass balance in the electrolysis process. Furthermore, online gas measurements give valuable information about process kinetics necessary for identifying optimal operational parameters and potential unwanted by-products (waste streams). In addition, emission data must be reported to document compliance with emission permits as well as for greenhouse gas accounting. The comparable electrolysis production of aluminium has for several decades worked with off gas analysis to understand the fundamental gas formation reactions to reduce the GHG footprint per kg metal produced and has achieved significant process improvements.

The main reaction for a generic rare earth (RE) electrolysis reaction is:

$$2\ RE_2O_3 + 3\ C \rightarrow 4\ RE + 2\ CO_2(g) \qquad (1)$$

While some examples of formation of undesired gases

$$2\ REF_3 + 3\ H_2O \rightarrow RE_2O_3 + 6\ HF(g) \qquad (2)$$

$$4\ REF_3 + 3\ C \rightarrow 4\ RE + 3\ CF_4(g) \qquad (3)$$

Based on reaction (1) no other gases than CO_2, or possibly CO needs to be evolved to produce the RE metals. Evolution of CO_2, a well-known greenhouse gas (GHG), is unavoidable to a certain extent as defined by the reaction stoichiometry. However, products from side reactions such as CF_4 evolution, reaction (2), are a result of oxide depletion at the anode surface and can theoretically be completely avoided with proper cell operations and good control of the oxide feeding. Formation of unnecessary CF_4 with a very high global warming potential (GWP) 7350 higher than CO_2 is highly unwanted.

GHG emissions from RE electrolysis requires national reporting as described in the 2019 refinement of the IPCC (Intergovernmental Panel on Climate Change) guidelines [1] and even very low CF_4 emissions will strongly affect the overall global warming footprint due to its high GWP. CF_4 formation can also result in temperature imbalance in the electrolysis cell mainly due to increased anodic overvoltage, and hence increased cell voltage.

Another fluoride loss mechanism is the formation of hydrogen fluoride gas (HF). HF will be generated according to reaction (3) when water or moisture get in contact with the electrolyte. Water can enter the electrolysis cell as adsorbed water on the oxide feed or as water vapour in the air. Although the HF gas is not part of the GHG inventory it is a highly toxic gas with 15 minutes Indicative Occupational Exposure Limit Values (IOLEV) at 3 ppm and 8 hours IOLEV at 1.8 ppm. Emissions of HF from plants are also strictly regulated, however with proper gas treatment and sufficient gas extraction from the electrolysis process it is possible to secure a good working environment together with low plant emissions.

Formation of any fluorine containing gas species will also result in a depletion of fluoride from the electrolyte, resulting in a chemical imbalance that could in worst case lead to partial bath solidification. To mitigate this all fluoride losses are compensated by additions of expensive rare earth fluorides to keep the electrolyte chemistry constant.

The concentration of CO/CO_2, CF_4 and HF in the off gas during RE electrolysis were recorded with a FTIR gas analyser and tuneable diode HF lasers, respectively. Measurements have been done both in the laboratory and in pilot scale production.

The results show that the formation of CF_4 can have a huge impact on the total CO_2 equivalents per kg metal, with an increase of more than 100 % in CO_2 equivalent emissions compared to the theoretical emissions required for the metal production if only CO_2 is produced. Furthermore, it is also proven that electrolysis of RE metals can be carried out for long periods without any CF_4 emissions. Efficient oxide feeding strategies, aided by online gas measurements to provide information on cell performance, are important to eliminate CF_4 emissions. Current measurements demonstrate the feasibility to operate the electrolysis process without any CF_4 evolution.

HF evolution, on the other hand, is more or less impossible to avoid and has to be captured by gas scrubbing. Fortunately, commercial solutions for cleaning the gas exists and measurements in a pilot facility with an industrial pilot electrolysis cell *demonstrated that commercial gas treatment technology can cut HF emissions by 98 %, bringing them down below acceptable permit levels for emissions in Europe.*

This work has shown how gas measurement methodologies can be used to obtain process events and gas response correlations and how the gas monitoring can be used for process optimisations

References

1. 2019 refinement to the 2006 IPCC guidelines for National Greenhouse Gas Inventories, INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE, 2019, https://www.ipcc-nggip.iges.or.jp/public/2019rf/index.html

Acknowledgement.

This work has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 776559