

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

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

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26 **fluoride systems**

27

28 **Abstract**

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

49 highlights the technological implications related to the PFC emissions measurements and
50 trends towards to set goals and develop strategies for GHG mitigation.

51 **Keywords:** Rare earth metal, electrolysis, greenhouse gases, perfluorocarbons emissions
52 factors, emission estimate technique.

53 **1. Introduction**

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

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

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

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

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

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

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

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

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

107 Therefore, the development of new equipment and techniques, associated with energy
108 conservation and environmental protection represents an inevitable path for the improvement
109 of RE metals industry [5]. As cleaner production technologies and recycling processes are
110 achieved, the importance of international standardization of the products in the RE chain is
111 highlighted. Indeed, in 2015, the International Organization for Standardization (ISO)
112 established a Technical Committee (ISO/TC 298) of RE, composed of 34 countries and, so
113 far, 5 working groups [13].

114 In this way, Chinese companies have been strongly incited to deploy significant work to
115 reduce the energy consumption and emissions from the RE fused salt electrolysis, in addition
116 to accomplish the environmental, occupational health and safety compliances. From this

117 perspective, this paper analyses the PFC emissions measurements and their role in the
118 production processes improvements of RE metals and sustainable production, with emphasis
119 on the neodymium (Nd) electrolysis oxide-fluoride system and GHG inventory.

120 The first section presents the state of art of the metallic Nd production, considering the main
121 technical aspects of RE electrolysis, as well as the analysis of the emissions reported from
122 previous publications. Then, is discussed the IPCC methods [14] and EPA and IAI protocols
123 [15] for quantifying PFC gases applied in the primary aluminum industry, known as
124 analogous process for RE electrolysis. Finally, the last section highlights, vis-à-vis standard
125 methodologies, the key issues for measurement of emission factors from the RE metal and
126 their alloys production and indicates the trends for evaluating and reducing GHG emissions.

127 **2. State-of-art**

128 **2.1. Fused oxide-fluoride electrolysis**

129 Like other elements of RE, neodymium (Nd) is transformed into metal by the oxide-fluoride
130 electrolysis into a fused salt electrolyte [5, 16, 17]. Usually, Nd oxides are dissolved in an
131 anhydrous electrolyte of Nd fluorides and Li fluorides (LiF) to improve electrical
132 conductivity and increase the fluidity. The electrolyte is maintained in the range of 800 °C to
133 1100 °C and is initially melted by resistance heating. Both the electrolyte and the deposited
134 metal can be kept liquid by the joule effect [18, 19].

135 On an industrial scale, the electrolytic cell (or furnace) operates in atmospheric conditions
136 with current densities of $\approx 6.5 \text{ A/cm}^2$ at the anode and $\approx 1 \text{ A/cm}^2$ at the cathode; features
137 graphite or molybdenum crucible, graphite anodes, molybdenum (Mo) or tungsten (W)
138 cathode and voltage conductive plates (**Fig. 1**). The cell is externally lined with layers of

139 insulating refractory materials and austenitic stainless steel. A potline is composed of a set of
140 cells electrically connected in series, normally installed in buildings named potroom.

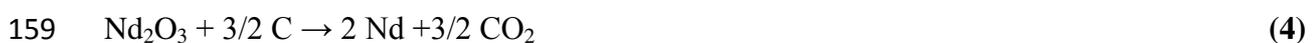
141 When Nd is prepared, carbon can be used in the anode and cathode. In the case of Nd alloys
142 (e.g. NdFe), graphite electrodes are used at the anode and Fe (including steel and low carbon
143 steel) at the cathode. In other words, if the desired product is metallic Nd, only the anode is
144 the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

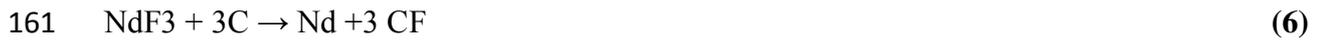
146 **[Fig.1-** Simplified diagram of 10 kA RE electrolytic cell – side view (adapted from Ref. [5]]

147 Particularly in relation to the consumption of the C anode, oxygen is released on the electrode
148 surface and converted to carbon oxides (reactions 1 and 2), namely CO and CO₂. These two
149 gases also react electrochemically with the cathode. Usually, the reaction occurs in a three-
150 phase interface (solid, liquid and gas), formed by the cathode, the electrolyte and the gas [20].



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





162 According to Stefanidaki et. al. [16], in fused $\text{LiF} - \text{Nd}_2\text{O}_3 - \text{NdF}_3$ systems, the neodymium
163 metal is probably produced by the electro-reduction of Nd fluorides in the cathode, while in
164 the anode occurs oxidation of Nd oxyfluorides generating oxygen (**Fig. 2**) conforming to the
165 following reactions (7) and (8):



168 [**Fig. 2**– Schematic diagram of partial electrochemical reactions of the Nd electrolysis under
169 smooth operation]

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

175 AE are manifested by the increase in voltage (V) of the electrolytic cell and if a power system
176 with limited voltage supply is used, also by the decrease in amperage (A). The increase in
177 voltage (overvoltage) can lead to an overheating of the electrolytic cell, which in turn,
178 promotes greater metallic Nd solubility and to excessive interactions of the metal with the
179 electrolyte elements. These occurrences prevent a smooth electrolytic operation and promote
180 the formation of non-metallic deposits (or similar to the slag) in the cathodes and other parts
181 of the cell [20], in addition to increasing energy consumption and decreasing the current
182 efficiency (CE).

183 **2.2. Anode effects and PFC emissions**

184 One of the main process parameters related to AE is the oxides concentration in the
185 electrolyte, in which the overvoltage can result from the oxides deprivation in a given region
186 of the cell. In the electrolysis of Nd oxide-fluorides, high levels of oxides in the electrolytic
187 cell produce the precipitation of oxyfluorides elements that cannot be reduced [18], while low
188 levels result in a decrease in electrical conductivity. In this way, the transport of electrical
189 charges is no longer supported by the standard (theoretical) reaction of Nd₂O₃ electrolysis.

190 Moreover, in the study conducted by Dorren et al. [24], during the electrolysis of molten
191 salts, a resistive C-F film formed on the anode surface can be decomposed to form the PFC
192 gases (reactions 5 and 6). Measured data reported in the literature on RE electrolysis indicate
193 that in the occurrence of AE, the gases CF₄ and C₂F₆ are released [25, 26]. The emissions of
194 CF₄ and C₂F₆ can be generated from the following reactions:



197 PFC can also be formed electrochemically by forming COF₂ and COF (reactions 11 and 12)
198 which are unstable and react spontaneously with C to form CF₄ and CO (reactions 13 and 14)
199 [4, 25,26], according to the reactions presented below:



204 In addition, depending on the replacement rate of LiF-NdF₃-Nd₂O₃ and the Nd₂O₃ solubility
205 in the electrolyte, other fluorine emissions occur. Under conditions of positive oxidizing
206 atmosphere, the F reacts with the water contained in the cell forming HF (reaction 15) [18,
207 27].The theoretical decomposition of Nd fluoride and H₂O producing HF [17] is presented
208 (reaction 16) below:



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

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

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

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

227 [Fig. 3 – Continuous off-gas measurement showing AE, LV-AE e NP-AE and related CO,
228 CO₂ and CF₄ emissions (adapted from Ref. [25].]

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

235 **2.3 Laboratory and industrial accounting of PFC emissions and GWP**

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

241 The figures below shows the emission factors of CF₄ and C₂F₆ in kg per RE kg metal and
242 alloy produced by fused salt electrolysis reported in the published literature and respective
243 CO_{2eq} emissions over time horizon of 20 years (**Fig. 4** and **5**) and time horizon of 100 years
244 (**Fig. 6** and **7**). In the figures, the number of cell technology (CT) is related to the production
245 of: Nd (1, 2, and 3); Nd-Pr (4, 5, and 6); Dy-Fe (7, 8) and La (9, 10).

246 The emission factor of both PFC are estimated based on: the operation of electrolytic cell
247 under laboratory conditions (CT: 1); measurements at production site (CT: 2, 3, 6, 7, 9); time
248 integrated and laboratory analysis (CT: 4, 5, 8, 10). The reference studies for CT: 1 [17]; 2,
249 3, 7 [31] and 4, 5, 6, 8, 9, 10 [4].

250 The colormap represents the intensity (quantity) of the respective PFC emissions converted
251 into CO_{2eq} (kg/RE kg) according to the metric values updated in IPCC Fifth Assessment
252 Report (AR5) as result of new scientific knowledge and also due to the changes in lifetimes
253 and radiative efficiency (RE) caused by changing atmospheric background conditions [33].
254 The values of global warming potential (GWP) relative to CO_{2eq} used for CF₄ and C₂F₆ are
255 given in the **table 1**.

256 [**Fig. 4** – CF₄ emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt
257 electrolysis – GWP time horizon of 20 years].

258 [**Fig. 5** – C₂F₆ emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt
259 electrolysis – GWP time horizon of 20 years].

260 [**Fig. 6** – CF₄ emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt
261 electrolysis – GWP time horizon of 100 years].

262 [**Fig. 7** – C₂F₆ emissions factors and respective CO_{2eq} (kg/RE kg) from RE fused salt
263 electrolysis – GWP time horizon of 100 years].

264 [**Table 1**. Lifetime and global warming potentials of CF₄ and C₂F₆]

265 Take into account the technical operation indicators, the differences between the emissions
266 factors and the same RE metal, e.g. kg CF₄ per kg Nd (from 9.50E-03 kg/kg to 7.39E-02
267 kg/kg), can be initially explained by the technological conditions of production of each RE
268 metal and the methods applied for measurement the air streams from the fused oxide-fluoride
269 system.

270 In the context of climate change, a critical issue regarding to the PFC emissions in the
271 electrolysis of Nd oxide-fluorides, including other RE metals and their alloys, is the absence

272 of standard methods or protocols for measuring the emission factors of these gases, similar to
273 the emission inventories applied in the primary aluminum industry, which allows an reliable
274 evaluation of CO₂ equivalent emissions from the RE metal and alloys production.

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

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

286 **3. IPCC Standard methodology for quantifying PFC emissions**

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

295 The IPCC Tier 2 and 3 methods, involve the statistical analysis of conventional AE
296 (frequency - AEF and duration - AED) and emissions coefficients (CF₄ slope coefficient and
297 mass ratio of C₂F₆ emissions in relation to CF₄). In general, calculations are carried out on the
298 monthly average data and then summed to obtain an annual issue. The emission factors of
299 CF₄ and C₂F₆ can be calculated using specific coefficients of the technology employed (Tier
300 2) and/or direct measurements performed at the smelter (Tier 3) [14].

301 The IPCC Tier 3 is applied to define a long-term relationship between the measured
302 emissions and the operating parameters and to verify the correlation of the AE and the
303 production levels. This method is recognized for presenting highest precision for building an
304 inventory of PFC emissions and provides two models for quantifying the gases: slope and
305 overvoltage. The slope is a parameter in which, when multiplied by the minutes of AE per
306 cell/day, it results in an industry-specific CF₄ emission factor (Eq. 1):

$$307 \quad EF_{CF_4} = S_{CF_4} * AEM * MP \quad (1)$$

308 Where:

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

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

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

312 MP: metal production (t)

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

$$316 \quad EF_{CF_4} = \frac{OVC * AEO * MP}{CE} \quad (2)$$

317 Where:

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

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

320 AEO: anode effect overvoltage (mV)

321 CE: current efficiency (%)

322 While the C₂F₆ emission factors can be determined as the mass fraction of the CF₄ emission
323 factor as show in Eq. (3):

$$324 \quad EF_{C_2F_6} = EF_{CF_4} * F_{C_2F_6} \quad (3)$$

325 Where:

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

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

328 F_{C₂F₆}: C₂F₆ weight ratio of CF₄ emission factor (kg C₂F₆/kg CF₄)

329 Whether using the slope method or overvoltage method, the weight fraction C₂F₆/CF₄ is
330 determined from individual facility-specific measurements or from average of measurements
331 factors from a number of facilities operating with similar technology. According to Dion et.
332 al. [30], since the TIER 3 methods are based on the average performance of a given industry,
333 the respective coefficients (S_{CF₄} or OVC_{CF₄}) and the weight ratio (F_{C₂F₆}) need to be
334 periodically redefined through continuous measurement campaigns in order to avoid large
335 deviations from the PFC values.

336 In 2008, a joint initiative by the US Environment Protection Agency (EPA), Voluntary
337 Aluminium Industry Partnership (VAIP) and the International Aluminium Institute (IAI)
338 developed a CF₄ and C₂F₆ Measurement Protocol for the primary aluminum industry that
339 incorporates a significant number of updates to the Tier 3 method in relation to the data
340 required for analysis, including methodological improvements in the collection and
341 quantitative measurement of primary and secondary PFC emissions flows [15].

342 **3.1 Measurement of CF₄ and C₂F₆ emissions based on EPA and IAI Protocol**

343 In the EPA and IAI protocol, two alternatives are given for the measurement and calculation
 344 of emissions of CF₄ and C₂F₆ per kg of metal, there are: 1) measurements of PFC carried out
 345 based on sampling using stainless steel bags or cylinders and 2) measurements conducted
 346 directly on the production site. In both, the slope and overvoltage coefficients and the mass
 347 ratio of C₂F₆/CF₄ can be evaluated. The recommended calculation procedures for the analysis
 348 of PFC emissions include information on how to measure:

- 349 • The gas flows from the cells exhaust ducts and the potroom area, weighting the speed,
 350 temperature, pressure, as well as the sectional area of the duct;
- 351 • The total emissions of CF₄ and C₂F₆ per minute of AE and sampling time (ST);
- 352 • The mass ratio or weight ratio of C₂F₆/CF₄;
- 353 • The total metal production as a function of ST;
- 354 • Calculation of PFC gases from secondary emissions in relation to ST;
- 355 • The secondary emissions and the adjustment of the quantity of CF₄ and C₂F₆ issued;
- 356 • The total emission factor of each PFC;
- 357 • The slope CF₄ emission coefficient and the CF₄ emission coefficient in overvoltage.

358 While primary (exhaust ducts) and secondary (fugitive) PFC emissions are analyzed based on
 359 sampling bags or onto sorbent columns and the exhaust gas collection efficiency (GC), the
 360 emission factors of the CF₄ and C₂F₆ gases are calculated by the following simplified Eq. (4):

$$361 \quad EF_{PFC} = \frac{E * M * F * T}{10^3 * MV * GC * \Sigma metal} \quad (4)$$

362 Where:

363 EF_{PFC}: CF₄ emission factor (kg/t/d)

364 E: average CF₄ concentration at sampling points (μlCF₄/l/Nm³/μlCF₄)

365 M= mass in kg per mol of CF₄ (0.088 kg/mol)

366 F: total gas flow at each sampling point (Nm³/h)

367 T= sampling time (h/d)
 368 MV= molar volume (22.4 l/mol)
 369 GC: gas collection efficiency (%)
 370 Σ_{Metal} : total metal produced over the sampling time (t/d *n° cells/d)

371 It is worthwhile to mention that the total amount of PFC (either CF₄ or C₂F₆ emissions) is the
 372 sum of each PFC emitted as primary and as secondary. The fugitive PFC can be calculated
 373 based on gas collection efficiency as a fraction of the total PFC emissions, according to the
 374 Eq. (5):

$$375 \quad PFC_{fugitive} = \frac{PFC_{duct} * F_{fugitive}}{1 - F_{fugitive}} \quad (5)$$

376 Where:

377 PFC_{fugitive}: PFC emitted as fugitive emissions (kg)
 378 PFC_{duct}: PFC emission measured in the duct by the instruments (kg)
 379 F_{fugitive}: fraction of fugitive emissions based on gas collection efficiency (%)

380 As long as the gas collection efficiency (GC) is greater than 90%, the total of PFC gases can
 381 be divided by GC as indicated in the Eq. (4). Otherwise, if the GC is less than 90% and the
 382 PFC fugitive emissions are measured by direct open path FTIR spectrometry, by the time
 383 average bag method or other methods shown to be capable of measuring the PFC emissions
 384 (both CF₄ and C₂F₆), the fraction of PFC emissions emitted as fugitive is calculate as follows
 385 (Eq. (6):

$$386 \quad F_{fugitive} = \frac{PFC_{fugitive}}{PFC_{fugitive} + PFC_{duct}} \quad (6)$$

387 Where:

388 F_{fugitive}: fraction of PFC emitted as fugitive (kg)
 389 PFC_{fugitive}: average PFC emitted measured as fugitive by total AE for the fugitive sampling time (kgCF₄/ AE
 390 min)

391 PFC_{duct} : total PFC emitted by total AE (potroom) for the duct sampling time (kgCF₄/ AE min)

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

$$394 \quad PFC_{total} = \frac{PFC_{duct}}{1 - F_{fugitive}} \quad (7)$$

395 Where:

396 PFC_{total} : total PFC emissions (kg)

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

398 $F_{fugitive}$: fraction of fugitive emissions based on gas collection efficiency (%) or measured by equipment
399 (kg)

400 It should be noted that since the fugitive emissions are measured, the Eq. (4) must be adjusted
401 in order to calculate PFC emission factor without the variable GC, avoiding underestimation
402 and oversized uncertainty. The same procedure given by the Eq.(4), (5) or (6) and (7) can be
403 applied for the quantification of the C₂F₆ emission factor, but replacing the value of the
404 variable M of the Eq. (4) with the corresponding number in kg per mol of C₂F₆ (0.138).

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

$$407 \quad S_{CF_4} = \frac{EF_{CF_4}}{\sum AE} \quad (8)$$

408 Where:

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

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

411 $\sum AE$: total AE min/cell/d over the sampling time

$$412 \quad OVC_{CF_4} = EF_{CF_4} * \frac{CE}{AEO} \quad (9)$$

413 Where:

414 OVC: overvoltage emission coefficient (kg CF₄/t/mV)
 415 EF_{CF₄}: CF₄ emission factor (kg CF₄/t)
 416 AEO: overvoltage for specific cells over the sampling time (mV)
 417 CE: current efficiency (%)

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

$$424 \quad U_{total} = \sqrt{U_1^2 + U_2^2 + \dots + U_n^2} \quad (10)$$

425 Where:

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

427 U_i²: the percentage uncertainties associated with each of the quantities, e.g. metal production, instrument
 428 measurement, duct flow rate, etc. (%).

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

$$433 \quad U_{total} = \sqrt{\frac{(U_1 \cdot X_1)^2 + (U_2 \cdot X_2)^2 + \dots + (U_n \cdot X_n)^2}{|X_1 + X_2 + \dots + X_n|}} \quad (11)$$

434 Where:

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

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

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

443 **4. Results and discussions**

444 **4.1. Key issues for evaluating of PFC emissions from RE metal production**

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

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

457 Additionally, there are transient circumstances, e.g. startup of a new cell and restart of the
458 potline due to the replacement of cells or their components (except exchange of anodes),

459 power outages and testing of raw material that do not characterize the process routine of the
460 RE production. Thus, care must be taken to ensure that AE measurements are representative
461 and to properly account for the PFC emissions and any reduction in collection efficiency.

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

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

473 Commonly, homogeneity is tested by injecting a small constant flow of a tracer gas into the
474 exhaust duct of one of the reduction cells, which is subsequently monitored at five points,
475 equally spaced along the duct sectional area. For an adequate definition of the sampling
476 point, the concentration of this gas cannot vary by more than 10% at any candidate sampling
477 point. This is particularly important for the definition of the emission coefficient in overvoltage
478 and the weight ratio of $\text{C}_2\text{F}_6/\text{CF}_4$. In either case, the measurement requires a minimum of 72
479 hours of gas collection and the inclusion of normal productive operation cycles, e.g. electrode
480 changes, among others [15].

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

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

494 In this way, additional caution related to the use of SF_6 as tracer gas must be considered since
495 it is used in electric power systems, in medium and high voltage switchgear for insulation and
496 breaking. Emissions of SF_6 from equipment operation can occur if subject, e.g. to high
497 ambient temperature and heat produced by the current passing through the circuit breaker and
498 corrosion due to the external environment, such as salt spray from the ocean and pollution
499 [36].

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

505 **4.2. Technological implications and trends**

506 Pang et. al. [5] claimed that RE oxide-fluoride electrolysis commercial technologies have
507 shown marked improvements over the past decade. Technical-economic indicators presented
508 to an increase of $\approx 10\%$ in CE and a reduction of $\approx 11\%$ in V, when comparing the 25 kA and
509 30 kA cells in relation to the 4 kA up to 6 kA.

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

515 In this way, take into account the view of quantifying the PFC emission factors regarding to
516 the technological class, the production of RE metals and their alloys via oxide-fluoride
517 electrolysis can be defined based on the cells technology capability in terms of amperes,
518 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
519 equal to or above 30 kA.

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

525 Besides, it establishes diverse compositions of the oxides and fluorides and the current
526 densities of the anodes and cathodes (A/cm^2) used in electrolysis. These parameters play an
527 important role in the generation of gases and particulate materials, influencing with greater or

528 lesser intensity the amount of PFC emissions, as stated before by Tamamura [18], Keller and
529 Larimer [20], Pang et.al [5], Vogel and Friedrich [25] and Kjos et.al. [26].

530 Technologies undertaken in electrolytic cells where the current is varied by hand control,
531 based on a visual estimation of cell temperature and feeding oxide is carry out manually,
532 results in significant temperature variations leading to an excesses generation of fluorine
533 gases, including HF [37] and consequently occupational health and safety effects and
534 environmental damages [38].

535 Furthermore, cells equal to or less than 6 kA, in which the gas collection system of the RE
536 production line is unique and located a few meters high from the electrolytic cells, may have
537 PFC emissions factors much lower than those in that the exhaust systems are coupled to the
538 cells individually. This is because the ventilation of gases, from all other cells in the potroom,
539 tends to dilute the emissions resulting from the AE of a cell and even change the gas
540 collection efficiency.

541 Consequently, within the same technological class, other operational particularities can
542 conduct to different outcomes of GHG emissions, as suggest the results of CO_{2eq} emissions
543 for time horizon of 20 years (see Fig.3) in the production of the Dy-Fe are 5.25 E02 kg/ RE
544 kg [31] and 6.76 E02 kg/ RE kg [4]. Recently, in the production systems of Nd-Pr, Dy-Fe and
545 La, operating in atmospheric conditions, the gas collection efficiency was found to be
546 approximately 57% [4].

547 Another relevant aspect is related to the LV-AE and NP-AE emissions. Even though the RE
548 fused salt RE electrolysis is very similar to primary aluminium metal process, sharing some
549 features, such as the use of carbon anodes and electricity for heating the electrolytic cell, a
550 major difference is the quantity of current applied for electrolysis that is determined

551 according to Faraday Law and by the current actually being used to electrodeposit the RE
552 metal [18].

553 As a basis for comparison, the anodic current density of high production aluminium cells is
554 maintained near 1 A/cm^2 [39, 40]. The increase in amperage leads to a greater probability of
555 different concentrations of the oxide within the cell and these conditions can limit the AE
556 propagation and consequently make the LV-AE and NP-AE more frequent in cells with high
557 amperage.

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

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

571 Moreover, in May 2019, the IPCC Task Force on National Greenhouse Inventories (TFI)
572 developed and published the Refinement for the 2006 IPCC Guidelines for National
573 Greenhouse Inventories [41] that affords an updated and sound scientific basis for supporting

574 the preparation and continuous improvement of national GHG inventories. It also provides
575 background and guidance for estimating PFC from generalized AE (also known as high
576 voltage anode effect) and LV-AE in the primary aluminium production using a range of
577 methods.

578 Thus, the development of specific EET for RE industry and laboratory analyses of fluorine-
579 containing compounds considering the production cycles is essential to determine the
580 potential indicators and variables for each technology were most likely associated with
581 different AE and respective PFC. This approach lets, primarily, to find the correlation
582 between the operating conditions and the emissions generated. Secondly, to evaluate the
583 necessary adjustments for the processes improvements, as well as the potential errors and the
584 general reliability related to the EET applied.

585 That is to say, the management of preconditions that generate PFC by e.g. control of the
586 materials feeding and dissolution in the electrolyte have been recognized as the best probably
587 way to prevent GHG emissions for the existing RE production technologies. On the other
588 side, the development and use of new technologies, such as Liquide State Cathode
589 Electrolysis (LSCE) and Solid Oxide Membrane Electrolysis (SOM), represents alternatives
590 for more efficient production and mitigation of GWP in the RE metals industry [42].

591 Pang et.al. [5] pointed out that since 2007 Chinese researchers have been conducting studies
592 with LSCE. Experimental results using this technology for the Nd production showed EC
593 from 87.1 up to 90.6% and a significant reduction in energy consumption and fluorine-
594 containing compounds emissions in the gas [5]. The SOM process, developed in the USA,
595 uses a membrane that conducts oxygen ions as part of the anode and does not produce PFC.
596 Recently, the application of this process for the production of Nd and Dy-Fe for the magnet
597 industry was reported by Guan et.al [42].

598 Finally, it is important to highlight that the studies on the emissions of fused oxide-fluoride
599 electrolysis discussed here contributed significantly for the advancement of knowledge
600 regarding to RE metal production. Research efforts by the academy, private sector and
601 governments together have accomplished substantial progress. However, an estimation of
602 GHG and respective contributions to the global warming from RE metals industries still
603 require performing a systematic and robust EET in other to define PFC emissions factors
604 specific for each currently RE metals technology, counting also their products and shares in
605 the RE supply chain.

606 **5. Conclusions**

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

621 combining the reduction of GHG emissions and socio-environmental risks with the resources
622 economy in the RE supply chain.

623 **Supplementary information**

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630 SHF: Formal analysis, writing, review, editing. F.J.G.L: Conceptualization, supervision,
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636 **Availability of data and materials**

637 The authors declare that all data supporting the findings of this study are available within the
638 article.

639 **Competing interest**

640 The authors declare that they have no competing interests.

Table 1. Lifetimes and global warming potentials of CF₄ and C₂F₆

Chemical Formula	Industrial Designation or Common Name	Lifetime (years) ⁽¹⁾	Global Warming Potential (GWP)	
			20 years horizon ⁽²⁾	100 years horizon ⁽²⁾
CF ₄	PFC -14	50000	4954	7349
C ₂ F ₆	PFC -116	10000	8344	12340

(1) IPCC Fourth Assessment Report – AR4 [6]
(2) IPCC Fifth Assessment Report – AR5 [33]

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Figures

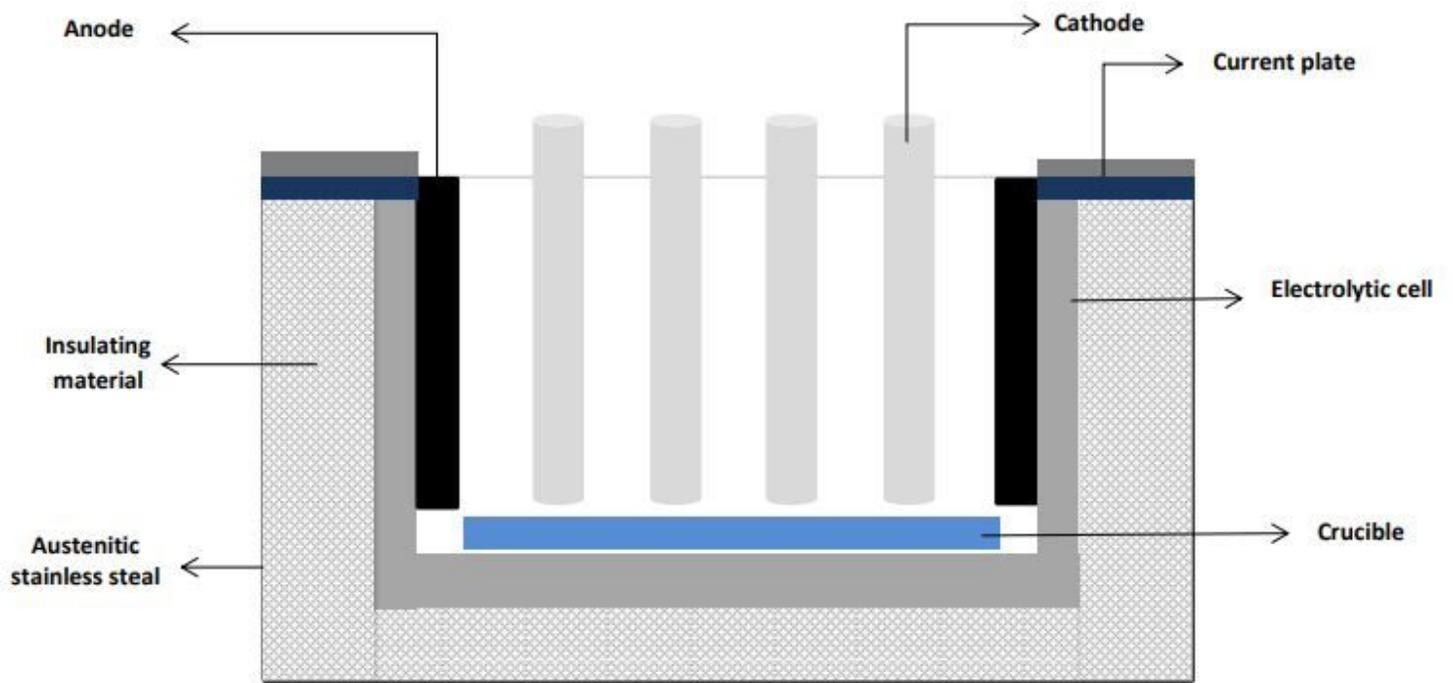


Figure 1

Simplified diagram of 10 kA RE electrolytic cell – side view (adapted from Ref. [5]).

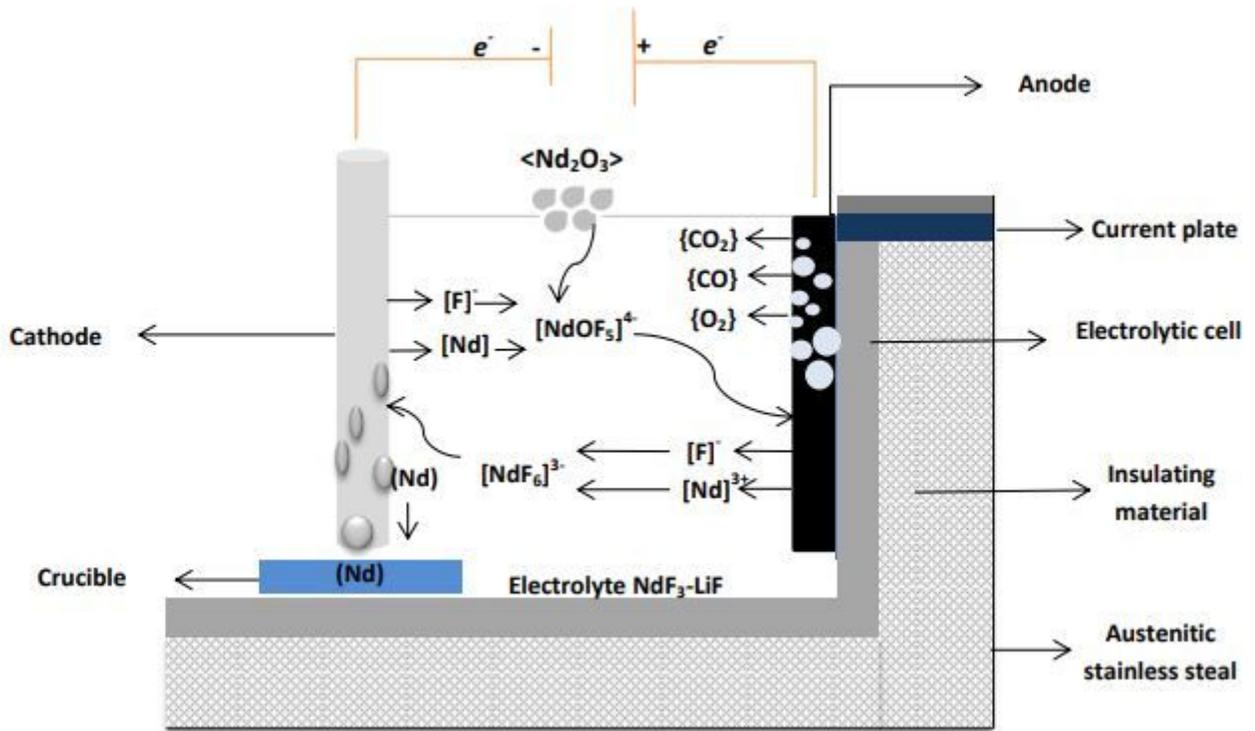


Figure 2

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

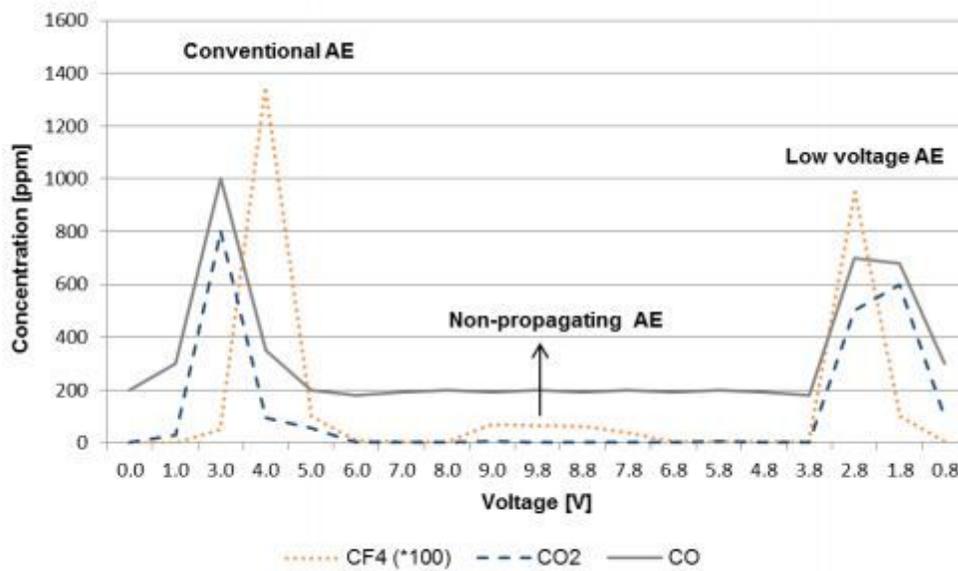


Figure 3

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

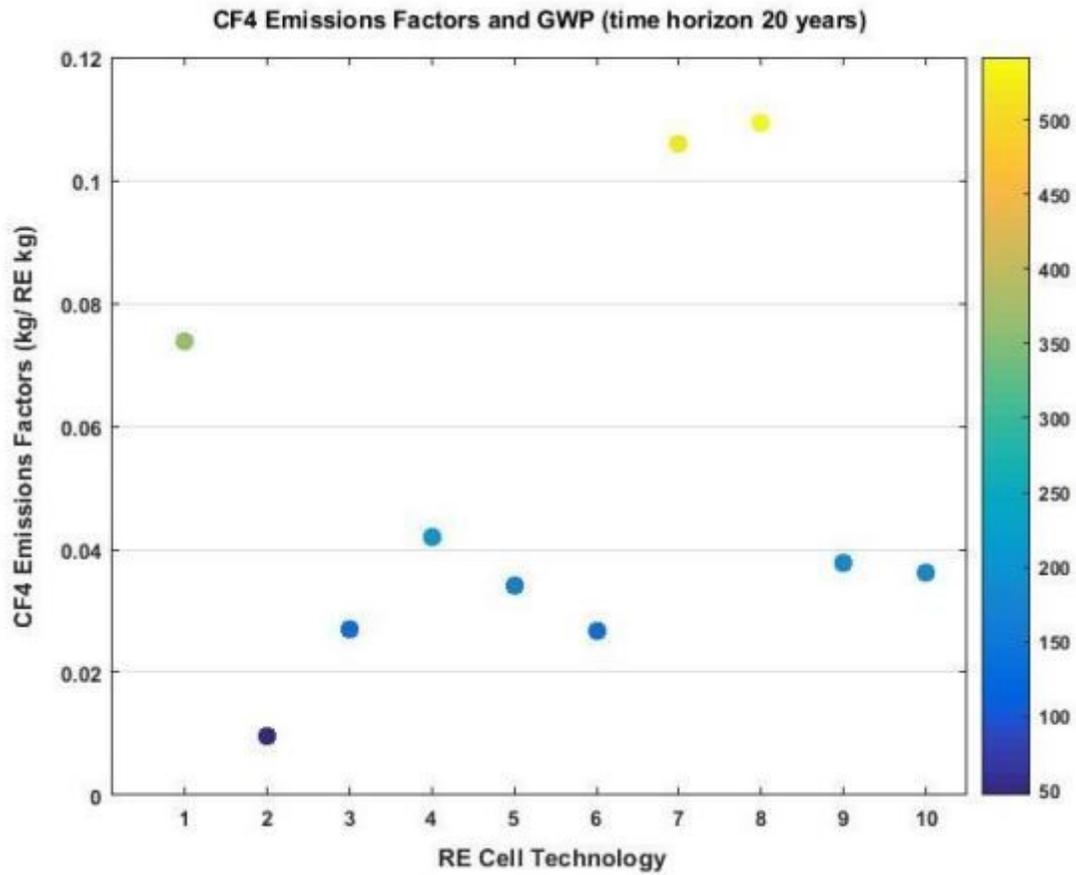


Figure 4

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

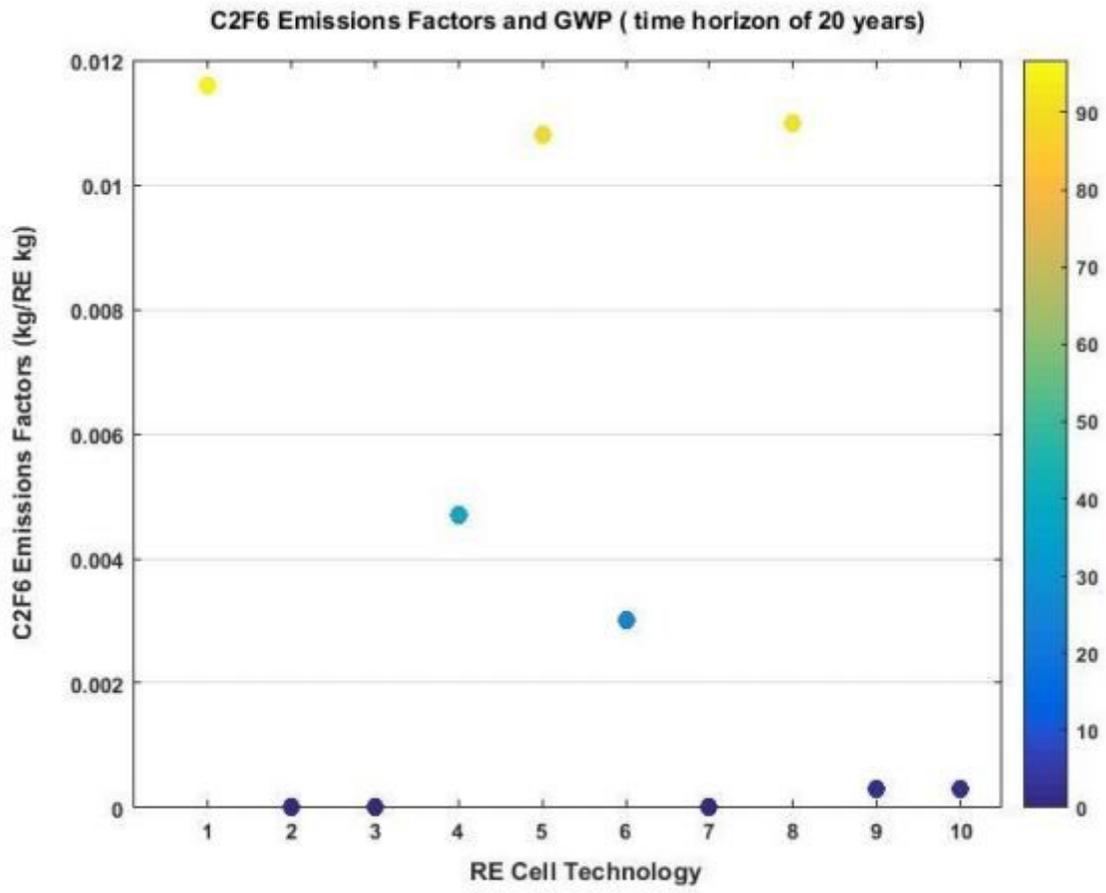


Figure 5

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

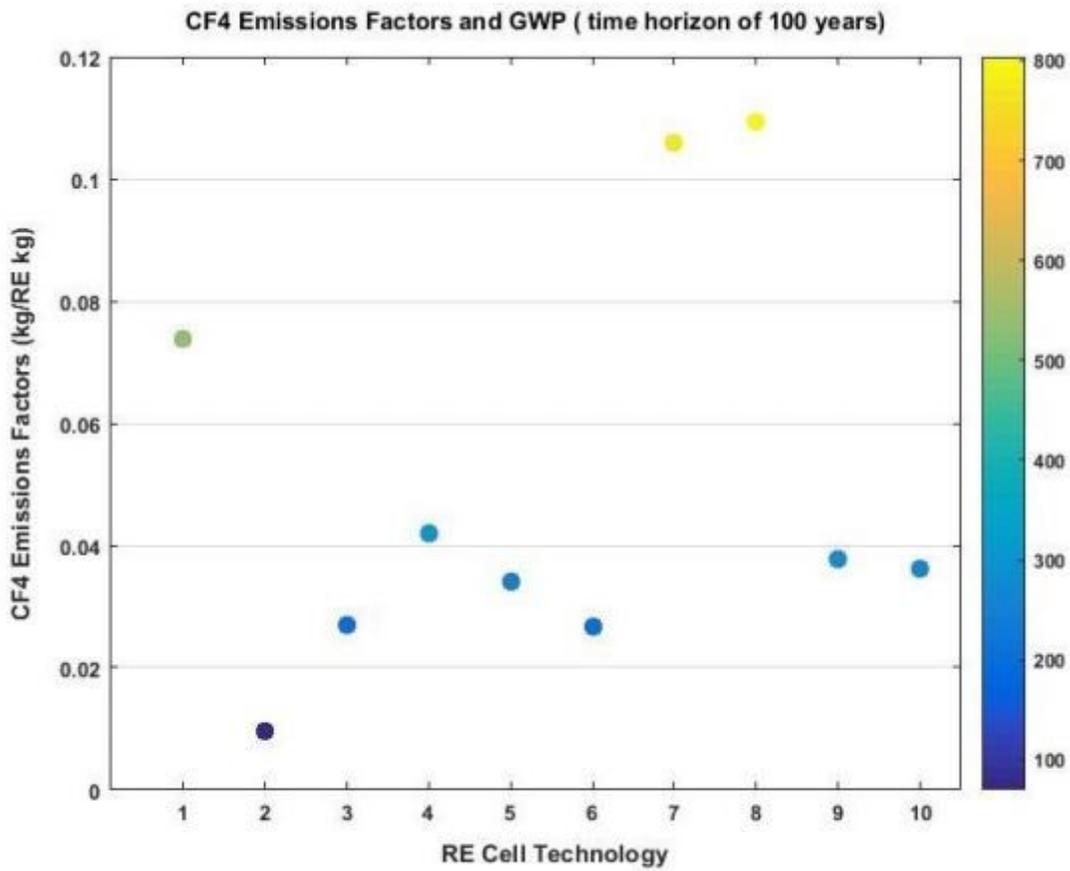


Figure 6

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

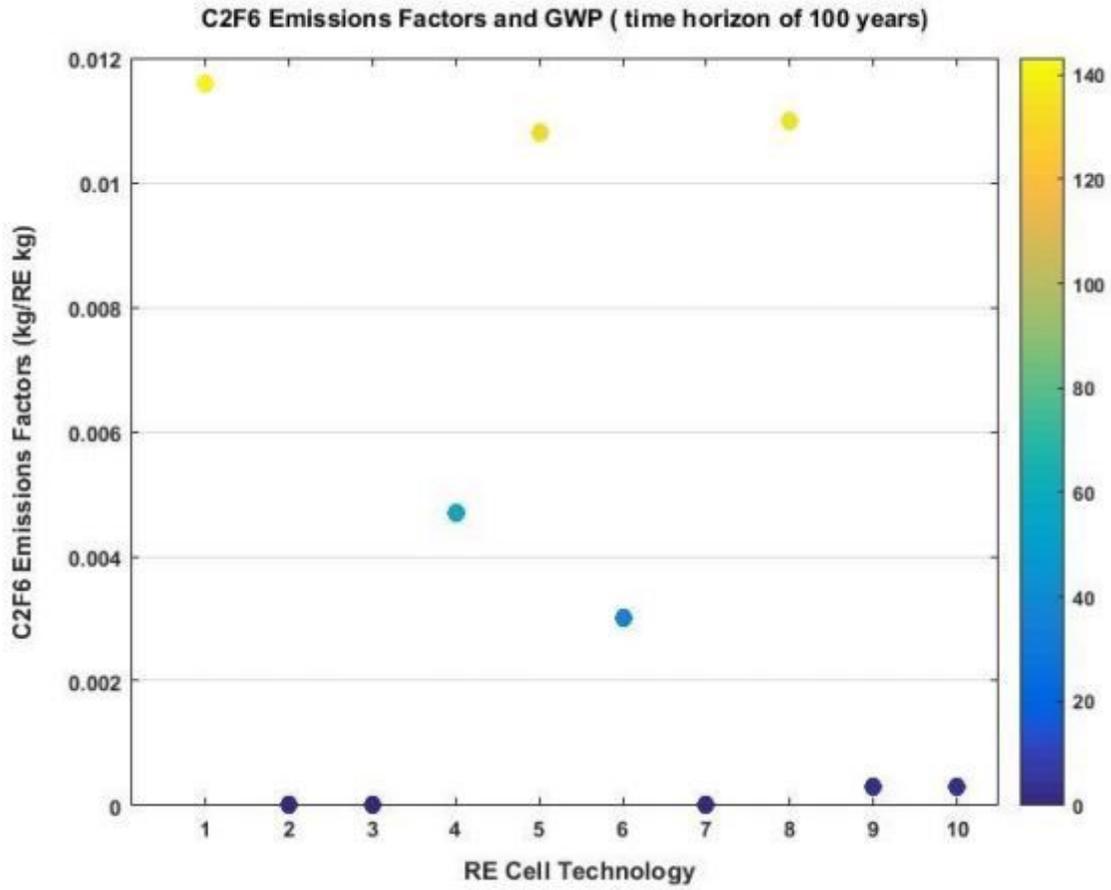


Figure 7

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