**Light Metals 2012** *Edited by: Carlos E. Suarez*
***TMS (The Minerals, Metals & Materials Society), 2012***

# Light Metals 2012

## ALUMINUM REDUCTION TECHNOLOGY

## Anode Effect, Process Control

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# Latest Results from PFC Investigation in China

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**Abstract**

In the first half year of 2011, PFC investigation has been conducted on five potlines whose line currents are at the range of 200~350kA. The total aluminum output is 1.35 million tons per year. Both PFC caused by anode effects and PFC unrelated to anode effects were monitored and calculated. $C_3F_8$ was observed during anode effects for the first time and its peaks were at the same location as $C_2F_6$ and $CF_4$ at the timetable. The weigh ratio of $C_3F_8/CF_4$ was 4.19%, and that of $C_2F_6/CF_4$ was 11.61%. $C_3F_8$ was observed only in the monitoring of two potlines and no $C_3F_8$ in the other three potlines. Concentration curves of $C_3F_8$ were plotted with $C_2F_6$. Percentage of Non Anode Effect PFC (NAE-PFC) of five potlines was calculated. The highest was 92.8% while the potline has the lowest anode effect frequency (AEF) and its AEF is 0.01 AEs/cell-day.

## Introduction

The Advanced Global Atmospheric Gases Experiment (AGAGE) published their report in the year of 2010 (1). They claimed that they had found much more $C_3F_8$ in the air by high-frequency in situ $CF_4$, $C_2F_6$, and $C_3F_8$ measurements in the vicinity of some important regional sources. Anthropogenic PFC sources are thought to be primary aluminum production, semiconductor manufacture and refrigeration use. United Nations Framework Convention on Climate Change (UNFCCC) $CF_4$ and $C_2F_6$ emission estimation are only about 30%~70% of global AGAGE top-down emissions, since non-Annex I countries with significant Al production (i.e., China, Brazil, South Africa, India, United Arab Emirates, Bahrain) and semiconductor manufacture are not included in UNFCCC data. UNFCCC $C_3F_8$ emission estimates are 8~32 times lower than AGAGE top-down emissions. The industrial production and usage of $C_3F_8$ should be investigated to find the missing emission sources.

Zhengzhou Research Institute of CHALCO (ZZRI), China National Engineering & Technology Research Centre for Aluminum, has mapped-out a research plan to investigate NAE-PFC and $C_3F_8$ emissions in China. The research plan covers 25% Chinese aluminum production whose line current is 200~400 kA. The PFC research is getting support from CHINALCO, CNIA and IAI.

PFC surveys were performed in China according to accepted IAI/US-EPA measurement methodology (2). Five potlines were investigated this year. All potlines are at normally-operated status. Three from five potlines have very low PFC emissions which are lower than IAI 2020 target 0.35 $tCO_2e/t\text{-}Al$ (3). NAE-PFC and $C_3F_8$ emissions were investigated and calculated (4).

## Measurement Equipment

The equipment is DX4000 Fourier transform infrared (FTIR) gas analyser which comes from Finland Gasmet Technologies Oy. DX4000 FTIR is particularly well suited for the measurement of PFC emissions at production sites (see figure 1). The unit is highly portable due to its rugged construction, relatively light weight, 13.9 kg, and has a detector that is cooled to a temperature of about -30 °C with a thermo-electrically cooled mercury cadmium telluride (MCT) detector. Its optical path length is 9.8 meters. The measurements can achieve parts-per-billion (ppb) detection levels. Gasmet portable sampling system is accompanying with the FTIR.

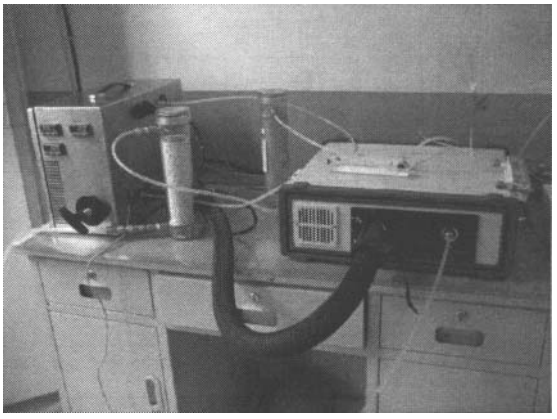

Figure 1 DX4000 in working

## Results and Discussions

Summary of PFC Surveys in 2011

During the first half of this year, ZZRI has finished PFC surveys on five potlines with line current of 200~350 kA. Their capacity is 1.35 million tons. AE-PFC and NAE-PFC were monitored at the same time.

Table I Proportion of Continuous $CF_4$ Emission

| potlines | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Line current, kA | 350 | 350 | 200 | 300 | 200 |
| AEF, AEs/cell-day | 0.01 | 0.10 | 0.16 | 0.08 | 0.04 |
| AED, min | 1.00 | 1.57 | 1.59 | 1.87 | 1.83 |
| PFC, $tCO_2e/t\text{-}Al$ | 0.22 | 0.90 | 0.77 | 0.18 | 0.21 |
| NAE-PFC, % | 92.80 | 85.53 | 75.94 | 46.27 | 34.02 |

PFC emissions from these potlines were calculated, the highest is 0.90 $tCO_2e/t\text{-}Al$ and the lowest is 0.18 $tCO_2e/t\text{-}Al$ (see Table I). Anode effect frequency is at the range of 0.01~0.39 AEs/cell-day. The best AEF is 0.01, median AEF is 0.1. Anode effect duration is at the range of 1.00~1.87 minutes. The best is 1 minute, median

AED is 1.59 minutes. Weight ratio of NAE-PFC is also calculated. The highest is 92.8% while the potline has best AE performance and its AEF is 0.01.

Mean PFC emission is 0.65 $tCO_2e$/t-Al, which is better than last year's data 0.69 $tCO_2e$/t-Al. $C_3F_8$ was observed only in the monitoring of fourth and fifth potlines and no $C_3F_8$ in the other three potlines.

Survey Results from the Fourth Potline

Line current of the 4# potline is 300 kA. The sampling location included exhaust gas from 84 cells. Monitoring duration was 85.68 hours. Its AEF was 0.08 anode effects per cell day and its AED was 1.87 minutes. During the survey, AE-PFC and NAE-PFC were investigated. The average concentration of NAE-$CF_4$ was 0.04ppm (see figure 2). $C_3F_8$ was observed during anode effects for the first time and its peaks were at the same location as $C_2F_6$ and $CF_4$ at the timetable (see figure 3 and figure 4).

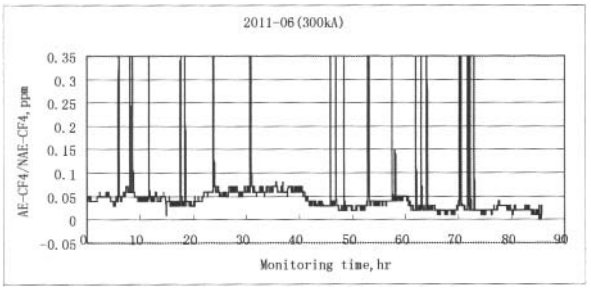


Figure 2 AE-$CF_4$ and NAE-$CF_4$ from 4# potline

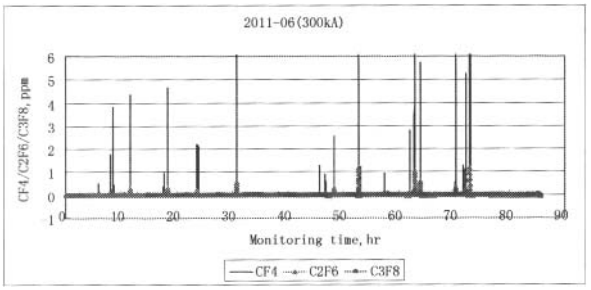


Figure 3 AE-PFC Peaks of 4# potline

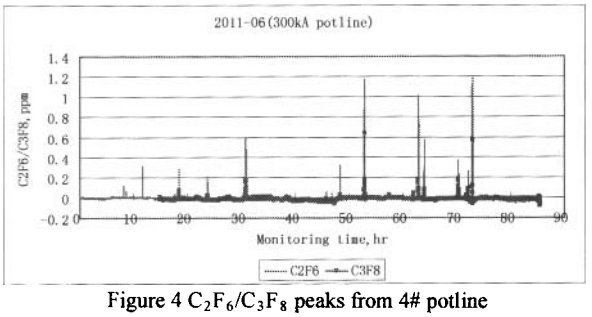


Figure 4 $C_2F_6/C_3F_8$ peaks from 4# potline

It can be seen from figure 2~figure 4 that baseline for $CF_4$ is always positive, but there is negative baseline of $C_2F_6$ and $C_3F_8$ concentration sometimes. Accumulative total concentration of three PFC compounds during anode effects is listed in Table II.

Table II AE-PFC Concentration from 4# Potline

| AE-PFC | AE-$CF_4$ | AE-$C_2F_6$ | AE-$C_3F_8$ |
|---|---|---|---|
| ppm | 685.99 | 51.01 | 12.03 |

From Table II, the weight ratio of $C_2F_6/CF_4$ and $C_3F_8/CF_4$ can be calculated according Tier 3 [2]. The weight ratio of $C_2F_6/CF_4$ is 11.66% and that of $C_3F_8/CF_4$ is 3.75%.

Survey Results from the Fifth Potline

Line current of the 5# potline is 200 kA. The sampling location included exhaust gas from 106 cells. Monitoring duration was 90.83 hours. Its AEF was 0.04 anode effects per cell day and its AED was 1.83 minutes. During the survey, AE-PFC and NAE-PFC was also investigated. The average concentration of NAE-$CF_4$ was 0.02ppm (see figure 5). $C_3F_8$ was also observed during anode effects (see figure 6 and figure 7).

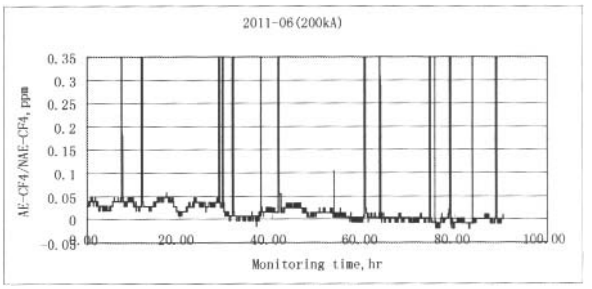


Figure 5 AE-$CF_4$ and NAE-$CF_4$ from 5# potline

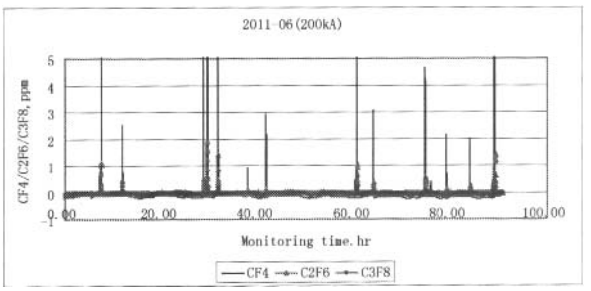


Figure 6 AE-PFC Peaks of 5# potline

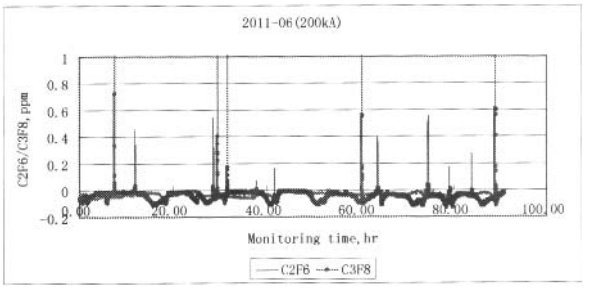


Figure 7 $C_2F_6/C_3F_8$ peaks from 5# potline

It can be seen from figure 5~figure 7 that baseline for $CF_4$ is always positive, but there was much more negative baseline of $C_2F_6$ and $C_3F_8$ concentration at the fifth potline than the fourth potline. The main reason is that there was much water vapor in the

gas sample which caused these negative deviations. There was continuous rain at site for almost one week forcing us to change dryer twice a day (see figure 8).

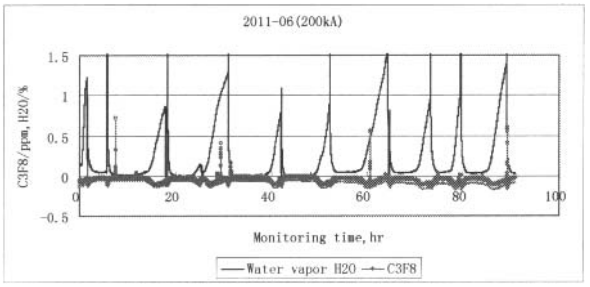


Figure 8 Water vapor and $C_3F_8$ from 5# potline

It can be seen clearly from figure 8 that when water vapor concentration in gas sample goes up, the baseline of $C_3F_8$ drops down.

Accumulative total concentration of three PFC compounds during anode effects is listed in Table III.

Table III AE-PFC Concentration of 5# Potline

| AE-PFC | AE-$CF_4$ | AE-$C_2F_6$ | AE-$C_3F_8$ |
|---|---|---|---|
| ppm | 639.48 | 47.19 | 13.89 |

From Table III, the weight ratio of $C_2F_6/CF_4$ and $C_3F_8/CF_4$ was also calculated. The weight ratio of $C_2F_6/CF_4$ was 11.57% and that of $C_3F_8/CF_4$ is 4.64%.

Results from Single-cell Measurements

Single-cell measurements were performed in order to learn further information about $C_3F_8$ and NAE-PFC emission. Two 300 kA cells were chosen for studying. Codes of two 300kA cells are 115# and 116#. Sampling location sketch map of single-cell measurement is plotted in figure 9.

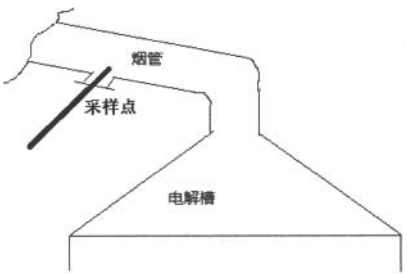


Figure 9 Sampling location of single-cell measurement

Results from 115# cell

Monitoring duration is 95.26 hours. Nine anode effects were monitored. The highest peaks of $CF_4$, $C_2F_6$ and $C_3F_8$ were 330.25ppm, 42.73ppm and 4.26ppm respectively (see figure 10 and figure 11). Accumulative total concentration of three PFC compounds during anode effects is listed in Table IV.

Table IV AE-PFC Concentration of 115# Cell

| AE-PFC | AE-$CF_4$ | AE-$C_2F_6$ | AE-$C_3F_8$ |
|---|---|---|---|
| ppm | 12530.73 | 1460.54 | 184.76 |

The weight ratio of $C_2F_6/CF_4$ and $C_3F_8/CF_4$ was also calculated. The weight ratio of $C_2F_6/CF_4$ was 18.28% and that of $C_3F_8/CF_4$ is 3.15%.

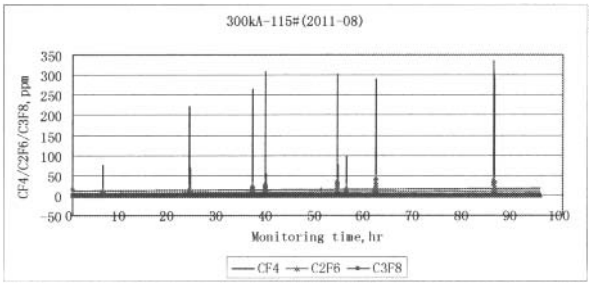


Figure 10 $CF_4/C_2F_6/C_3F_8$ peaks of 115# cell

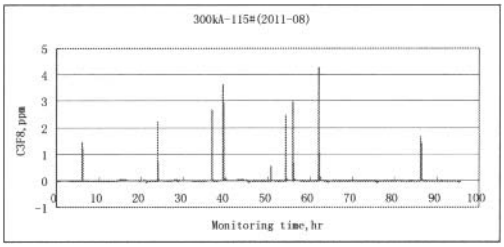


Figure 11 $C_3F_8$ peaks of 115# cell

It can be seen from figure 10~figure 11 that highest peaks of $C_2F_6$ were not always at the same time point as those of $CF_4$. Similar situation happened to $C_3F_8$. To our surprise, more than two peaks of $C_3F_8$ were observed during anode effects (see figure 12). The average concentration of NAE-$CF_4$ was 0.055ppm (see Figure 13).

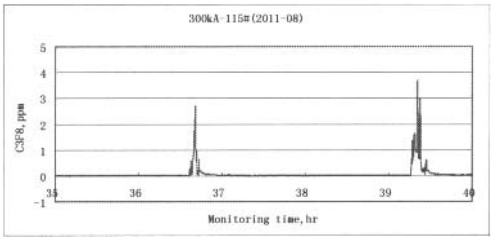


Figure 12 $C_3F_8$ peaks during anode effects

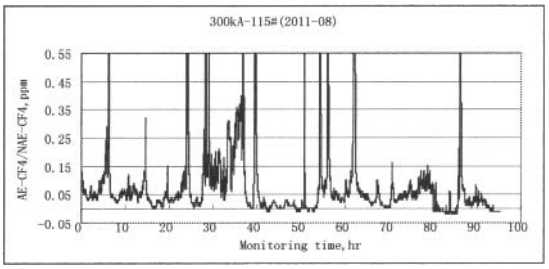


Figure 13 AE-$CF_4$ and NAE-$CF_4$ from 115# cell

Results from 116# cell

116# cell locates at the same potline as 115# cell and next to 115# cell. Monitoring duration is 15.90 hours. Two anode effects were monitored. The highest peaks of $CF_4$, $C_2F_6$ and $C_3F_8$ were

308.63ppm, 29.37ppm and 3.92ppm respectively (see figure 14 and figure 15). Accumulative total concentration of three PFC compounds during anode effects is listed in Table V.

Table V AE-PFC Concentration of 116# Cell

| AE-PFC | AE-$CF_4$ | AE-$C_2F_6$ | AE-$C_3F_8$ |
|---|---|---|---|
| ppm | 3786.70 | 390.75 | 57.08 |

The weight ratio of $C_2F_6/CF_4$ and $C_3F_8/CF_4$ was also calculated from Table V. The weight ratio of $C_2F_6/CF_4$ was 16.18% and that of $C_3F_8/CF_4$ is 3.22%.

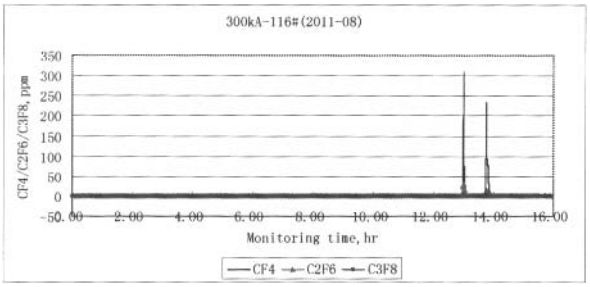


Figure 14 $CF_4/C_2F_6/C_3F_8$ peaks of 116# cell

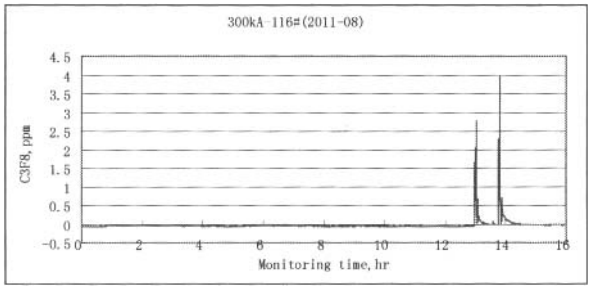


Figure 15 $C_3F_8$ peaks of 116# cell

It can be seen from figure 14~figure 15 that highest peaks of $C_3F_8$ were not always at the same time point as those of $CF_4$. More than two peaks of $C_3F_8$ were observed as well during anode effects (see figure 15). The average concentration of NAE-$CF_4$ was 0.22ppm (see Figure 16).

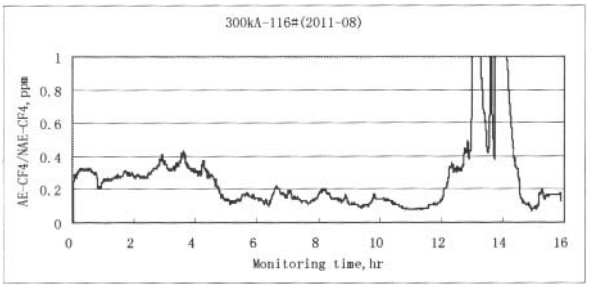


Figure 16 AE-$CF_4$ and NAE-$CF_4$ from 116# cell

## Conclusions

PFC surveys has been conducted on five potlines whose line currents are at the range of 200~350kA. AE-PFC and NAE-PFC were monitored. Percentage of NAE-PFC from five potlines was calculated while the highest was 92.8% and the lowest was 34.02%.

$C_3F_8$ was observed during anode effects for the first time and its peaks were at the same location as $CF_4$ at the timetable. Different potlines had different $C_3F_8/CF_4$ weight ratio. The average weight ratio of $C_3F_8/CF_4$ was 4.19% and that of $C_2F_6/CF_4$ was 11.61%. $C_3F_8$ was observed only in fourth and fifth potlines and no $C_3F_8$ in the other three potlines. Concentration curves of $C_3F_8$ were plotted with $CF_4$ and $C_2F_6$.

Single-cell measurements were performed in order to learn further information about $C_3F_8$ and NAE-PFC. Different cells had different $C_3F_8/CF_4$ weight ratio. $C_3F_8/CF_4$ weight ratio of 115# cell and 116# cell were 3.15% and 3.22%, respectively. Those of $C_2F_6/CF_4$ were 18.28% and 16.18%. Highest peaks of $C_3F_8$ were not always at the same time point as those of $CF_4$. Furthermore, more than two peaks of $C_3F_8$ were observed during anode effects.

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