

INVESTIGATION ON FORMATION MECHANISM OF NON-ANODE EFFECT RELATED PFC EMISSIONS FROM ALUMINUM REDUCTION CELLS

Chen Xiping, Li Wangxing, Zhang Yanfang, Qiu Shilin
 (Zhengzhou Research Institute of CHALCO, Zhengzhou China 450041)
 (China National Engineering & Technology Centre for Aluminum, Zhengzhou China 450041)

Chris Bayliss
 (The International Aluminium Institute, London SW1Y 4TE, UK)

Keywords: Non-anode effect, PFC emissions, Formation mechanism, Aluminum reduction cells

Abstract

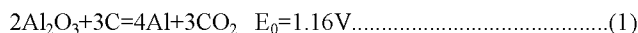
Influencing factors on PFC (perfluorocarbon) emission were investigated in Chinese smelters. The formation mechanism of non-anode effect related PFC emissions (short as NAE-PFC) from aluminum reduction cells were discussed. Anodic overvoltage has an obvious influence on NAE-PFC formation, CF_4 will emit when anodic overvoltage is higher than 2.55 volts, C_2F_6 will be generated when anodic overvoltage surpasses 2.68 volts. Alumina concentration in bath with anodic current density also has a clear influence on NAE-PFC formation. Alumina fluctuates in large cells from the metal-tapping-end to the flue-end. Alumina always distributes unevenly in the bath because of bath flow driven by magnetic fields, which will also cause NAE-PFC formation. NAE-PFC will emit when there is not enough alumina under certain anode's bottom. The limit alumina concentration is 75% of normal level which is 2.0-3.5% in Chinese smelters. Cells will generate NAE-PFC when any anode's current density is higher than 1.5 times of normal level which is 0.72-0.80A/cm² in Chinese smelters.

Introduction

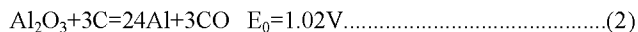
Each aluminum reduction cell emits PFCs (perfluorocarbons) when an anode effect occurs. PFC investigations were performed in China since 2008. Low levels of PFC were observed when no anode effects arise in aluminum reduction cells [1]. This type of PFC is different from PFC related to anode effect (short as AE-PFC). NAE-PFC has much lower concentration than AE-PFC [2]. Dr Jerry Marks also observed CF_4 unrelated to anode effects in smelters outside China [3]. PFC emissions unrelated to anode effects were defined as NAE-PFC or continuous PFC. NAE-PFC emission characteristic is not similar to that of AE-PFC. More attention has been given to NAE-PFC since then..

Formation Mechanism of NAE-PFC

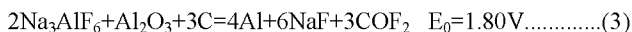
Carbon anodes are easily polarized during the aluminum electrolysis process. When anodic current density is at normal level, anodic reactions will generate CO_2 (see reaction 1).



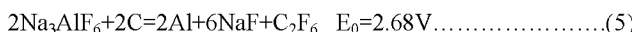
When anodic current density is a little lower than normal, anodic reactions will generate CO (see reaction 2).



When anodic current density is much lower than normal, anodic reactions will generate COF_2 (see reaction 3). COF_2 is an unstable compound and will easily decompose and form CF_4 .



When anodic polarization worsens, anodic reactions will generate CF_4 and C_2F_6 (see reactions 4 and 5).



Anodic polarization will cause anodic overvoltage. When anodic overvoltage reaches formation electric potential of CF_4 , CF_4 will be generated. C_2F_6 will be generated if anodic overvoltage goes up further.

Theory of Anodic Overvoltage

With respect to H-H aluminum reduction process, anodic overvoltage generally includes reaction overvoltage and diffusion overvoltage. Reaction overvoltage, usually accompanying with anodic reactions, can be denoted by equation (1).

$$\eta_{RA} = - \frac{RT}{\alpha nF} \ln \frac{i_A}{i_O} \quad (1)$$

Where:

- η_{RA} = Reaction overvoltage
- T = Bath temperature, K
- R, F = Constant
- n = Electrons transferring in electrode reactions, n = 2
- α = Electric charge transferring coefficient, usually at the range of 0.52~0.56
- i_A = Anodic current density, A/cm²
- i_O = Exchanging current density, the function of alumina concentration, A/cm²

When alumina concentration in bath is at the range of 2%~5% (wt), i_O can be expressed by equation (2).

$$i_O = 0.002367 + 0.000767(Al_2O_3\%) \dots\dots\dots(2)$$

Where:

- $Al_2O_3\%$ = Alumina concentration in the cell

When alumina concentration drops continuously, diffusion overvoltage will appear on the surface of carbon anode. Equation (3) is the expression of diffusion overvoltage.

$$\eta_{CA} = -\frac{RT}{2F} \ln \frac{i_{cr}}{i_{cr} - i_A} \quad (3)$$

Where:

η_{CA} = Diffusion overvoltage or concentration overvoltage
 i_{cr} = Limit anodic current density, A/cm². It can be expressed by the following experiential formula.

$$i_{cr} = [5.5 + 0.018(T - 1323)]A^{-0.1} [(Al_2O_3\%)^{0.5} - 0.4] \quad (4)$$

Where:

A = Bottom area of single anode, cm²
 T = Bath temperature, K

Above-mentioned equations (1)-(4) described interdependences among anodic current density, anodic overvoltage and alumina concentration. Their interdependences are plotted in Figure 1.

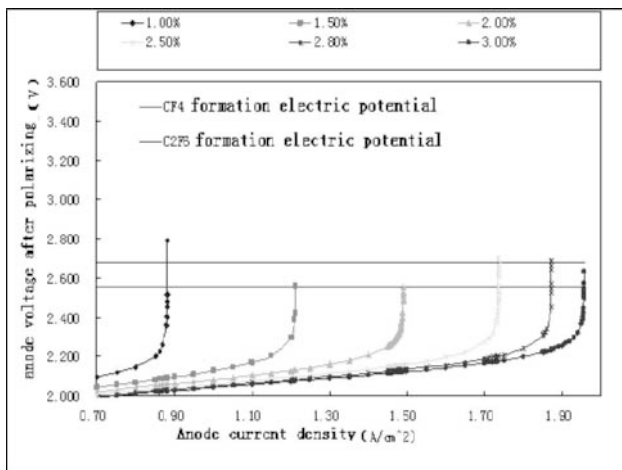


Figure 1. Interrelation between polarized anode voltage, alumina concentration (%) and anodic current density

When aluminum reduction cells run under stated alumina concentrations, anode polarization will worsen with rising of anodic current density. When anodic current density continues to rise and reaches the limits shown, anodic overvoltage will rise sharply. When anodic overvoltage reaches the formation electric potential of PFC, PFC will generate in the cells. The higher alumina concentration is, the higher is the limit of i_A . On the opposite, if alumina concentration is low, the limit of i_A which can cause PFC will be low.

Rising anodic overvoltage is the inducement which causes generation of PFC. Anodic overvoltage will increase sharply if alumina concentration is low enough or i_A is high enough. NAE-PFC has characteristic of much lower level than AE-PFC. This suggests NAE-PFC will generate at partial area in the cell when i_A is high enough or alumina concentration is low enough.

Theory of Alumina Diffusion

Flow Field in Aluminum Reduction Cells

Flow field in aluminum reduction cells includes flow field of aluminum liquid and flow field of electrolyte. Flow fields of aluminum liquid and electrolyte were simulated and plotted in Figure 2.

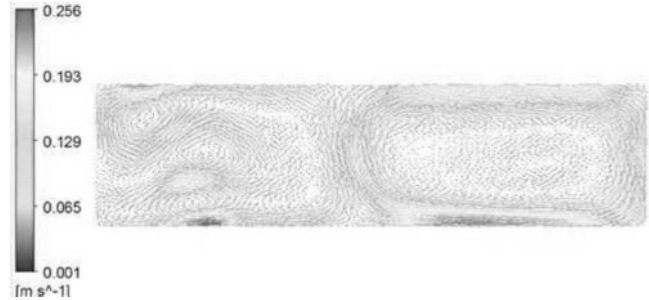


Figure 2a. Flow field distribution of aluminum liquid

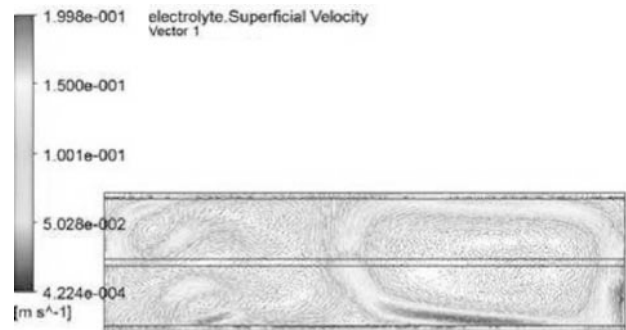


Figure 2b. Flow field distribution of electrolyte

Simulation of Alumina Movement

The simulation model was designed based on industrial aluminum reduction cells. Line current is 300kA. There are six feeders in the 300kA aluminum reduction cell normally. Each feeder feeds 1.8 kilograms alumina into the cell every time. Figure 3 is sketch map of feeders' position.

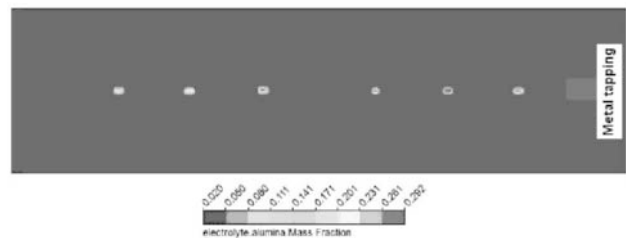


Figure 3. Alumina feeding locations of a 300kA cell

Alumina feeding and diffusion were demonstrated in order to study alumina concentration distribution in aluminum reduction cells. First, electromagnetic force was obtained via calculation by ANSYS electromagnetic field model. Electromagnetic force would be used as driven force for flow field model. Then, flow field model was set up via simulation calculation by CFX equal two-phase flow model with free flow based on CFX software.

Finally, alumina concentration distributing maps were got via simulation calculation by VOF momentary diffusion model based on VOF elements (see Figure 4).

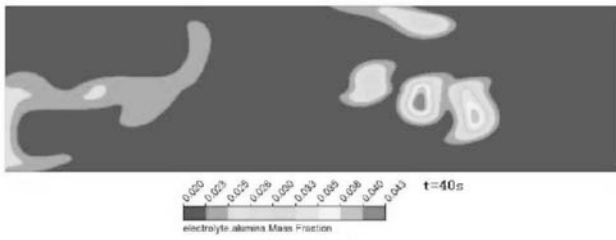


Figure 4a

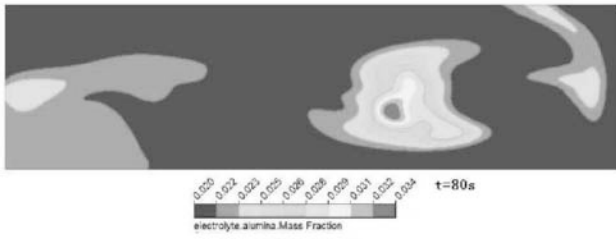


Figure 4b

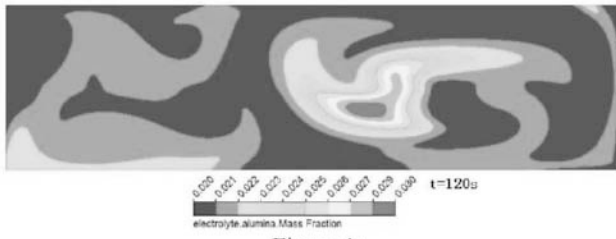


Figure 4c

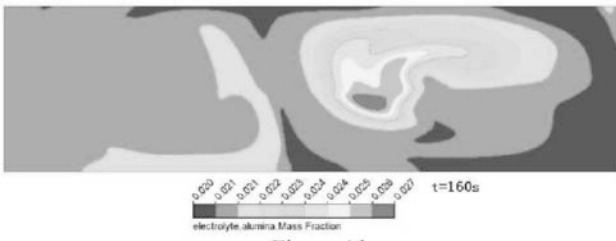


Figure 4d

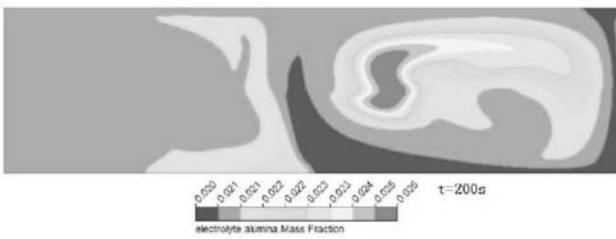


Figure 4e

Figure 4. Diffusion and distribution status of alumina

It can be seen obviously from Figure 4 that alumina can diffuse all over the cell at 200 seconds after feeding. Alumina concentration is high in red area coverage and low in blue area coverage. In Chinese smelters, feeding cycle is usually 100

seconds. That means alumina will settle much more easily during overfeeding and some other places will be short of alumina.

Diffusion movement status of alumina has close correlation to flow field distribution. Distribution characteristic of alumina at different position is dependent on flow status of electrolyte at this place. If electrolyte flow at certain place is fast, alumina will move with the flow quickly, thus alumina concentration will be low at the place. If the electrolyte flow is slow and not enough to drive alumina, alumina will settle at the place. Alumina easily settles at the center of flow burbles and nearby feeders.

Results and Discussion

Influences of Alumina Concentration on NAE-PFC

Influences of alumina concentration on NAE-PFC were discussed. Research object is one 300kA aluminum reduction cell. Six-hole sampling and twelve-hole sampling tests were implemented respectively. Electrolyte was sampled once per hour and oxygen content in the electrolyte was determined and alumina concentration was calculated. Oxygen content was measured with LECO-RO500C. Figure 5 is sketch map of holes in six-hole sampling test. Median alumina concentration from the test was plotted in Figure 6.

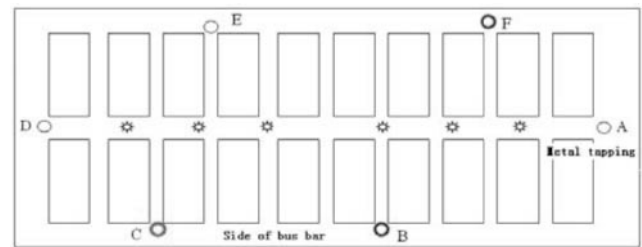


Figure 5. Sketch map of six-hole sampling

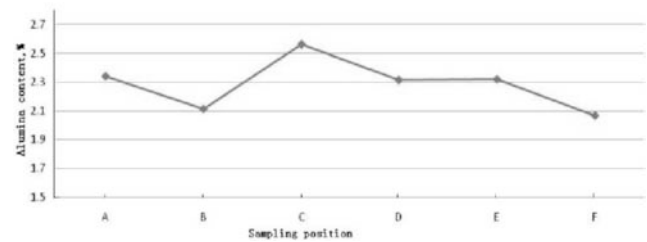


Figure 6. Alumina concentration of six-hole sampling

It can be seen clearly from Figure 6 that alumina concentration was at the range of 2.0%~2.6% and alumina concentration was low at positions B and F.

Figure 7 is sketch map of holes in twelve-hole sampling test. Median alumina concentration from the test was plotted in Figure 8.

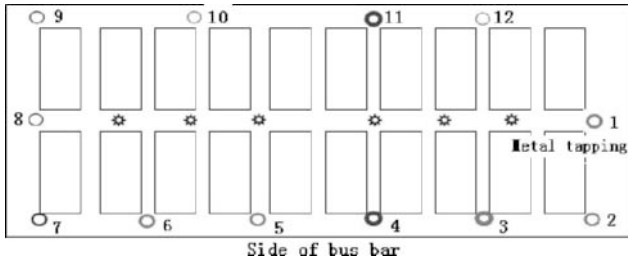


Figure 7. Sketch map of twelve-hole sampling

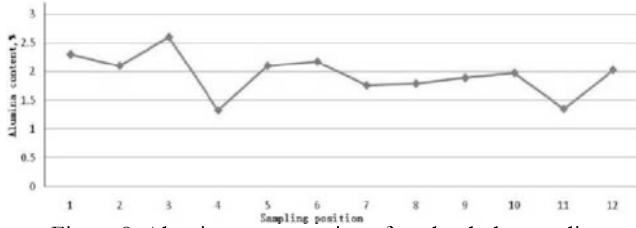


Figure 8. Alumina concentration of twelve-hole sampling

It can be seen obviously from Figure 8 that alumina concentration was at a wider range of 1.3%~2.6%. Alumina concentration was low at positions 4 and 11. More practical alumina concentration can be got from twelve-hole sampling than six-hole sampling. Results from alumina concentration tests were consistent with simulation results.

Alumina concentration has a good relativity to NAE-PFC. Their relation can be described by the following experiential formula and plotted in Figure 9. It seemed that CF₄ would not generate when C_{Al₂O₃} was higher than 2.0%, normal level in Chinese industrial aluminum reduction cells.

$$Y=0.1941-0.822/C_{Al_2O_3}+0.8835/(C_{Al_2O_3})^2 \dots\dots\dots (5)$$

Where:

C_{Al₂O₃}: alumina concentration, wt%

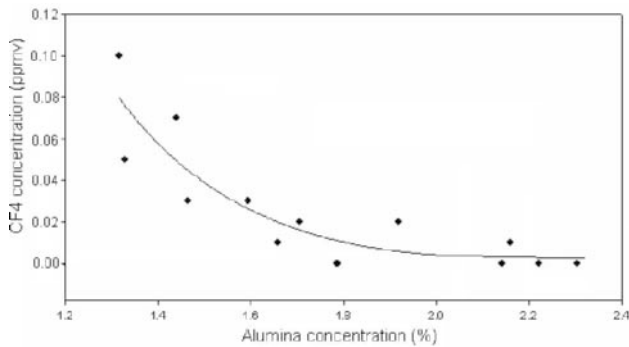


Figure 9. Interrelation of NAE-PFC to C_{Al₂O₃}

Influences of alumina concentration on NAE-PFC were studied on 300kA aluminum reduction cells. Results from measurements are demonstrated in Figure 10.

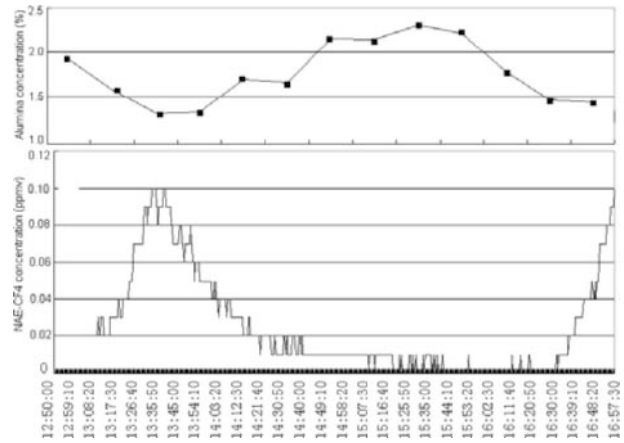


Figure 10. Curves of NAE-CF₄ and alumina concentration

It can be observed from Figure 10 that NAE-CF₄ would emit when alumina concentration in cells was lower than 1.5%, 75% of normal level 2.0%. NAE-CF₄ would drop to zero when alumina concentration in cells went up over 2.0%, the normal level. Results from investigations on industrial aluminum reduction cells had excellent accordant trend to that in Figure 9.

Influences of Anodic Current Density on NAE-PFC

Anode current of cells was usually measured with a millivolt fork. Voltage drop is measured on every anode rod between two probes at fixed distance apart. The current in each rod is:

$$I_i = \frac{\Delta V_i}{R_i} = \frac{\Delta V_i A}{\rho(T_i)L} \dots\dots\dots(6)$$

Where:

- ΔV_i = mV drop
- R_i = Resistance of the rod between the fork tines
- A = Cross-section of the rod
- ρ_i = Resistivity of the rod (function of rod temperature T_i between the tines)
- L = Distance between fork tines

In cell control practice it is assumed that all the rods have the same temperature. Then, the resistance is the same in each rod and will fall out in the calculation. The sum of measured electric currents in individual rods is then easily normalized to the line current. Measured current distribution in anode rods is normalized to line current in the following way:

$$I_{i-norm} = \frac{(\Delta V)_i}{\sum_1^N (\Delta V)_i} I_{Line} \dots\dots\dots(7)$$

Where:

- I_{i-norm} = Normalized current in each anode rod, kA
- I_{Line} = Line current, kA
- (ΔV)_i = Individual rod voltage, mV
- N = Number of anode rods.

Anodic current density also has a close connection with alumina concentration described in the following experiential formula and plotted in Figure 11.

$$i_a = -0.0733 \cdot (C_{Al_2O_3})^2 + 0.8268 \cdot C_{Al_2O_3} - 0.1509 \dots \dots \dots (8)$$

Where, i_a is anodic current density.

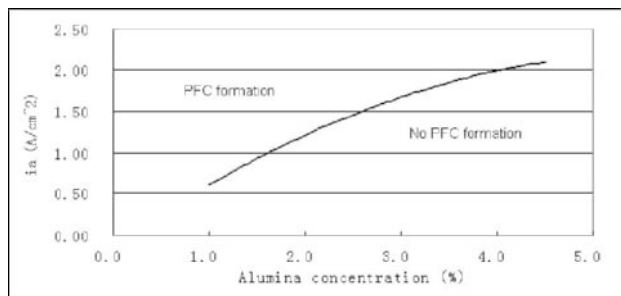


Figure 11. Connection of i_a to $C_{Al_2O_3}$

In Chinese smelters, normal level of anodic current density is 0.75-0.8A/cm². Sometimes anodic current density would rise because of anodic polarization. PFC would emit when anodic current density was higher than 1.2A/cm², 1.5 times of normal level. It can be seen from Figure 11 that PFC easily emit on the left side of the curve and would not generate on the right side of the curve.

PFC measurements were performed on 300kA cells in order to study influences of anodic current density on NAE-PFC. Results were demonstrated in Figure 12.

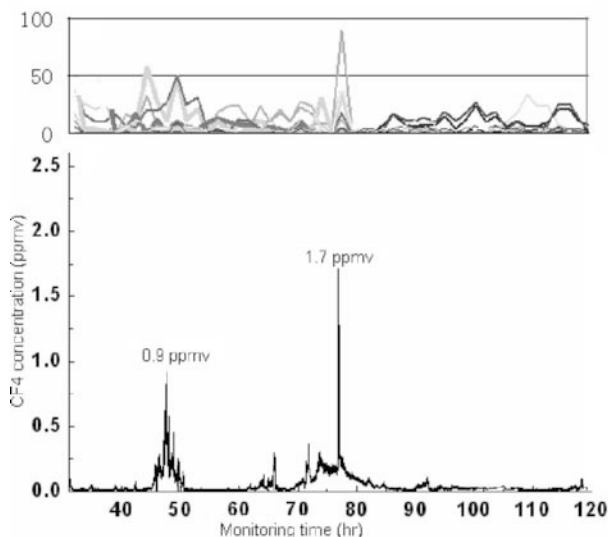


Figure 12. Influences of anodic current density on NAE-PFC

PFC easily emitted when anodic current density of certain anodes went up (see Figure 12).

Conclusions

Anodic current density has an obvious influence on NAE-PFC. PFC would emit when anodic current density was higher than 1.2A/cm², 1.5 times of its normal level. Generation of NAE-PFC also has a close connection with alumina concentration. NAE-PFC arose when alumina concentration was lower than 1.5w%,

75% of its normal level. Anodic overvoltage can influence formation of NAE-PFC. With worsening of anodic polarization, PFC would form when anodic overvoltage reached formation electric potential of PFC.

Acknowledgement

This work is supported by The National Natural Science Foundation of China (No. 50974127) and The National Key Technology R&D Program (No. 2009BAB45B03).

References

1. Li Wangxing, Chen Xiping, and Chris Bayliss, "On Continuous PFC Emission Unrelated to Anode Effects", *Light Metals 2011*, 309-314.
2. Li Wangxing and Chen Xiping, "Latest Results from PFC Investigation in China" *Light Metals 2012*, 619-622.
3. Chen Xiping, Li Wangxing, and Jerry Marks, "PFC Investigations in Chinese Smelters" (Report ZZRI/2012-01, Zhengzhou Research Institute of Chalco, August 2012).
4. Jerry Marks, "Perfluorocarbon Emissions and Primary Aluminum Production", February 2010
5. Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production. (U.S. EPA (Washington, D.C.) and IAI (London, U.K.). April 2008)