Rare Earth Electrolysis: key issues for measurement of greenhouse gases from oxide-fluoride systems

Sandra Harumi Fukurozaki (✉ sharumi@alumni.usp.br)

National Institute for Science and Technology - Rare Earth Magnets Processing and Applications for High-Tech Industry https://orcid.org/0000-0001-5861-7538

Fernando José Gomes Landgraf

Department of Metallurgical and Materials Engineering; Polytechnic School, University of São Paulo https://orcid.org/0000-0001-5390-0879

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Abstract

Over the past decade, the reduction of greenhouse gases (GHG) has been recognized as one of the key factors for sustainable primary metal production, in which the rare earth (RE) industry can be affected both in terms of price and use by GHG reduction policies and non-tariff technical barriers. From environmental and economic standpoint, the perfluorocarbons (PFC) emissions generated in RE electrolysis during events known as anode effects (AE) are strong infrared-absorbing GHG and play an important role for RE metals process improvements. However, there is no standard methodology to account these GHG emissions from RE metal production industry and the assessment of the contribution of PFC emissions from different technologies to the global warming is urgently needed. This paper focuses on the analysis of PFC measurements from RE metal production in terms of GHG inventory and sustainable production. The state of art of RE fused oxide-fluoride electrolysis, particularly of neodymium electrolysis, provides the technical fundamentals for the evaluation of PFC emissions factors reported in scientific articles. Based on International Panel on Climate Change (IPCC) standard methods and US Environmental Protection Agency (EPA) and International Aluminium Institute (IAI) protocol applied to analogous industrial process, the analysis of key issues for estimate CF_4 and C_2F_6 emission factors from electrolytic RE production indicates the additional refinements are necessary to optimize the accuracy of total PFC emission amount from each currently RE technology. Additionally, the selection of emission estimation technique (EET) or mix EET should be considered on case-by-case basis as to their purposes and suitability for a particular process and facility. Finally, this paper highlights the technological implications related to the PFC emissions measurements and trends towards to set goals and develop strategies for GHG mitigation.

1. Introduction

Rare earth elements (REE) are recognized as essential transition resources for high-tech industries and have attracted worldwide attention from countless productive sectors. The unique qualities of REE, such as chemical stability, excellent thermal conductivity, high ductility and corrosion resistance, have made these metals an important material in many of the modern renewable energy, transportation, communication, medical and alloy industries, structural steel, among others [1, 2].

On the other hand, the advance of urbanization and the construction of new structures, the electronics use and the change to cutting-edge and low-carbon technologies impose, in addition to a continuous demand, a series of technological challenges when this issue is associated with a sustainable primary metals production [1, 3], especially in relation to the REE.

Nowadays, fused salt electrolysis has been used on a large scale for the industrial production of RE metals (lanthanum, cerium, praseodymium, neodymium, dysprosium) and their alloys (Nd-Pr, Pr-Nd-Dy, Dy, Nd-F, among others) in which the oxides-fluorides electrolysis became the main manufacturing method and China the world producer, consumer and major exporter [4].

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However, even in the face of several technical and economic advances achieved in the production of RE metals, over more than 80 years of exploration and practice in the Chinese industry, still persist problems related to high energy consumption and air pollution. Given the different types of RE and their respective alloys, on average energy consumption is approximately 10 kWh/kg and the fluorine-containing compounds gas emission factor is 0.03 kg/kg [5].

Fluorine-containing compounds, specifically perfluorocarbons (PFC) - CF_4, C_2F_6 and C_3F_8 are emitted during the RE metals production and from processes that range from the semiconductors industry to the primary aluminum production. The PFC is considered one of the major greenhouse gas (GHG) due their high global warming potentials (GWP), even at a few parts per trillion, and long atmospheric lifetimes [6].

Although concentrations of PFC in the atmosphere were near zero a few decades ago, including other halogenated gases that not natural abundances have been found and natural abundances have been assumed to be insignificant [7], these gases have increased rapidly as they have been incorporated into a variety industrial process and commercial and household uses. When PFC is counted in terms of CO_2 eq, the GWP values are thousands to ten thousands higher [6, 7].

As a result of the high potentials for long-term impacts in relation to climate change, international efforts have been made to reduce emissions not only from PFC, but also from hydrofluorocarbons (HFC) and sulfur hexafluoride (SF_6) [8]. Initiatives in the aluminium and semiconductor industries have conducted several researches and technical studies in order to mitigating PFC emissions and concomitantly, improving the efficiency of control systems and gases treatment in the production process [9].

Additionally, Mancheri et.al [10] outlines that new policies with stricter environmental standards, illegal mine closure and comparatively high cost of importing concentrates around the world, reduce the advantages of China with low production costs and low prices of REE for domestic industries at upstream of the RE supply chain. That is to say, the rational use of resources can certainly affect the capital expenditure (CAPEX) and operational expenditure (OPEX) of these companies in the long term and promote the use of more efficient technologies with less environmental impact [11].

Besides, over the last decade, the number of disputes over actions, or inaction, related to climate mitigation and adaptation efforts have grown in importance. As of July 2020 climate change cases have been filed in 38 countries, with at least 1550 litigations. These cases are forcing greater climate disclosures, ending greenwashing on the subject of climate change and energy transition. Moreover, the laws codifying national and international responses to climate change have recognized new rights and created new duties, compelling governments and corporate actors to purse more ambitious climate change mitigation and adaptation actions [12].

Therefore, the development of new equipment and techniques, associated with energy conservation and environmental protection represents an inevitable path for the improvement of RE metals industry [5]. As cleaner production technologies and recycling processes are achieved, the importance of international ...ted. Indeed, in 2015, the International

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Organization for Standardization (ISO) established a Technical Committee (ISO/TC 298) of RE, composed of 34 countries and, so far, 5 working groups [13].

In this way, Chinese companies have been strongly incited to deploy significant work to reduce the energy consumption and emissions from the RE fused salt electrolysis, in addition to accomplish the environmental, occupational health and safety compliances. From this perspective, this paper analyses the PFC emissions measurements and their role in the production processes improvements of RE metals and sustainable production, with emphasis on the neodymium (Nd) electrolysis oxide-fluoride system and GHG inventory.

The first section presents the state of art of the metallic Nd production, considering the main technical aspects of RE electrolysis, as well as the analysis of the emissions reported from previous publications. Then, is discussed the International Panel on Climate Change (IPCC) methods [14] and US Environmental Protection Agency (EPA) and International Aluminium Institute (IAI) protocols [15] for quantifying PFC gases applied in the primary aluminum industry, known as analogous process for RE electrolysis. Finally, the last section emphasized, vis-à-vis standard methodologies, the key issues for measurement of emission factors from the RE metal and their alloys production and indicates the trends for evaluating and reducing GHG emissions.

2. State-of-art

2.1. Fused oxide-fluoride electrolysis

Like other elements of RE, neodymium (Nd) is transformed into metal by the oxide-fluoride electrolysis into a fused salt electrolyte [5, 16, 17]. Usually, Nd oxides are dissolved in an anhydrous electrolyte of Nd fluorides and Li fluorides (LiF) to improve electrical conductivity and increase the fluidity. The electrolyte is maintained in the range of 800 ^{o}C to 1100 ^{o}C and is initially melted by resistance heating. Both the electrolyte and the deposited metal can be kept liquid by the joule effect [18, 19].
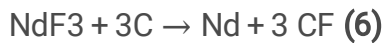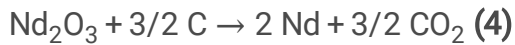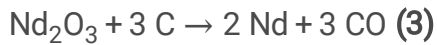
On an industrial scale, the electrolytic cell (or furnace) operates in atmospheric conditions with current densities of $\approx$ 6.5 A/cm^2 at the anode and $\approx$ 1 A/cm^2 at the cathode; features graphite or molybdenum crucible, graphite anodes, molybdenum (Mo) or tungsten (W) cathode and voltage conductive plates (Fig. 1). The cell is externally lined with layers of insulating refractory materials and austenitic stainless steel. A potline is composed of a set of cells electrically connected in series, normally installed in buildings named potroom.

When Nd is prepared, carbon can be used in the anode and cathode. In the case of Nd alloys (e.g. NdFe), graphite electrodes are used at the anode and Fe (including steel and low carbon steel) at the cathode. In other words, if the desired product is metallic Nd, only the anode is the consumable electrode. On the other side, when the NdFe alloy is prepared both electrodes are consumed in the process.

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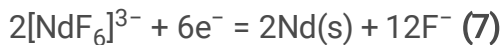
Particularly in relation to the consumption of the C anode, oxygen is released on the electrode surface and converted to carbon oxides (reactions 1 and 2), namely CO and CO_2. These two gases also react electrochemically with the cathode. Usually, the reaction occurs in a three-phase interface (solid, liquid and gas), formed by the cathode, the electrolyte and the gas [20].

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad \textbf{(1)}$$

$$C + O^{2-} \rightarrow CO + 2e^- \quad \textbf{(2)}$$

Several studies on the fused salts electrolysis using halogenated RE compounds (oxide-chlorides and oxide-fluorides) have been reported in the literature in last decades [16, 17, 21, and 22]. Comparatively, the Nd electrodeposition from oxide-fluorides is considered more attractive for mass metal production in which the possible decomposition reactions of the oxides-fluorides can be simplified as follows:

$$Nd_2O_3 + 3\ C \rightarrow 2\ Nd + 3\ CO \quad \textbf{(3)}$$

$$Nd_2O_3 + 3/2\ C \rightarrow 2\ Nd + 3/2\ CO_2 \quad \textbf{(4)}$$

$$NdF_3 + 3/2C \rightarrow Nd + 3/2\ CF_2 \quad \textbf{(5)}$$

$$NdF3 + 3C \rightarrow Nd + 3\ CF \quad \textbf{(6)}$$

According to Stefanidaki et. al. [16], in fused $LiF - Nd_2O_3 - NdF3$ systems, the neodymium metal is probably produced by the electro-reduction of Nd fluorides in the cathode, while in the anode occurs oxidation of Nd oxyfluorides generating oxygen (Fig. 2) conforming to the following reactions (7) and (8):

$$2[NdF_6]^{3-} + 6e^- = 2Nd(s) + 12F^- \quad \textbf{(7)}$$

$$3[NdOF_5]^{4-} + 6e^- = 3/2O_2\ (g) + 3Nd^{3+} + 15F^- \quad \textbf{(8)}$$

[Fig. 2− Schematic diagram of partial electrochemical reactions of the Nd electrolysis under smooth operation]

Despite numerous physicochemical and electrochemical properties of the oxide-fluoride electrolysis process have been extensively studied, still remains the challenge for address environmental and economic burdens which significantly reduce the so-called anodic effects (AE) that interfere in the operation of the cell and consequently, to a rise in emissions of fluorine-containing compounds [23].

AE are manifested by the increase in voltage (V) of the electrolytic cell and if a power system with limited voltage supply is used, also by the decrease in amperage (A). The rise in voltage (overvoltage) can lead to an overheating of the electrolytic cell, which in turn, promotes greater metallic Nd solubility and to excessive interactions of the metal with the electrolyte elements. These occurrences prevent a smooth electrolytic operation and promote the formation of non-metallic deposits (or similar to the slag) in the

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cathodes and other parts of the cell [20], in addition to increasing energy consumption and decreasing the current efficiency (CE).

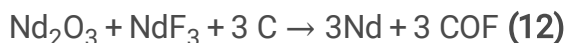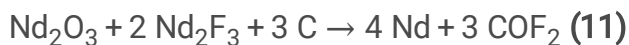## 2.2. Anode effects and PFC emissions

One of the main process parameters related to AE is the oxides concentration in the electrolyte, in which the overvoltage can result from the oxides deprivation in a given region of the cell. In the electrolysis of Nd oxide-fluorides, high levels of oxides in the electrolytic cell produce the precipitation of oxyfluorides elements that cannot be reduced [18], while low levels result in a decrease in electrical conductivity. In this way, the transport of electrical charges is no longer supported by the standard (theoretical) reaction of Nd_2O_3 electrolysis.

Moreover, in the study conducted by Dorren et al. [24], during the electrolysis of molten salts, a resistive C-F film formed on the anode surface can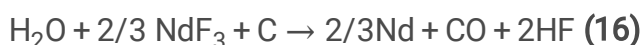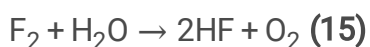 be decomposed to form the PFC gases (reactions 5 and 6). Measured data reported in the literature on RE electrolysis indicate that in the occurrence of AE, the gases CF_4 and C_2F_6 are released [25, 26]. The emissions of CF_4 and C_2F_6 can be generated from the following reactions:

$NdF_3 + 3/4C \rightarrow Nd + 3/4\ CF_4$ **(9)**

$NdF_3 + 3/4C \rightarrow Nd + 1/2\ C_2F_6$ **(10)**
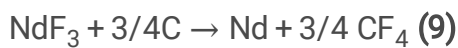
PFC can also be formed electrochemically by forming COF_2 and COF (reactions 11 and 12) which are unstable and react spontaneously with C to form CF_4 and CO (reactions 13 and 14) [4, 25, 26], according to the reactions presented below:

$Nd_2O_3 + 2\ Nd_2F_3 + 3\ C \rightarrow 4\ Nd + 3\ COF_2$ **(11)**

$Nd_2O_3 + NdF_3 + 3\ C \rightarrow 3Nd + 3\ COF$ **(12)**

$2COF_{2\ +}\ C \rightarrow CF_4 + 2\ CO$ **(13)**

$4COF + C \rightarrow CF_4 + 4\ CO$ **(14)**

In addition, depending on the replacement rate of $LiF-NdF_3-Nd_2O_3$ and the Nd_2O_3 solubility in the electrolyte, other fluorine emissions occur. Under conditions of positive oxidizing atmosphere, the F reacts with the water contained in the cell forming HF (reaction 15) [18, 27]. The theoretical decomposition of Nd fluoride and H_2O producing HF [17] is presented (reaction 16) below:

$F_2 + H_2O \rightarrow 2HF + O_2$ **(15)**

$H_2O + 2/3\ NdF_3 + C \rightarrow 2/3Nd + CO + 2HF$ **(16)**

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Recently, analyzes conducted on a laboratory and industrial scale have indicated that the generation of PFC can also take place at low voltage [4, 25, 26]. This particular process, known as low voltage AE (LV-AE) or partial AE (P-AE) or smooth AE (S-AE), can happen over a long period of time, with little or no indication of interference in the metal deposition and a marked increase in the voltage of the electrolytic cell.

The LV-AE is analogous to that seen in recent years in the Hall Heroult process, in which the LV-AE of aluminum primary production occurs through the same fundamental mechanisms as conventional AE. However, one of the main differences regarding AE is related to the probability of how and when LV-AE is propagated within the cell [28, 29].

Another category of AE, discussed in the literature (mostly in the aluminum industry) are the so-called no propagating AE (NP-AE), these refer to the slow movement of PFC levels in the background which in terms of magnitude are much smaller when compared to the PFC peaks resulting from AE and LV-AE [28].

Nonetheless, in the investigation carried out by Vogel et.al. [25] the presence of NP-AE during the continuous monitoring of the outlet gases can be noted in the electrolysis of fused Nd salts (Fig. 3).

[Fig. 3 – Continuous off-gas measurement showing AE, LV-AE e NP-AE and related CO, CO_2 and CF_4 emissions (adapted from Ref. [25].]

In summary, the emission of PFC is inherent to the process and their rate can be highly variable, depending on the concentration of oxides, current density of the anode and the occurrence of AE. All of these parameters are interrelated and will dictate whether eventually the LV-AE will exceed the limit of the voltage required to generate AE [30]. Usually, PFC concentrations rise during conventional AE and rapidly, depending on the production control system and technology, decrease to atmospheric levels when this effect ceases [31, 32].

2.3 Laboratory and industrial accounting of PFC emissions and GWP

In response to the requirements for a sustainable metals management concerning their technical bases for process improvements, i.e. set goals and develop strategies for reducing GHG contributions from RE metals production to the global warming and climate change, Vogel and Friedrich [17, 32], Zhang et. al. [31], Cai et. al. [4], Kjos et. al. [26] carried out analyzes of PFC emissions on a laboratory and industrial scale.

The figures below shows the emission factors of CF_4 and C_2F_6 in kg per RE kg metal and alloy produced by fused salt electrolysis reported in the published literature and respective CO_{2eq} emissions over time horizon of 20 years (Figs. 4 and 5) and time horizon of 100 years (Figs. 6 and 7). In the figures, the number of cell technology (CT) is related to the production of: Nd (1, 2, and 3); Nd-Pr (4, 5, and 6); Dy-Fe (7, 8) and La (9, 10).

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The emission factor of both PFC are estimated based on: the operation of electrolytic cell under laboratory conditions (CT: 1); measurements at production site (CT: 2, 3, 6, 7, 9); time integrated and laboratory analysis (CT: 4, 5, 8, 10). The reference studies for CT: 1 [17]; 2, 3, 7 [31] and 4, 5, 6, 8, 9, 10 [4].

The colormap represents the intensity (quantity) of the respective PFC emissions converted into CO_{2eq} (kg/RE kg) according to the metric values updated in IPCC Fifth Assessment Report (AR5), as result of new scientific knowledge and also due to the changes in lifetimes and radiative efficiency (RE) caused by changing atmospheric background conditions [33]. The values of global warming potential (GWP) relative to CO_{2eq} used for CF_4 and C_2F_6 are given in the Table 1.

Table 1
Lifetimes and global warming potentials of CF_4 and C_2F_6

Chemical Formula	Industrial Designation or Common Name	Lifetime[(1)] (years)	Global Warming Potential (GWP)	
			20 years horizon [(2)]	100 years horizon [(2)]
CF_4	PFC – 14	50000	4954	7349
C_2F_6	PFC – 116	10000	8344	12340
(1) IPCC Fourth Assessment Report – AR4 [6]				
(2) IPCC Fifth Assessment Report – AR5 [33]				

[Fig. 4 – CF_4 emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 20 year.].

[Fig. 5 – C_2F_6 emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 20 year.].

[Fig. 6 – CF_4 emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 100 year.].

[Fig. 7 – C_2F_6 emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 100 year.].

[Table 1. Lifetime and global warming potentials of CF_4 and C_2F_6]

Take into account the technical operation indicators, the differences between the emissions factors and the same RE metal, e.g. kg CF_4 per kg Nd (from 9.50E-03 kg/kg to 7.39E-02 kg/kg), can be initially

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explained by the technological conditions of production of each RE metal and the methods applied for measurement the air streams from the fused oxide-fluoride system.

In the context of climate change, a critical issue regarding to the PFC emissions in the electrolysis of Nd oxide-fluorides, including other RE metals and their alloys, is the absence of standard methods or protocols for measuring the emission factors of these gases, similar to the emission inventories applied in the primary aluminum industry, which allows an reliable evaluation of CO_2 equivalent emissions from the RE metal and alloys production.

Generally, industries and government have used GHG inventories to support benchmarking and process improvement initiatives in which the development of strategies to mitigate PFC emissions in industrial units is perceived as the basis for a well-formulated processes improvement plan. Under the umbrella of United Nations Framework Convention on Climate Change, the measurements of PFC enables creation of more accurate inventory through use of facility specific emissions factors rather than default uses [15].

Inventories of PFC emissions are also important for several market mechanisms of Kyoto Protocol, including emissions trading, Clean Development Mechanism (CDM) and Joint Implementation (JI). Precise and verifiable emissions reductions are required to participate in the sale of credits generated under these programs. That is, accepted and validated measurements procedures are important to verify reductions and facilitate trading [15].

3. Ipcc Standard Methodology For Quantifying Pfc Emissions

In the primary aluminum industry, three methods established by the IPCC 2006 Guidelines for National Greenhouse Inventories are used to quantify PFC emissions [14]. The IPCC Tier 1 method comprises the estimation of PFC emissions from the smelter by the multiplication of the annual metal production with a given coefficient based on the technological class used, namely: Center Worked Prebake (CWPB), Side Worked Prebaked (SVPB), Vertical Stud Soderberg (VSS) and Horizontal Stud Soderberg (HSS). This method is applied in industries where there is no system for monitoring and recording AEs and is less accurate than the IPCC Tier 2 and 3 methods.

The IPCC Tier 2 and 3 methods, involve the statistical analysis of conventional AE (frequency - AEF and duration - AED) and emissions coefficients (CF_4 slope coefficient and mass ratio of C_2F_6 emissions in relation to CF_4). In general, calculations are carried out on the monthly average data and then summed to obtain an annual issue. The emission factors of CF_4 and C_2F_6 can be calculated using specific coefficients of the technology employed (Tier 2) and/or direct measurements performed at the smelter (Tier 3) [14].

The IPCC Tier 3 is applied to define a long-term relationship between the measured emissions and the operating parameters and to verify the correlation of the AE and the production levels. This method is recognized for presenting highest precision for building an inventory of PFC emissions and provides two

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models for quantifying the gases: slope and overvoltage. The slope is a parameter in which, when multiplied by the minutes of AE per cell/day, it results in an industry-specific CF_4 emission factor (Eq. 1):

$$EF_{CF4} = S_{CF4} * AEM * MP$$

1

Where:

EF_{CF4}: CF_4 emission factor (kg /t)

S_{CF4}: slope emission coefficient (kg CF_4/t) / (AE min/cells/d)

AEM: anode effect minutes per cell-day (AE min/cells/ d)

MP: metal production (t)

In the case of companies with AEO (anode effect overvoltage) control systems but without AEF and AED registration, the calculation method used includes data on excess voltage in relation to normal operating conditions, according to Eq. (2):

$$EF_{CF4} = \frac{OVC*AEO}{CE}$$

2

Where:

EF_{CF4}: CF_4 emission factor (kg /t)

OVC: overvoltage emission coefficient (kg CF_4/t/mV)

AEO: anode effect overvoltage (mV)

CE: current efficiency (%)

While the C_2F_6 emission factor can be estimated as the mass ratio of the CF_4 emission factor as show in Eq. (3):

$$EF_{C2F6} = EF_{CF4} * F_{C2F6}$$

3

Where:

EF_{C2F6}: emission factor (kg C_2F_6/t)

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EF_{CF4}: CF_4 emission factor (kg /t)

F_{C2F6}: C_2F_6 mass ratio of CF_4 emission factor (kg C_2F_6/kg CF_4)

Whether using the slope method or overvoltage method, the C_2F_6 emission factor is determined from individual facility-specific measurements or from average of measurements factors from a number of facilities operating with similar technology. According to Dion et. al. [30], since the TIER 3 methods are based on the average performance of a given industry, the respective coefficients S_{CF4} or OVC $_{CF4}$ and the EF_{C2F6} need to be periodically redefined through continuous measurement campaigns in order to avoid large deviations from the PFC values.

In 2008, a joint initiative by the US EPA, Voluntary Aluminium Industry Partnership (VAIP) and IAI developed a CF_4 and C_2F_6 Measurement Protocol for the primary aluminum industry that incorporates a significant number of updates to the Tier 3 method in relation to the data required for analysis, including methodological improvements in the collection and quantitative measurement of primary and secondary PFC emissions flows [15].

3.1 Measurement of CF_4 and C_2F_6 emissions based on EPA and IAI Protocol

In the EPA and IAI protocol, two alternatives are given for the measurement and calculation of emissions of CF_4 and C_2F_6 per kg of metal, there are: 1) measurements of PFC carried out based on sampling using stainless steel bags or cylinders and 2) measurements conducted directly on the production site. In both, the slope and overvoltage coefficients and the mass ratio of C_2F_6/CF_4 can be evaluated. The recommended calculation procedures for the analysis of PFC emissions include information on how to measure:

- The gas flows from the cells exhaust ducts and the potroom area, weighting the speed, temperature, pressure, as well as the sectional area of the duct;
- The total emissions of CF_4 and C_2F_6 per minute of AE and sampling time (ST);
- The mass ratio or weight ratio of C_2F_6/CF_4;
- The total metal production as a function of ST;
- Calculation of PFC gases from secondary emissions in relation to ST;
- The secondary emissions and the adjustment of the quantity of CF_4 and C_2F_6 issued;
- The total emission factor of each PFC;
- The slope CF_4 emission coefficient and the CF_4 emission coefficient in overvoltage.

While primary (exhaust ducts) and secondary (fugitive) PFC emissions are analyzed based on sampling bags or onto sorbent columns and the exhaust gas collection efficiency (GC), the emission factors of the

CF_4 and C_2F_6 gases are calculated by the following simplified Eq. (4):

$$EF_{PFC} = \frac{E * M * F * T}{10^3 * MV * GC * \sum metal}$$

4

Where:

EF_{PFC}: CF_4 emission factor (kg/t/d)

E: average CF_4 concentration ppm by volume at sampling points (μICF_4/l/Nm^3/μICF_4)

M = mass in kg per mol of CF_4 (0.088 kg/mol)

F: total gas flow at each sampling point (Nm^3/h)

T = sampling time (h/d)

MV = molar volume (22.4 l/mol)

GC: gas collection efficiency (%)

$\sum_{Metal}$: total metal produced over the sampling time (t/d *n° cells/d)

It is worthwhile to mention that the total amount of PFC (either CF_4 or C_2F_6 emissions) is the sum of each PFC emitted as primary and as secondary. The fugitive PFC can be calculated based on gas collection efficiency as a fraction of the total PFC emissions, according to the Eq. (5):

$$PFC_{fugitive} = \frac{PFC_{duct} * F_{fugitive}}{1 - F_{fugitive}}$$

5

Where:

$PFC_{fugitive}$: PFC emitted as fugitive emissions (kg)

PFC_{duct}: PFC emission measured in the duct by the instruments (kg)

$F_{fugitive}$: fraction of fugitive emissions based on gas collection efficiency (%)

As long as the gas collection efficiency (GC) is greater than 90%, the total of PFC gases can be divided by GC as indicated in the Eq. (4). Otherwise, if the GC is less than 90% and the PFC fugitive emissions are measured by direct open path FTIR spectrometry by the time average bag method or other methods

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shown to be capable of measuring the PFC emissions (both CF_4 and C_2F_6), the fraction of PFC emissions emitted as fugitive is calculate as follows (Eq. (6):

$$F_{fugitive} = \frac{PFC_{fugitive}}{PFC_{fugitive} + PFC_{duct}}$$

6

Where:

$F_{fugitive}$: fraction of PFC emitted as fugitive (kg)

$PFC_{fugitive}$: average PFC emitted measured as fugitive by total AE for the fugitive sampling time ($kgCF_4$/ AE min)

PFC_{duct}: total PFC emitted by total AE (potroom) for the duct sampling time (kg CF_4/ AE min)

Then, the total PFC emission is adjusted to include fugitive emissions, estimated based on GC or measured by equipment, as shown in the Eq. (7):

$$PFC_{total} = \frac{PFC_{duct}}{1 - F_{fugitive}}$$

7

Where:

PFC_{total}: total PFC emissions (kg)

PFC_{duct}: PFC emission measured in the duct by the instruments (kg)

$F_{fugitive}$: fraction of fugitive emissions based on gas collection efficiency (%) or measured by equipment (kg)

It should be noted that since the fugitive emissions are measured, the Eq. (4) must be adjusted in order to calculate PFC emission factor without the variable GC, avoiding underestimation and outsized uncertainty. The same procedure given by the Eq. (4), (5) or (6) and (7) can be applied for the quantification of the C_2F_6 emission factor, but replacing the value of the variable M of the Eq. (4) with the corresponding number in kg per mol of C_2F_6 (0.138).

The slope and overvoltage emission coefficients presented before in the Eqs. (1) and (2) are calculated according to the Eqs. (8) and (9) below:

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$$S_{CF4} = \frac{EF_{CF4}}{\sum AE}$$

8

Where:

S_{CF4}: slope coefficient (kg CF_4/t)

EF_{CF4}: CF_4 emission factor (kg /t)

$\sum AE$: total AE min/cell/d over the sampling time

$$OVC_{CF4} = EF_{CF4} * \frac{CE}{AEO}$$

9

Where:

OVC: overvoltage emission coefficient (kg CF4/t/mV)

EF_{CF4}: CF_4 emission factor (kg CF4/t)

AEO: overvoltage for specific cells over the sampling time (mV)

CE: current efficiency (%)

Regardless of whether fugitive PFC emissions are estimated based on GC or measured by the equipment, the uncertainty values associated with the results achieved must be computed to indicate the uncertainty coefficient of the Tier 3 method application. One statistical approach estimates uncertainties by using error propagation equation [15, 34]. The approximation is used to combine emission factor, activity data and other estimation parameter ranges by categories and GHG (Eq. 10):

$$\bigcup total = \sqrt{U_1^2 + U_2^2 + \cdots + U_n^2}$$

10

Where:

U_{total}: the percentage uncertainty in the product of the quantities that are added (%).

U_i^2 : the percentage uncertainties associated with each of the quantities, e.g. metal production, instrument measurement, duct flow rate, etc. (%).

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Under typical circumstances, the approximate of all random variables is accurate as long as the coefficient variation is less than 0.3. Where uncertain quantities are be combined by addition or subtraction, a simple equation can be derived for the uncertainty of the sum, expressed in percentage terms (Eq. 11):

$$U_{total} = \sqrt{\frac{\left(U_{1}.X_{1}\right)^{2} + \left(U_{2}.X_{2}\right)^{2} + \cdots + \left(U_{n}.X_{n}\right)^{2}}{|X_{1} + X_{2} + ...X_{n}|}}$$

11

Where:

U_{total}: the percentage uncertainty in the sum of the quantities that are added (%). This term uncertainty is based upon 95 percent confidence interval.

U_i and x_i: the percentage uncertainties and uncertain quantities associated with them, respectively (%).

From the perspective of applying the PFC measurement protocol (Tier 3) proposed by the EPA & IAI, it is emphasized that the current technologies in the primary aluminum industry present gas collection efficiency between 80 to $\geq$ 97%. That is, the PFC emissions that are not collected directly from the cell's exhaust duct and escape into the environment often vary from 3% to a maximum of 20%, depending on the technology [15].

4. Results And Discussions

4.1. Key issues for evaluating of PFC emissions from RE metal production

Face the standard methods applied in the primary aluminium and the published PFC emission results from the RE metals electrolysis process, the analysis of PFC emission factors requires exceptional attention to some methodological aspects underlined here, namely: 1) the AE data correlation with the emissions measured in the exhaust ducts and fugitive emissions, 2) analysis of emissions in the background, 3) evaluation of the flow homogeneity in the ducts system for collecting the gases from the cell and releasing to the atmosphere, as well as sampling time.

The proper correlation of the AE data with the measured PFC emissions presupposes the statistical analysis of the conventional AE monitored on the potline by the production control systems. This allows determining the conditions considered normal or stable operation of the potline and the process parameters (e.g. percentage of AE manual termination, cell control and feeding strategy) that can affect the Tier 3 coefficients during the measurements.

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Additionally, there are transient circumstances, e.g. startup of a new cell and restart of the potline due to the replacement of cells or their components (except exchange of anodes), power outages and testing of raw material that do not characterize the process routine of the RE production. Thus, care must be taken to ensure that AE measurements are representative and to proper account the PFC emissions and any reduction in collection efficiency.

On the other hand, background sampling aims to identify all interference that may occur in the analyte signal coming from locations close to the potroom or industrial site. The levels of background emissions of CF_4 and C_2F_6 must be insignificant when comparing the average concentrations of the primary and secondary emissions. Interference in the analyte signal can be observed in the study by Zhang et.al [31], in which the C_2F_6 emissions data resulted in negative values, after deducting the emissions in the background (see Figs. 5 and 7).

Regarding to the flow homogeneity, the evaluation of this variable aims to avoid measurement errors that can be caused due to the sampling points and concentration of the gases. Experiences in the aluminum industry have indicated that PFC concentrations diverge across the sectional area of the duct, as the gas flows collected from the cell by the exhaust system can remain segregated for a certain distance even after being merging [15].

Commonly, homogeneity is tested by injecting a small constant flow of a tracer gas into the exhaust duct of one of the reduction cells, which is subsequently monitored at five points, equally spaced along the duct sectional area. For an adequate definition of the sampling point, the concentration of this gas cannot vary by more than 10% at any candidate sampling point. This is particular important for the definition of the emission coefficient in overvoltage and the weight ratio of C_2F_6/CF_4. In either case, the measurement requires a minimum of 72 hours of gas collection and the inclusion of normal productive operation cycles, e.g. electrode changes, among others [15].

An indication of significant variation in homogeneity in the gas flow can be observed in the experiments conducted by Kjos and collaborators [26], in which the gases produced by electrolytic cells used for the production of various RE alloys resulted in values of CF_4 extremely high and above the capacity of the measuring equipment, even operating without signal from conventional AE. Thus, the homogeneity and the sampling point aims to determine a value of the emission coefficient reliable and conforming to the cycles of the production process.

The tracer gas can also be used to analyze the flow volumetric rate (velocity in Nm^3/min) from the duct upstream of the sampling point [35]. This method is particularly advantageous as it allows the evaluation of short-term variations in the duct flow and when the measuring instruments can quantify the tracer gas and the PFC simultaneously. The tracer compound is selected based on knowledge of the process and must be stable, non-reactive gas that is not otherwise found in the native air stream.

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In this way, additional caution related to the use of SF_6 as tracer gas must be considered since it is used in electric power systems, in medium and high voltage switchgear for insulation and breaking. Emissions of SF_6 from equipment operation can occur if subject, e.g. to high ambient temperature and heat produced by the current passing through the circuit breaker and corrosion due to the external environment, such as salt spray from the ocean and pollution [36].

Therefore, in the absence of the emission coefficients standard values for each RE metal and their alloy, the selection of emission estimation technique (EET), e.g. sampling or direct measurement, mass balance, mathematical models or other engineering calculations, or even the mix of EET should be carefully considered on case-by-case basis as to their purposes and suitability for a particular technology (types of cell) and facility site.

4.2. Technological implications and trends

Pang et. al. [5] claimed that RE oxide-fluoride electrolysis commercial technologies have shown marked improvements over the past decade. Technical-economic indicators presented to an increase of $\approx$ 10% in CE and a reduction of $\approx$ 11% in V, when comparing the 25 kA and 30 kA cells in relation to the 4 kA up to 6 kA.

Specifically in relation to Nd production, the increase in amperage has conducted to a relative reduction in electricity consumption (from 11−13 kWh/kg up to 9.5−11 kWh/kg). Although, the voltage still remains high (8−10V) compared to the aluminum industry, the changes in the cell design, with focus on energy conservation and reduction of PFC emissions, lead to the upturn in CE (from 65% up to 80%) and better productivity [5].

In this way, take into account the view of quantifying the PFC emission factors regarding to the technological class, the production of RE metals and their alloys via oxide-fluoride electrolysis can be defined based on the cells technology capability in terms of amperes, named here: cells of 3 up to 3.5 kA, cells of 4 up to 6 kA, cells of 10 and 25 kA, and cells equal to or above 30 kA.

These technologies are used for the production of different RE metals and their alloys (e.g., La, Pr, Nd, Dy-Fe, Gd-Fe) and have different CE which, in other terms, reflects the differences in the control systems for conventional AE and oxide feeding, the industrial design of cells and its component materials that is intrinsically related with the type of cell and the typical products which result from their use.

Besides, it establishes diverse compositions of the oxides and fluorides and the current densities of the anodes and cathodes (A/cm^2) used in electrolysis. These parameters play an important role in the generation of gases and particulate materials, influencing with greater or lesser intensity the amount of PFC emissions, as stated before by Tamamura [18], Keller and Larimer [20], Pang et.al [5], Vogel and Friedrich [25] and Kjos et.al. [26].

Technologies undertaken in electrolytic cells where the current is varied by hand control, based on a

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js carry out manually, results in significant

temperature variations leading to an excesses generation of fluorine gases, including HF [37] and consequently occupational health and safety effects and environmental damages [38].

Furthermore, cells equal to or less than 6 kA, in which the gas collection system of the RE production line is unique and located a few meters high from the electrolytic cells, may have PFC emissions factors much lower than those in that the exhaust systems are coupled to the cells individually. This is because the ventilation of gases, from all other cells in the potroom, tends to dilute the emissions resulting from the AE of a cell and even change the gas collection efficiency. Recently, in the production systems of Nd-Pr, Dy-Fe and La, operating in atmospheric conditions, the gas collection efficiency was found to be approximately 57% [4].

Another relevant aspect is related to the LV-AE and NP-AE emissions. Even though the RE fused salt RE electrolysis is very similar to primary aluminium metal process, sharing some features, such as the use of carbon anodes and electricity for heating the electrolytic cell, a major difference is the quantity of current applied for electrolysis that is determined according to Faraday Law and by the current actually being used to electrodeposit the RE metal [18]. The increase in amperage leads to a greater probability of different concentrations of the oxide within the cell and these conditions can limit the AE propagation and consequently make the LV-AE and NP-AE more frequent in cells with high amperage.

Hence, it is important to note that PFC emissions from AE and LV-AE represents not only an operational process expense [16], but also a capital cost for the RE metal production industry and an environmental cost for the governments and society. These AE represents disturbances in the process of electrolysis that has a long-term impact on the operation of the cell efficiency [28] and environment, reducing the lifetime of electrolytic cell components and the quality of product, increasing the energy and materials consumption and the generation of waste stream.

In order to overcome potential challenges related to the anode effect and PFC monitoring, some precise estimation methods uses linear models quantifying the total amount of PFC based on a single cell parameter (e.g. AE, polarized AE duration, etc.). Similarly, innovative and non-linear models using an approach that identify and account the PFC emissions related to AE, L-AE and N-AE have been developed and applied to estimate the total amount of PFC emissions in the smelter industry [30].

Moreover, in May 2019, the IPCC Task Force on National Greenhouse Inventories (TFI) developed and published the Refinement for the 2006 IPCC Guidelines for National Greenhouse Inventories [39] that affords an updated and sound scientific basis for supporting the preparation and continuous improvement of national GHG inventories. It also provides background and guidance for estimating PFC from generalized AE (also known as high voltage anode effect) and LV-AE in the primary aluminium production using a range of methods.

Thus, the development of specific EET for RE industry and laboratory analyses of fluorine-containing compounds considering the production cycles is essential to determine the potential indicators and

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js   l with different AE and respective PFC. This

approach lets, primarily, to find the correlation between the operating conditions and the emissions generated. Secondly, to evaluate the necessary adjustments for the processes improvements, as well as the potential errors and the general reliability related to the EET applied.

That is to say, the management of preconditions that generate PFC by e.g. control of the materials feeding and dissolution in the electrolyte have been recognized as the best probably way to prevent GHG emissions for the existing RE production technologies. On the other side, the development and use of new technologies, such as Liquide State Cathode Electrolysis (LSCE) and Solid Oxide Membrane Electrolysis (SOM), represents alternatives for more efficient production and mitigation of GWP in the RE metals industry [40].

Pang et.al. [5] pointed out that since 2007 Chinese researchers have been conducting studies with LSCE. Experimental results using this technology for the Nd production showed EC from 87.1 up to 90.6% and a significant reduction in energy consumption and fluorine-containing compounds emissions in the gas [5]. The SOM process, developed in the USA, uses a membrane that conducts oxygen ions as part of the anode and does not produce PFC. Recently, the application of this process for the production of Nd and Dy-Fe for the magnet industry was reported by Guan et.al [40].

Finally, although research efforts by the academy, private sector and governments together have accomplished substantial progress, an estimation of GHG and respective contributions to the global warming from RE metals industries still require performing a systematic and robust EET in other to define PFC emissions factors specific for each currently RE metals technology, counting also their products and shares in the RE supply chain.

5. Conclusions

Studies on PFC emissions from RE metal industry production have emerged as an important feature of ongoing efforts to promote process improvements, cleaner production and GHG mitigation. This owes in large part to the growing number of environmental concerns regard to the climate change and sustainability of primary metal production. It is possible to observe that in recent years, the industry of RE earth metals and their alloys production has achieved significant improvements in the reduction of energy consumption and emissions of GHG. However, the analysis of estimate amount of PFC, related GHG emissions and GWP from RE metal production reported in scientific database shows that EET applied in the studies demands further investigations to establish a robust GHG inventory. In order to perceive a base for continuous process enhancements and hold the climate change mitigation and adaptation goals is essential the development of a standard methodology to account the PFC of different RE metal technologies. In this way, contrary to common sense, public and private sector initiatives on a national and global scale associated with GHG mitigation policies can lead and have leading to the development of new techniques, processes and materials, combining the reduction of GHG emissions and socio-environmental risks with the resources economy in the RE supply chain.

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Declarations

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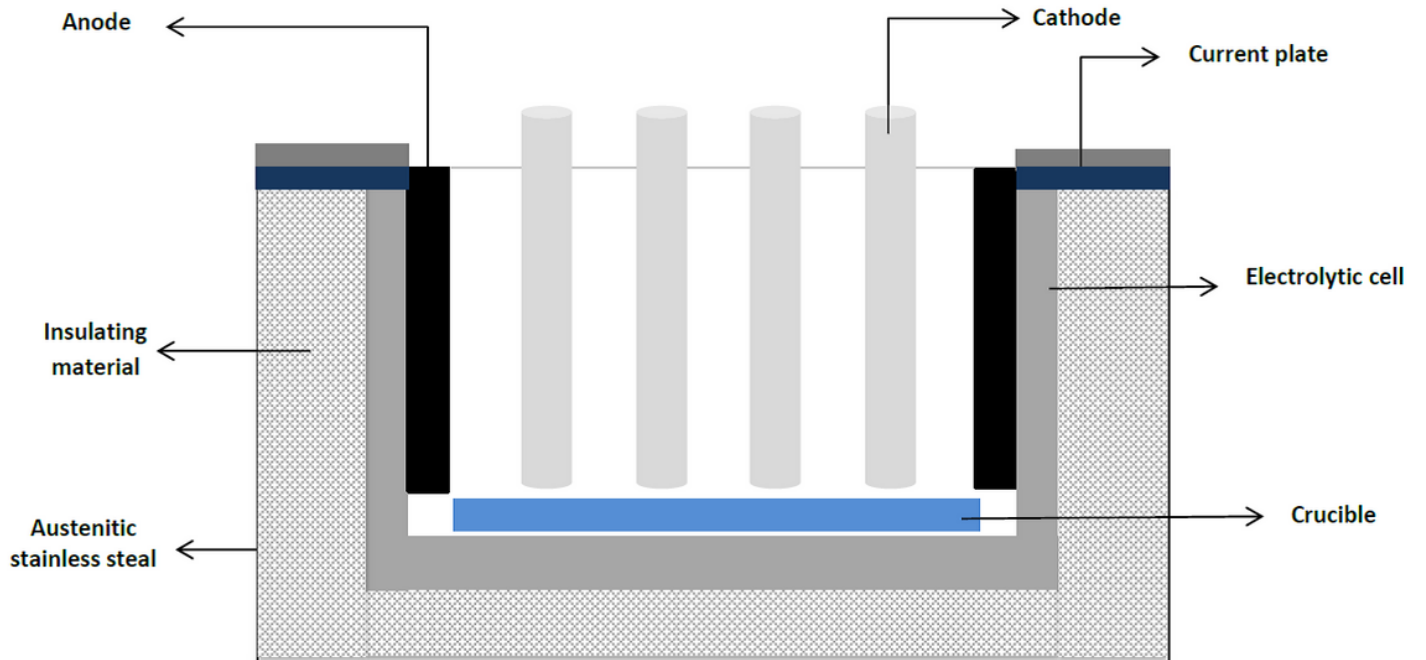
Figures

Figure 1

Simplified diagram of 10 kA RE electrolytic cell − side view (adapted from Ref. [5].
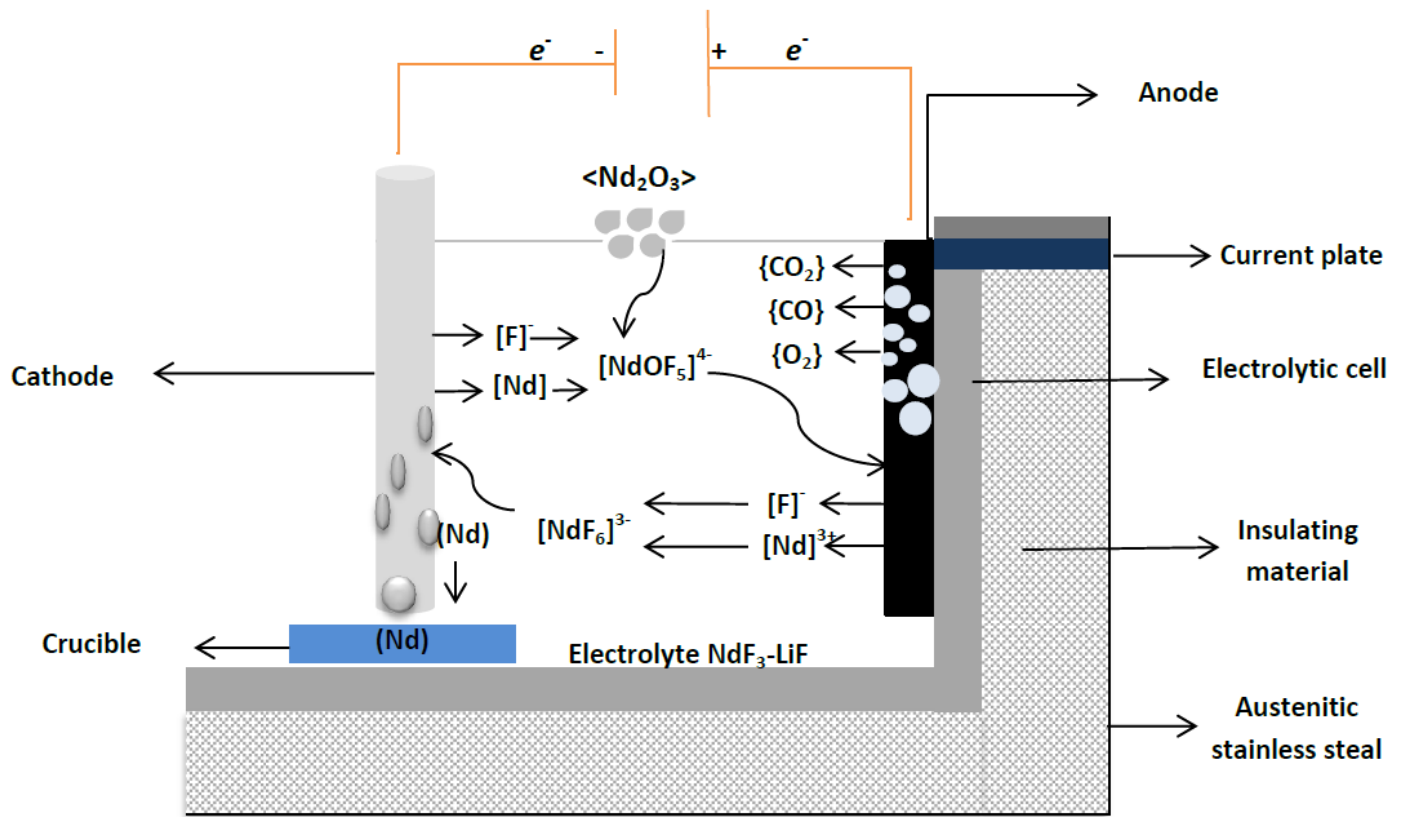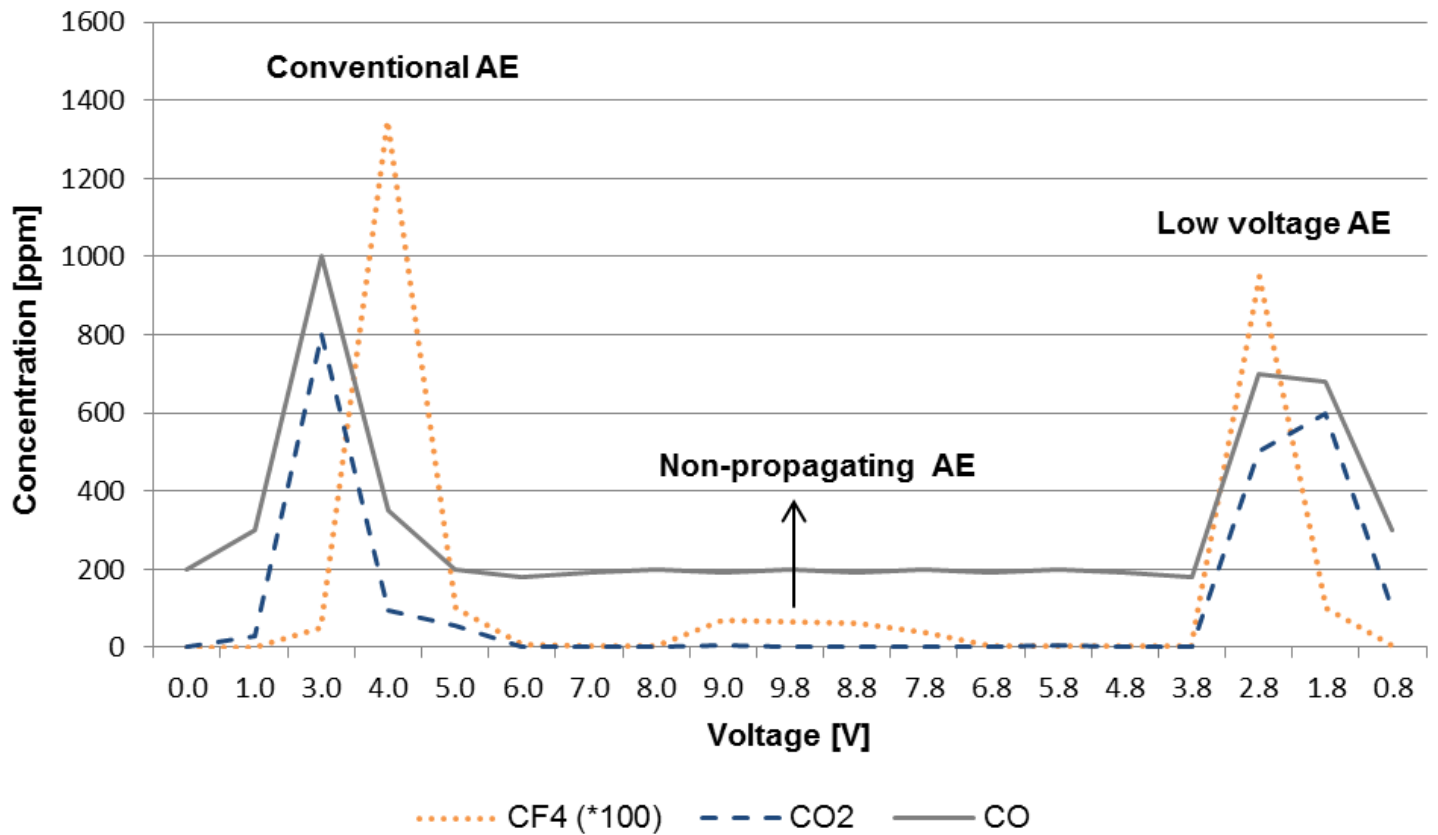
Figure 2

Schematic diagram of partial reactions of the Nd electrolysis under smooth operation

Figure 3

Continuous off-gas measurement showing AE, LV-AE e NP-AE and related CO, CO2 and CF4 emissions (adapted from Ref. [25]).
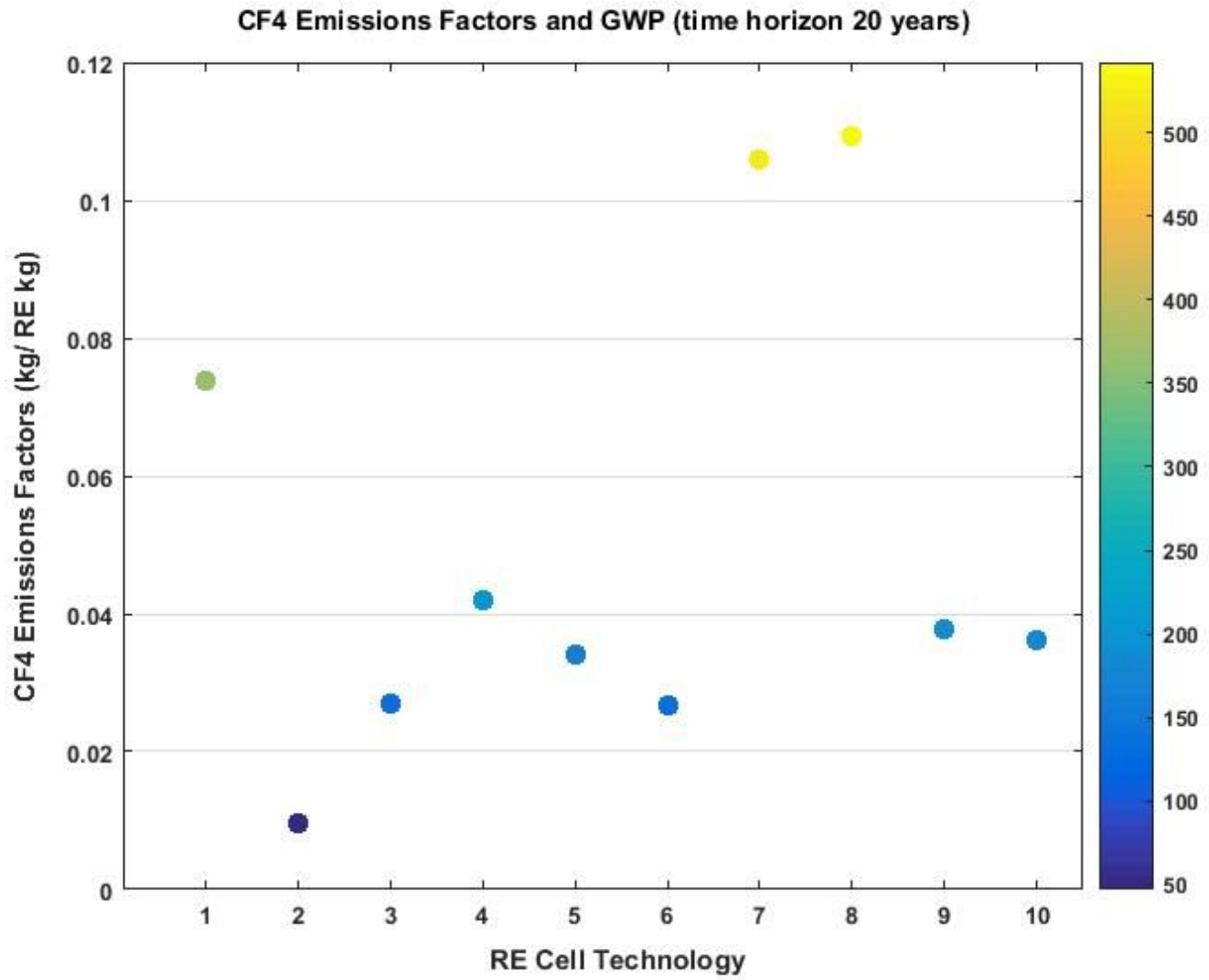
Figure 4

CF4 emissions factors and respective CO2eq (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 20 years.
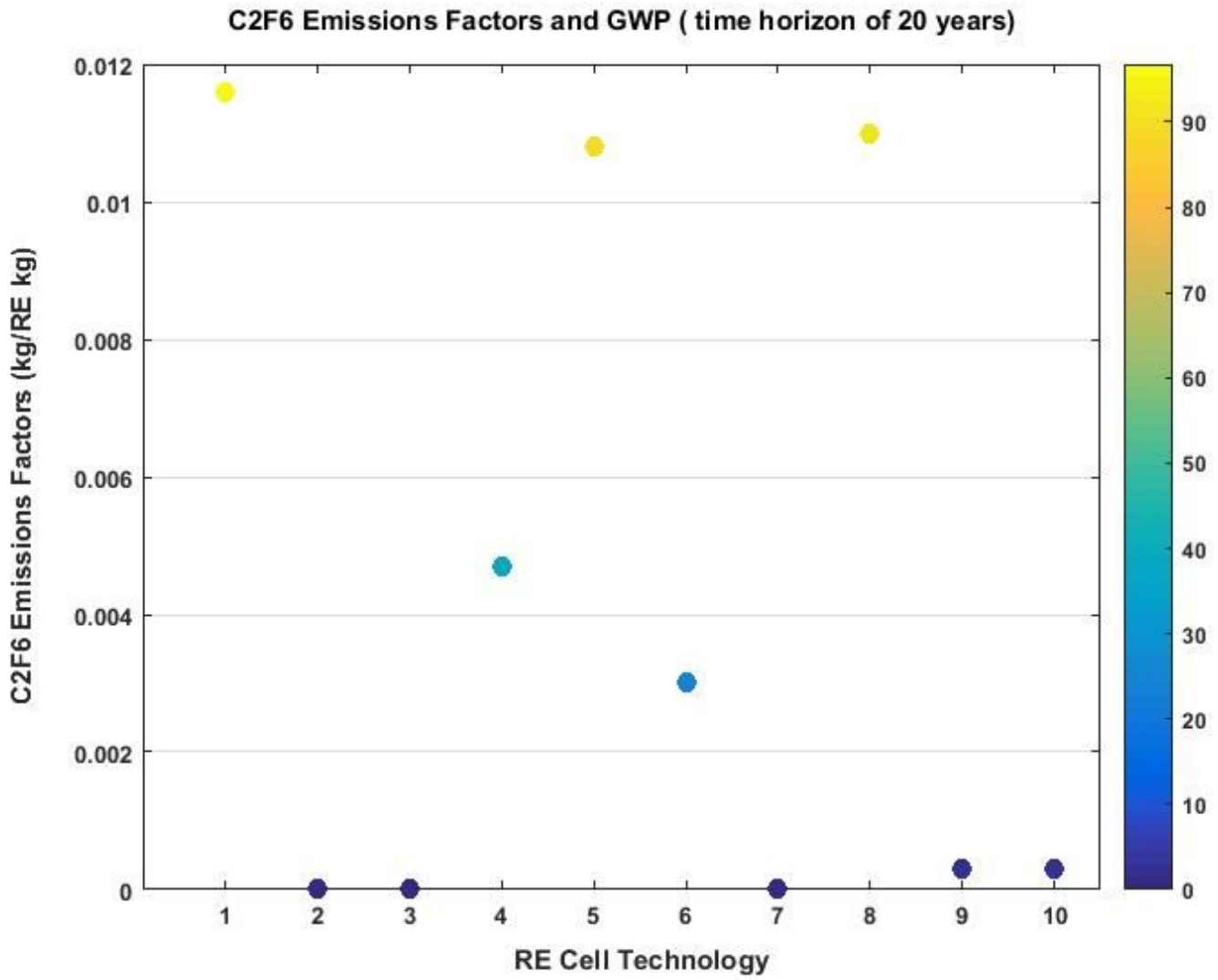
C2F6 Emissions Factors and GWP (time horizon of 20 years)

Figure 5

C2F6 emissions factors and respective CO2eq (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 20 years.
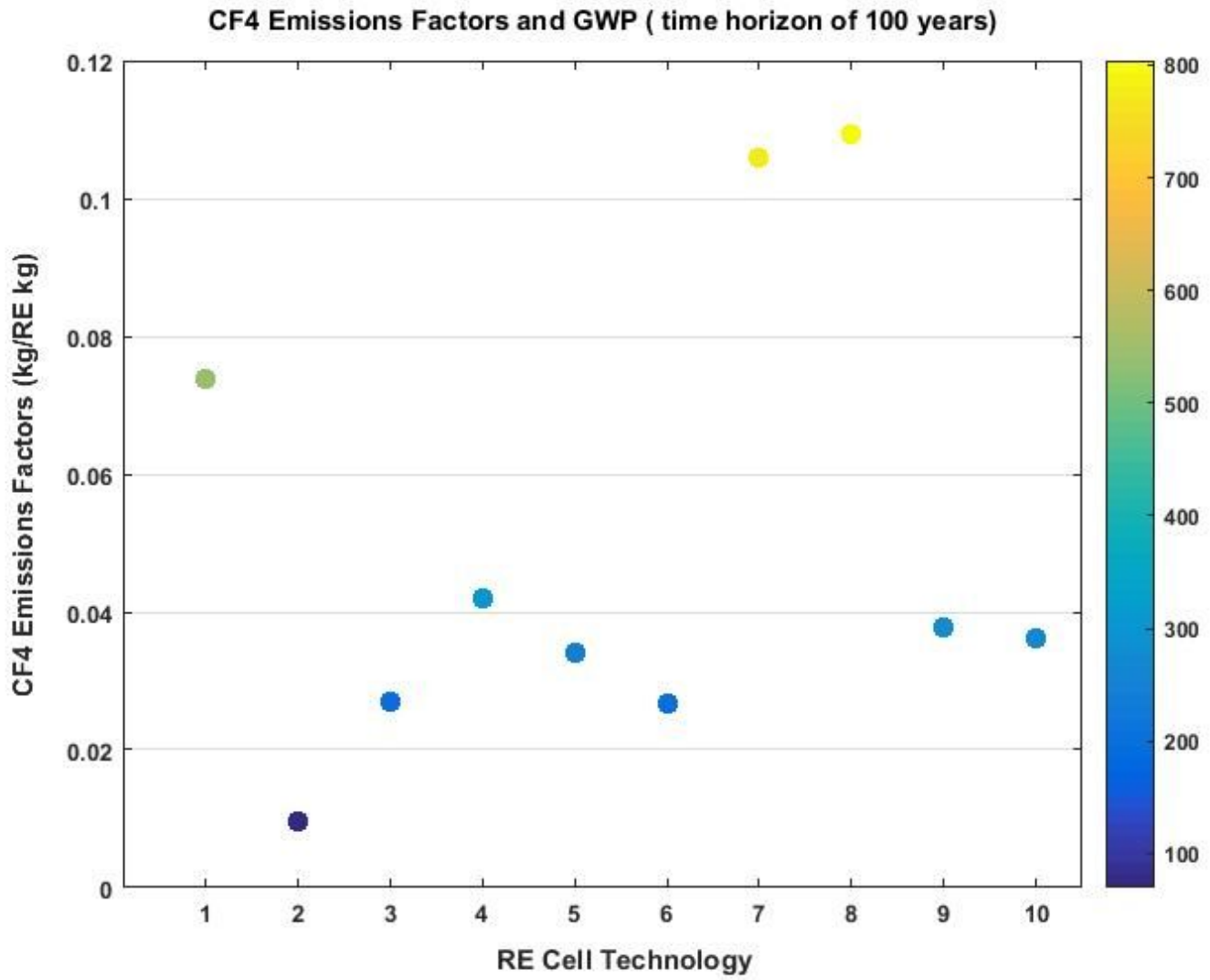
Figure 6

CF4 emissions factors and respective CO2eq (kg/RE kg) from RE fused salt electrolysis − GWP time horizon of 100 years.

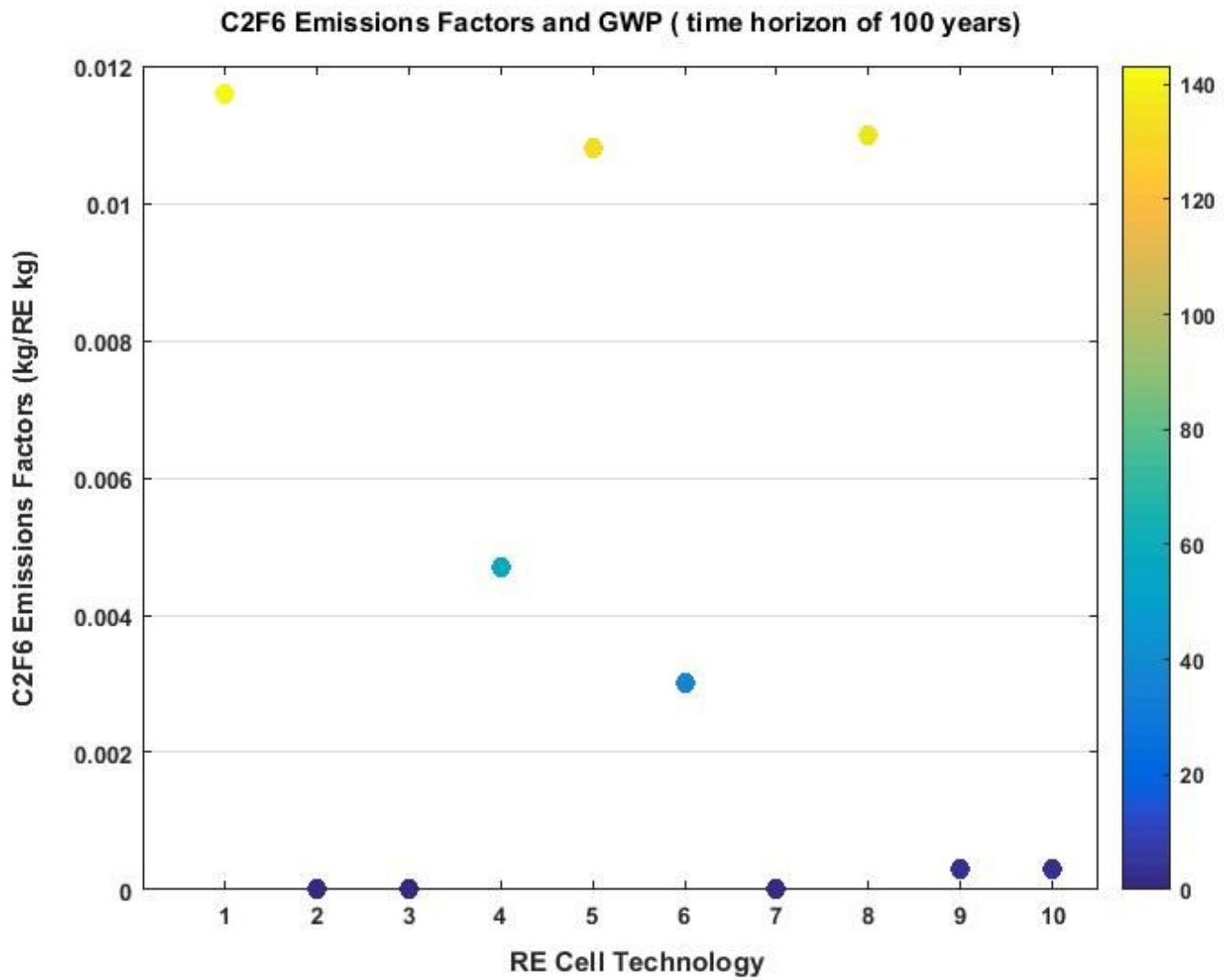**C2F6 Emissions Factors and GWP (time horizon of 100 years)**

Figure 7

C2F6 emissions factors and respective CO2eq (kg/RE kg) from RE fused salt electrolysis – GWP time horizon of 100 years.

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