

## ON THE MECHANISM BEHIND LOW VOLTAGE PFC EMISSIONS

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### Abstract

Recently there have been several reports on PFC emissions (CF<sub>4</sub> + C<sub>2</sub>F<sub>6</sub>) during normal operation of aluminium cells. Laboratory recordings of the so-called “critical current density” for the initiation of anode effect on carbon anodes in cryolite-alumina melts can be helpful to understand this phenomenon. When gradually raising the anodic potential, the anodic current density then increases until the alumina concentration at the anode surface approaches zero, whereby the current abruptly drops back to a much lower value, and PFC is being evolved. In an aluminium cell operating at low alumina concentration, alumina depletion may occur at one or more anodes, whereby PFC emission is initiated by this mechanism. Due to the low current density the local ohmic drop decreases, allowing the higher anode polarization needed for PFC evolution. The remaining anodes evolving CO<sub>2</sub>, may sustain normal electrolysis close to normal cell voltage. How to avoid this harmful condition is discussed.

PFC emission at close to normal cell voltage has also been observed in electrowinning of neodymium in a fluoride melt.

### Introduction

During the last 20 years strong efforts have been made in order to reduce the emission of PFC (perfluorocarbon) gases from the aluminium industry. These gases are being emitted during the so-called anode effect, which occurs when the concentration of dissolved alumina in the bath gets too low (< 0.5-2 wt%). The cell voltage then rises abruptly to 15-40 V, and an anode effect is on [1]. In order to extinguish anode effects alumina is being fed and the bath is being agitated in various ways, e.g. by inserting wooden poles or by repeatedly raising and lowering the anodes.

The PFC emissions from any given plant are being reported to the national environmental protection agency. It is being calculated by taking the time on anode effect and multiply it by an empirical factor, named “the slope”. The units are ton CO<sub>2</sub> eq./ton Al. The time on anode effect is normally recorded as the time above 8 V cell voltage. This data is being reported due to the fact that the PFC gases, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, are very potent greenhouse gases contributing to global warming. CF<sub>4</sub> is 6500 times and C<sub>2</sub>F<sub>6</sub> is 9200 times stronger greenhouse gases than CO<sub>2</sub>. The initiative for this reporting comes from “The United Nations Intergovernmental Panel on Climate Change” (IPCC), and the data are being collected and reported by the International Aluminium Institute (IAI) in London. IAI has reported that the average PFC emissions have been reduced from close to 5 ton CO<sub>2</sub> eq./ton Al in 1990 down to 0.70 in 2010, and a goal of 0.34 in set for 2020 [2].

This remarkable achievement is the result of impressive efforts made by the aluminium industry over the years by introducing

new technology and improved cell control and cell operation. This is really a success story. But is it the whole story?

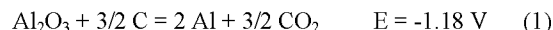
Apparently it is not the whole story. In recent years there have been several reports [2-5] showing that under certain circumstances PFC emissions are also being detected during normal operation. It has been named “non-anode effect PFC emissions” or simply “low voltage PFC emissions”.

According to our knowledge it was first observed by the late Warren Haupin of Alcoa in an internal Alcoa report in 1995 [6]. As shown below the normal cell voltage (3.7-4.5 V) is high enough to permit PFC emissions during certain operating conditions, but at that time (1990ies) we tended to think that although being possible, Haupin’s observation must have been a very extraordinary and rare event.

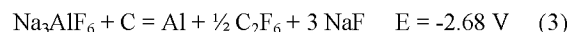
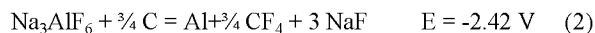
Now we know better, because several reports have come out telling the same story, i.e. that PFC emissions during normal operation is a problem, which the industry is facing. It has been reported that it tends to occur during anode changing and at the end of an underfeeding period [5]. According to Chinese data, it can amount to 34 to 93% of the total PFC emissions [3-4], the average being 70% [2]. As shown in the following, an explanation of the phenomenon can be offered based on laboratory studies of the initiation of anode effects.

### The Critical Current Density

In the normal cell reaction the anode product is CO<sub>2</sub>,



By alumina depletion, the cryolite-based electrolyte may start to be decomposed,



As shown in Fig. 1, when increasing the imposed voltage on a graphite anode, the current density increases up to a certain peak value (c), named the “critical current density”. Thereafter the current density drops back to a very low value ( $\approx 0.04 \text{ A/cm}^2$ ) at a voltage above about 3 V. This voltage is high enough to sustain the PFC formation according to reactions (2) and (3). This is exactly what happens. In a paper published in 1974 [7] we showed that in the potential range 3-3.4 V the anode gas from a cryolite melt contained 10-30 % CF<sub>4</sub> (at that time we did not have the means to detect C<sub>2</sub>F<sub>6</sub>). An alumina-containing melt would probably show lower CF<sub>4</sub> contents, but not zero.

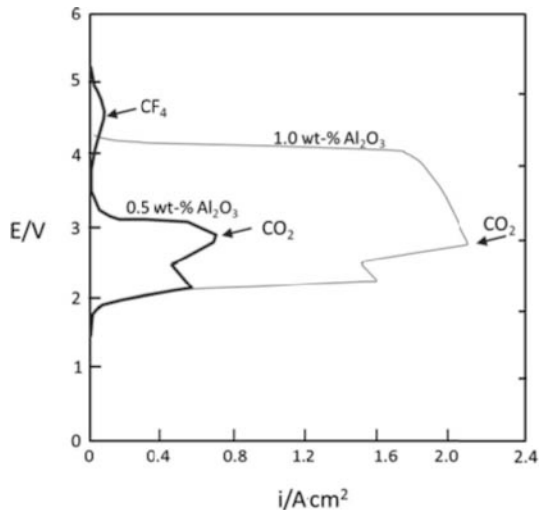


Figure 1. Linear potential sweep curves obtained with graphite anodes in cryolite melts at 1020 °C [7]. Curve I: 0.5 wt% Al<sub>2</sub>O<sub>3</sub>, Curve II: 1 wt% Al<sub>2</sub>O<sub>3</sub>.

If we now turn to an industrial cell with multiple prebaked anodes, we may have the case that one or more anodes are subjected to alumina depletion. The current density on such an anode then decreases due to a shortage of oxygen ions. This implies that the ohmic voltage drop through the anode assembly and the bath decreases, and the anode potential referred to aluminium rises accordingly. It may now pass the critical current density, as shown in Fig. 1, and enter the low current density/high voltage range shown to the left in the figure (marked by CF<sub>4</sub>). The anode may stay in this mode until a fresh supply of dissolved alumina arrives.

In Fig. 2 we illustrate this situation showing one anode sustaining normal electrolysis and one “starved” anode that in addition produces PFC gas.

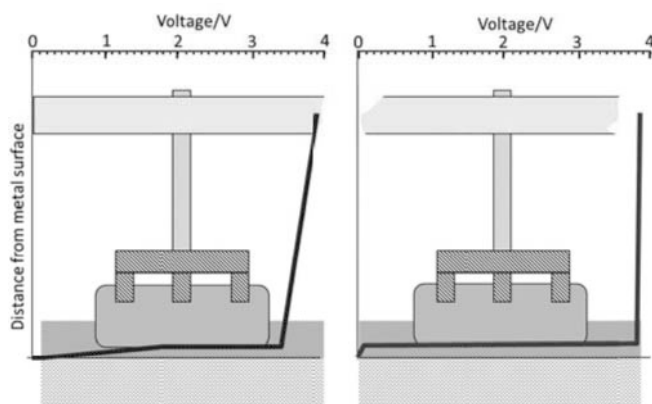


Figure 2. Schematic presentation of the voltage profile between the cathode and anode bar for an anode with normal current (left; anodic polarization voltage ~1.7 V) and an anode with low current (right; anodic polarization voltage ~3.8 V).

The real situation may be more complicated than described here, but this treatment gives at least a plausible explanation of what has been observed.

If it is so that alumina depletion is the cause of the problem, one can propose ways how to abate it. The following measures may be considered:

1. Improve the alumina distribution in the cells (install more feeders?).
2. Continuous monitoring of the current distribution on all anodes, using available automatic devices [8].
3. Run at higher average alumina concentration. Today the alumina concentration is squeezed, because it is known that a higher current efficiency can be achieved by running at low alumina. However, one might choose to sacrifice current efficiency in order to reduce harmful PFC emissions.

### Electrowinning of rare earth metals

Rare earth metals, such as, e.g., neodymium, can be produced by dissolving their oxides in fluoride melts and performing electrolysis using carbon or graphite anodes. Keller and Larimer (9) studied electrowinning of neodymium from neodymium oxide in a fluoride melt. The composition of the anode gas coming off the graphite anode is shown in Fig. 3. A relatively high voltage (and current) produced high contents of CF<sub>4</sub> -- and hence would require NdF<sub>3</sub> to be added to a cell in an industrial neodymium production. This situation can be remedied by selecting a large anode surface area, i.e. maintaining a low current density at the anode (10).

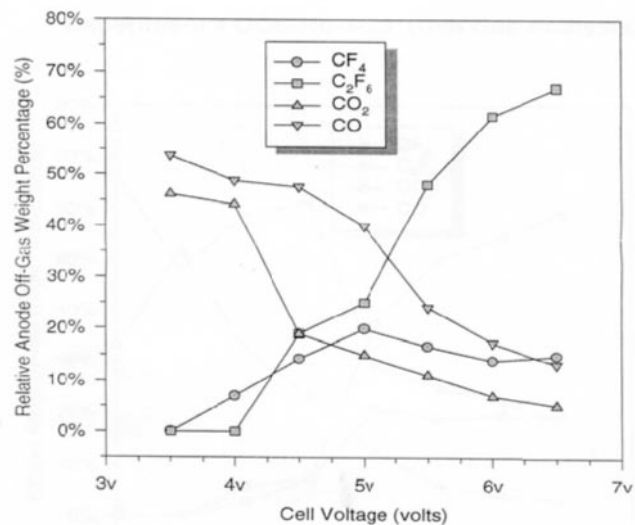


Figure 3. The composition of gas coming off a graphite anode by electrowinning neodymium from neodymium oxide dissolved in a fluoride melt (60 wt% NdF<sub>3</sub>, 20 wt% CaF<sub>2</sub>, 20 wt% LiF, with 1 wt% Nd<sub>2</sub>O<sub>3</sub> added) [9].

### Conclusions

1. It appears that the phenomenon of low voltage PFC emissions can be understood on the basis of the critical current density being reached on one or more anodes that have been subjected to alumina depletion.
2. Ways should be found in order to reduce low voltage PFC emissions.
3. Procedures must be found on how to detect and monitor low voltage PFC emissions.

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