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Perfluorocarbon emissions from electrolytic reduction of rare earth metals in fluoride/oxide system

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ABSTRACT

Perfluorocarbons (PFC) are important greenhouse gas. In the aluminum electrolysis industry, PFC emission had been valued. The electrolytic reduction of rare earth metals in fluoride/oxide system with carbon anode and tungsten cathode also has PFC emission. But the PFC emission in rare earth metals industry received less attention. The PFC emissions during the electrolysis were studied by tracking the change of CF_4 concentration in the flue gas of neodymium electrolysis and dysprosium-iron alloy electrolysis. The results showed that there were continuous CF_4 overflows in the electrolysis process. The CF_4 was outburst when anode effect occurred. The anode effect was always accompanied with the low electrolysis temperature. In addition, because of the electrolytic dysprosium-iron alloy requires higher cell voltage, the PFC emissions are higher than rare earth electrolysis. In general, PFC emissions from rare earth metal electrolysis are quite same as the aluminum electrolysis industry.

1. Introduction

Perfluorocarbons (PFC) are important greenhouse gases, include tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) et al. Because of the very durable C–F bond, the PFC is difficult to decompose. The PFC has a strong infrared band absorption capacity, and can absorb considerable surface and low-level heat radiation (Environmental Protection Agency U.S.A., 2008). Global warming potential (GWP), a relative measure of how much heat a greenhouse gas traps in the atmosphere, compares the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by similar mass of CO_2 (whose GWP is standardized to 1). In the Fourth Assessment Report (AR4) of the Intergovernmental Panel on Climate Change (IPCC),[1] CF_4 has a lifetime of 50 thousand years and with climate-carbon feedbacks a global warming potential of 7390 over 100 years in response to emissions. The corresponding C_2F_6 has a lifetime of 10 thousand years and GWP is 12200 (Intergovernmental Panel on Climate Change, 2007). The electrolysis industry with fluoride salts using carbon anodes is one of the major sources of emissions of perfluorocarbons, especially in the electrolytic aluminum industry. In the year 2015, total global aluminum production 57.89 million tons and 31.41 million tons in China. The average measured PFC emissions is 0.43 t-CO_2 by one ton aluminum and the statistical output accounts for 35% of global production (International Aluminium Institute, 2016).

QianDong Rare Earths Group Co. Ltd is a group company that combines rare earth basic materials, functional materials, application products and rare earth processing equipment manufacturer. We produce about 4.2 thousand tons of rare earth metals and 0.8 thousand tons of rare earth alloy by electrolysis annual. In the recent years, total global rare earth metal/alloy production is about 50 thousand tons and 45 thousand tons in China. Qiandong output accounts for 10% of global rare earth production. In order to deeply understand the environmental impact of rare earth electrolytic production process, we took the lead in carrying out relevant research work in the rare earth industry in China.

Compared with the PFC emissions from the aluminum industry (Zhao et al., 2008; Chen et al., 2010; Xiang, 2011; Gao, 2013), there are few studies on the emission of PFC in rare earth fluoride electrolysis with carbon anodes and fluoride molten salt electrolysis systems. There is no definite industrial production of rare earth

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[1] We have used AR4 GWP's data to calculate t-CO_2e/t, to compare with the aluminum industry data in IAI report, which uses AR4 GWP's. The data in the AR5 are 6630 for CF_4 and 11100 for C_2F_6 (Myhre et al., 2013).

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metal electrolysis PFC emissions research reports. Previous research on neodymium electrolysis process and mechanism indicates sustained PFC emissions during the electrolysis and bursts of PFC emissions during anode events (Liu et al., 2001; Wang et al., 2007; Thonstad et al., 2013; Vogel and Friedrich, 2015; Lee et al., 2015). PFCs emissions in the electrolysis of rare earth metals may be produced in the following manner (Nd, for example):

$$4NdF_3 + 3C = 4Nd + 3CF_4$$

$$4LiF + C = 4Li + CF_4$$

$$2NdF_3 + 2C = 2Nd + C_2F_6$$

$$6LiF + 2C = 6Li + C_2F_6$$

Many of the published works were studied under laboratory conditions, or so called industry experimental. No PFC emissions measurement in rare earth commercial electrolysis factory was reported at present.

2. Testing and evaluation method

All the tests were conducted on the basis of conventional industrial production. The sketch of electrolytic cell was showed in Fig. 1. The same type of electrolytic cell was used for neodymium and dysprosium-iron alloy electrolysis.

For the neodymium electrolysis, the fused electrolytes were combined with 85% of NdF_3, 10% of LiF and 5% of Nd_2O_3 (w/w). A tungsten rod was used as cathode. The electrolytic cell voltage was 8–9 V and current was 5000–6000 A. The typical operation temperature was around 1420 K. During the electrolysis process, accompanied Nd_2O_3 was added to the fused electrolytes slowly, neodymium gradually deposited on the cathode and finally fall in to the crucible. At a certain period of time, the cathode was raised by the cathode lift. A hand tool was used to life the crucible and poured the metal into the mold. The crucible and cathode were returned to their original position and the electrolysis was carrying on.

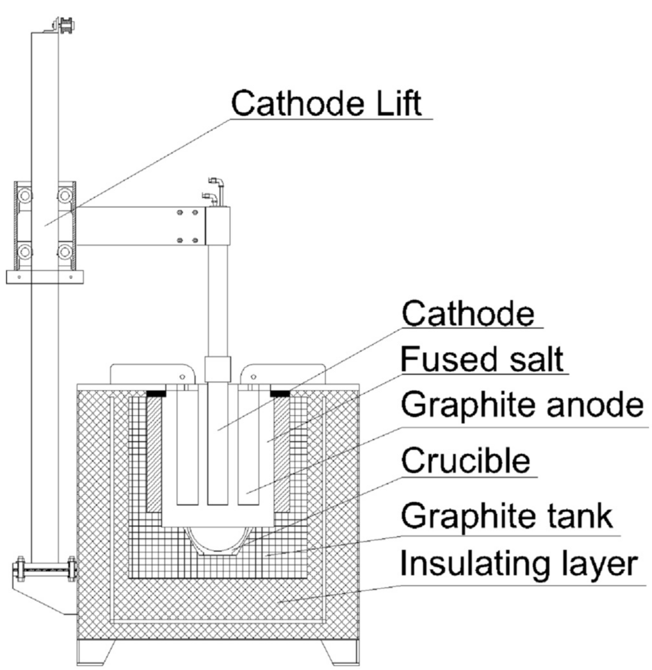

Fig. 1. The electrolytic cell both neodymium and dysprosium-iron alloy electrolytic cell.

The dysprosium-iron alloy electrolysis was quite the same as previous expect that an iron rod was used as cathode. 85% of DyF_3, 10% of LiF and 5% of Dy_2O_3 (w/w) were combined the fused electrolytes. The voltage, current and temperature for the cell were 10–11 V, 3500–4500 A and 1470 K. The voltage and temperature were higher than the neodymium electrolysis. During the electrolysis process, accompanied Dy_2O_3 was added to the fused electrolytes slowly, dysprosium gradually deposited on the cathode and dysprosium-iron alloy finally fall in to the crucible. At a certain period of time, the cathode was raised by the cathode lift. A hand tool was used to life the crucible and poured the alloy into the mold. The crucible and cathode were returned to their original position and the electrolysis was carrying on.

There are two graphite anodes in one cell. The anode is consumed in the electrolysis process. It causes the production of CO_2. At regular interval, the anode needs to be replaced one by one. When replaced anode or cathode rose, the electrolysis process is in an unconventional state or interrupted. The non-normal production status of the electrolysis reaction causes the decrease of CO_2 concentration. We use CO_2 concentration to monitor the electrolysis reaction state. High CO_2 concentration means the electrolysis reaction is in progress and the low CO_2 concentration means the reaction is different or stopped. The temperature of the cell is maintained by the thermal effect of the electrolysis reaction and current. There is no external hearting equipment. The non-normal status of electrolysis reaction also causes the fused electrolytes temperature drops.

PEC emission measurement and evaluation are based on the Protocol for Measurement of CF_4 and C_2F_6 Emissions from Primary Aluminum Production (Environmental Protection Agency U.S.A., 2008), which is recommendation by the Intergovernmental Panel on Climate Change (IPCC), International Aluminum Institute (IAI), and U.S. Environmental Protection Agency (US-EPA), and Measuring and Calculation Methods for Perfluorocarbon Emissions Resulting from a Group of Cells (Chinese Stander YS/T 801-2012) (People 's Republic of China Nonferrous Metals Industry Standard, 2012). MKS MG2030 Fourier Transform Infrared Spectrometer was used as the test equipment. We collected both CF_4 and C_2F_6 concentrations at the same time during the data collection window. But the C_2F_6 concentration was too low. After deducting the background, most of the data was negative. So we ignore the C_2F_6 data, use CF_4 data as the main PFC emissions and the evaluation source. Although COF_2 has been found as a precursor to CF_4 and C_2F_6 gas in aluminum (Dion et al., 2016), we are not able to get useful data from the FTIR spectrum to support the COF_2 component.

The PFC emissions of rare earth metal industry have not got enough attention yet. There is no corresponding emission limit in China. Here we introduce the “Perfluorocarbon Emission Limits of Electrolytic Aluminum Production (draft)” (National Standardization Technical Committee of nonferrousmetals, 2012), which will be promulgated as a Chinese National Standard in the near future, as a reference. The standard set three levels of emission quotas: the qualifying level, the new plant level and the target level. The qualifying level delegates that all existing aluminum plants' PFC emission must below that value. The new plant level indicates that all new aluminum plants' PFC emissions must not exceed that value. The target level represents the PFC emission goals of all the aluminum plant should achieve in the future. The corresponding data are listed in Table 2.

We set up three test point to do the research. 1# test point was over the neodymium electrolytic cell, 1 meter above the smelt salts, in the branch exhaust pipe inlet. 2# test point was over the dysprosium-iron alloy electrolytic cell, 1 meter above the smelt