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REDUCTION STRATEGIES FOR PFC EMISSIONS FROM CHINESE SMELTERS

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Abstract

Perfluorocarbon (PFC) formation mechanism was investigated and strategies for PFC reduction in China were developed. Alumina concentration in bath has a strong effect on PFC evolution. Anodic overvoltage and current density also have an obvious influence on PFC. Narrow alumina concentration controlling mode, small dose feeding mode, alumina level pre-estimating and verifying mode were developed in order to reduce PFC emissions. PFC can be reduced by keeping alumina level in bath in the range between 2% and 3%, not low enough to cause anode effect or high enough to deposit in cells. Small dose feeding mode controls both fixed and movable small dose feeders, which can supply alumina into cells at right time. Alumina level pre-estimating & verifying mode includes pre-estimating modules and verifying modules, which can calculate alumina level by equations related to anodic current density and alumina concentration. If alumina is low, numerical modules will send feeding command to feeders.

Introduction

With the development of aluminum smelting technology, aluminum reduction cells become bigger and bigger and it becomes more difficult for alumina to diffuse and dissolve uniformly in the cell. Alumina concentration distribution has various gradients in the cell [1]. Sometimes alumina level may be very low in particular area of the cell. Non-anode effect PFC [NAE-PFC] may be generated if alumina is low enough [2]. Change in alumina concentration controlling mode to achieve optimized control of feeding system is a good way to reduce NAE-PFC. NAE-PFC has a close relation to alumina level in cells. New alumina concentration controlling technology has been developed by optimizing controlling software. Narrow alumina concentration controlling mode was designed and put into the control system. Thus alumina concentration range was narrowed from 1.5%-3.5% to 2.0%-3.0%.

Cell-Controlling modes in Smelters

Shortcomings of Conventional Control Mode

Cell resistance (R) has a close relation to alumina concentration (C) which can be described by R-C curve. R-C curve shape can be shifted left-and-right, which is influenced by bath temperature and alumina concentration in cells, and also moved up-and-down which is influenced by anode current density (see Figure 1). When bath temperature is low, alumina will diffuse and dissolve slowly and the R-C curve shifts to the right. When anode current density is low, the R-C curve shifts down. When anode current density is high, the curve will be steep. Thus, alumina concentration cannot be estimated via cell resistance, but can be calculated based on dR/dt. So alumina feeding algorithm could be adjusted by improving the control band. An improved control strategy is necessary in order to obtain needed alumina level in the bath.

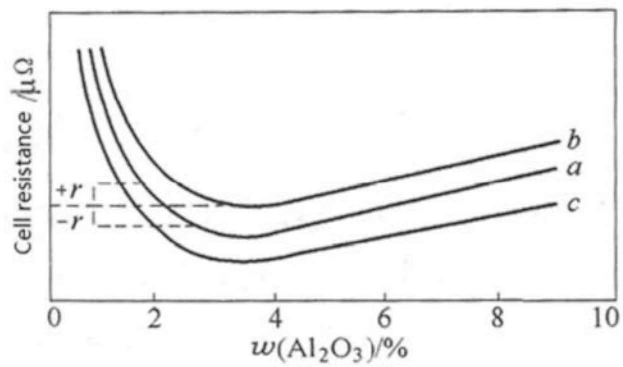

Figure 1. Former R-C curve

Improved Control Mode

Anode current density controlling mode and narrow alumina concentration controlling mode were designed and added into new control strategy. Anode current distribution and alumina level in bath can be maintained through online monitoring and control.
Alumina concentration control mode includes pre-estimating module and verifying module. Its controlling principle is described as follows. Alumina concentration in cells has a close relation to anode current density [3]. Anode current was usually measured with a millivolt fork. When anode current signal is sent to CPU, anode current density is calculated based on anode area. Alumina concentration in bath is pre-estimated using the equation $\mathbf{i_A} = -0.0733*(C_{Al2O3})^2 + 0.8268*C_{Al2O3} - 0.1509$. Here $\mathbf{i_A}$ is anode current density, A/cm^2. C_{Al2O3} is alumina concentration, % [3]. If alumina concentration is lower than the target value, CPU would send feeding instruction to a small dose feeder. After feeding, the feeding module would send back feeding signal to CPU, CPU would verify actual alumina concentration in aluminum reduction cells (see equation 9). If alumina concentration is still low, CPU would repeat these operations until alumina concentration in cells is within the control range. A schematic diagram of new control strategy and small dose feeders is presented in Figure 2.

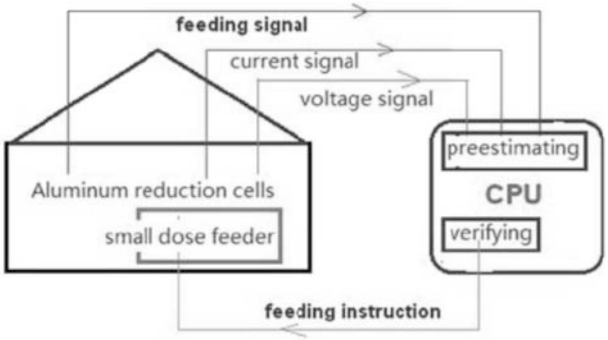

Figure 2a. Control logic for improved alumina concentration control.

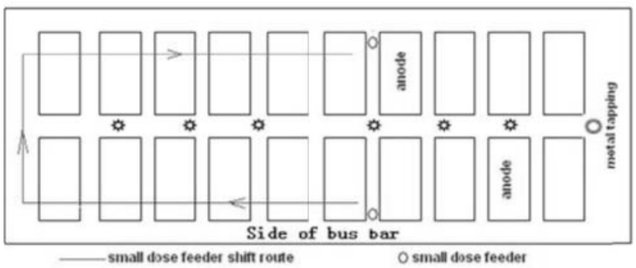

Figure 2b. Schematic diagram of small dose feeding

Real time control software was modified and anode current distribution monitoring software was added to CPU based on millivolt fork method. Alumina control algorithm was improved and narrow alumina concentration control range was achieved. New control algorithm can receive and analyze current signal, voltage signal and monitor feeding status continuously. Alumina concentration in aluminum reduction cells can be pre-estimated and verified in real time. Alumina can be fed into cells via movable small dose feeders continuously. Low alumina concentration zones would be reduced and cells would be more stable. Therefore, NAE-PFC formation can be depressed.

New Alumina Concentration Control Technology

Alumina Concentration Control Range

More advanced control strategy was needed for alumina concentration control mainly because alumina level in bath cannot be measured on-line. It is necessary to explore qualitative relation between alumina concentration (C) and cell resistance (R). Figure 3 shows C-R diagram with different alumina concentration regions are marked in the plot.

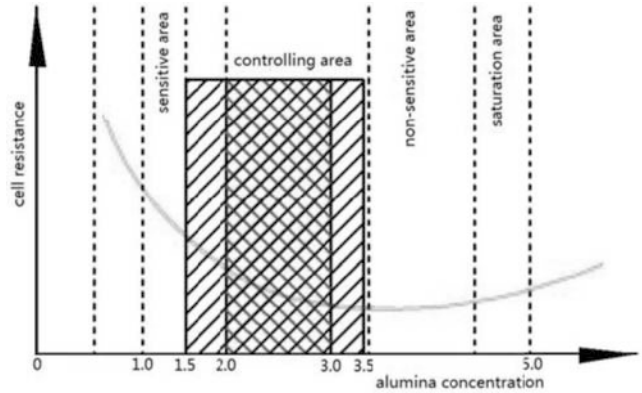

Figure 3. Relationship between alumina concentration and cell resistance

The change in cell resistance with alumina concentration can be divided into four characteristic areas which are described as follows.

- Saturation area: R will go up slowly with increasing of C. When C reaches saturation, alumina will deposit in cells.
- Non-sensitive area: R is not sensitive to C and alumina concentration is not easily followed or estimated.
- Controlling area: R rises with falling C,and R is strongly related to C. Alumina concentration can be monitored easily and held within desired control range.
- Sensitive area: R rises sharply with falling C. Alumina concentration drops to the limiting C value at which NAE-PFC emission would occur.
- Effect area: R rises sharply with falling C. Anode effects easily occur.

Based on different alumina concentration regime characteristics, optimized alumina concentration control mode can be chosen, alumina concentration shift trend can be identified accurately, control strategy can be improved and the desired alumina concentration range can be maintained. Thus the formation of NAE-PFC, which depends on alumina concentration, can be depressed.

Alumina Concentration Control Logic

In the conventional alumina control approach, the relation between cell resistance and alumina concentration can be expressed by the following equation:

$$R=a\times C_{Al2O3}^{2}+b\times C_{Al2O3}+R_0 \quad \ldots\ldots(1)$$

Where,
R_0: target cell resistance
C_{Al2O3}: current alumina concentration in the cell.
R: cell resistance at current time point.

Based on formula (1), an estimating method for current alumina concentration can be obtained and expressed as:

$$(dR/dt)=2a\times(C_{Al2O3}-C_0)dC_{Al2O3}/dt \quad \ldots\ldots(2)$$

Where,
dC_{Al2O3}/dt: Rate of alumina concentration change with time.
dR/dt: can be calculated on the basis of measured data.
C_0: target alumina concentration

C_{Al2O3}: current alumina concentration in the cell.

Increment of alumina concentration during a period of time can be calculated based on formula (2).
For the time point T_1,

$$(dR/dt)_1=2a\times(C_{Al2O3}-C_0)_1\times dC_{Al2O3}/dt \ldots\ldots(3)$$

For the time point T_2,

$$(dR/dt)_2=2a\times(C_{Al2O3}-C_0)_2\times dC_{Al2O3}/dt \ldots\ldots(4)$$

At the same time,

$$(C_{Al2O3}-C_0)_2=(C_{Al2O3}-C_0)_1+dC_{Al2O3}/dt\times(T_2-T_1) \ldots\ldots(5)$$

From equations (3), (4) and (5), formulae (6) and (7) can be derived:

$$2\times a=((dR/dt)_2-(dR/dt)_1)\div((T_2-T_1)\times(dC_{Al2O3}/dt)^2) \ldots\ldots(6)$$

$$(C_{Al2O3}-C_0)_1=(dR/dt)_1\times((T_2-T_1)\times(dC_{Al2O3}/dt)\div((dR/dt)_2-(dR/dt)_1)) \ldots\ldots(7)$$

$(C_{Al2O3}-C_0)_1$ and $(C_{Al2O3}-C_0)$ at any time point can be calculated based on equations (6) and (7). Thus alumina concentration at certain time can be calculated.

Calculation of dC_{Al2O3}/dt Alumina level in bath changes continuously with time. Increment of alumina concentration per hour can be described by the following expression.

$$dC_{Al2O3}/dt=m\times60\times60\times(1/t_1-1/t_2)/M\times100\% \quad (\%/h) \ldots\ldots(8)$$

Where,
m: mass of alumina per feed shot (kg).
M : gross mass of bath in the cell (kg).
t_1: time interval of normal-feeding (s).
t_2: time interval of under-feeding (s).

Pre-estimation of Alumina Concentration at Certain Point Alumina level in bath changes continuously with alumina consumption. Alumina concentration at current time point can be calculated based on equation (9).

$$(C_{Al2O3}-C_0)_2=(dR/dt)_1\times(T_2-T_1)\times(dC_{Al2O3}/dt)\div((dR/dt)_2-(dR/dt)_1))+dC_{Al2O3}/dt\times(T_2-T_1) \ldots\ldots(9)$$

The relationship between feed rate, dR/dt and alumina concentration can be understood from expressions (2)-(9). The control algorithm based on equations (2)-(9) was added to the improved control strategy. Alumina concentration in aluminum reduction cells can be pre-estimated fairly easy in real-time. Alumina level in bath can be kept in the range between 2.0% and 3.0% (wt).

Effect of Improved Alumina Control Technology

An improved alumina concentration control technology was developed and its effect on alumina concentration in the bath is shown in Figure 4. Figure 4 presents alumina concentration optimization course (~1 year) of one 300 kA potline before and after adjusting control mode. Plots are mean daily alumina % of 45 cells. It can be seen from Figure 4 that alumina concentration in cells shifted from a wide range of 1.5%~3.5% to a more narrow range of 2%~3%.

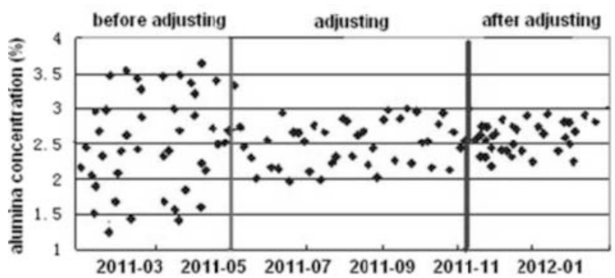

Figure 4. Alumina concentration of one 300 kA potline before and after adjusting control mode

Figure 5 and Figure 6 show running curves for a 300 kA line (current, voltage, resistance, slope, swing and feed signals) for the control system before and after the improvement. It is much easier to achieve an accurate control of alumina concentration under the improved control technology compared to the former control technology.

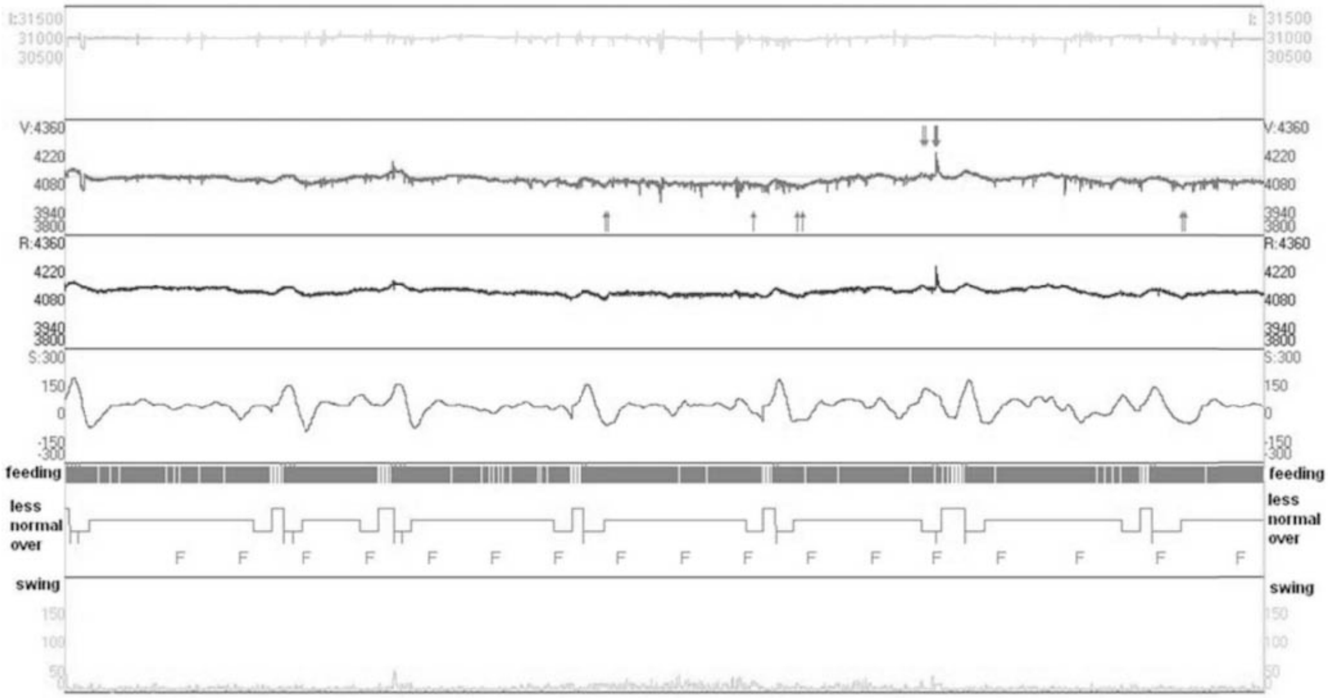

Figure 5. Running curves for new control technology (300 kA potline)

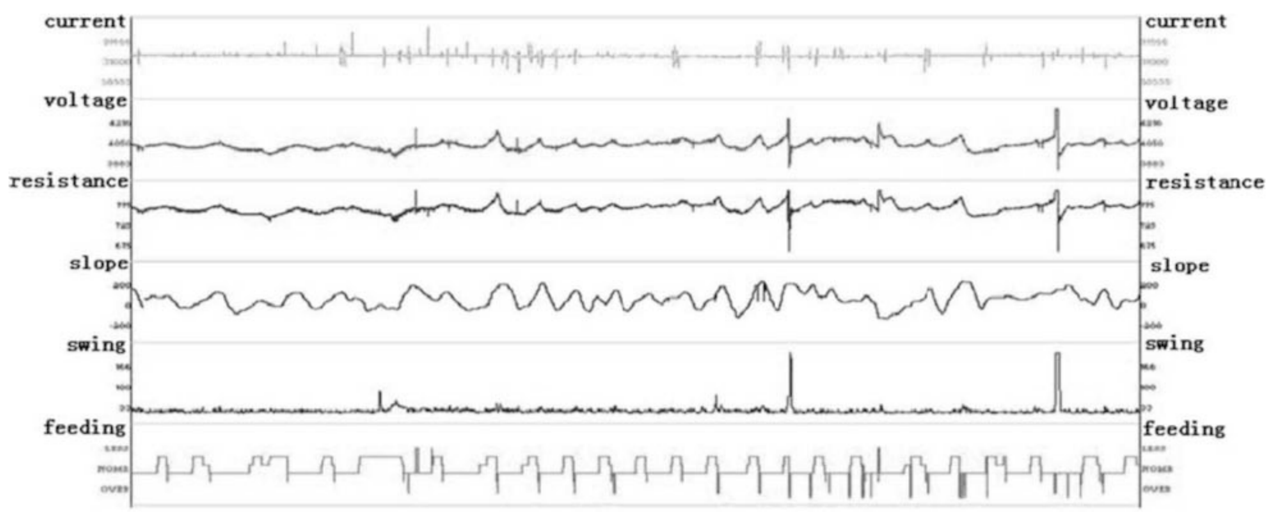

Figure 6. Running curve for former control technology (300 kA potline)

Application to PFC Reduction

PFC reduction technology was developed and its core content includes alumina concentration pre-estimating, narrow alumina concentration control and small dose feeding. The new technology has been put into industrial application. Two potlines were chosen as test base. One is 300 kA potline and the other is 350 kA potline.

Results from 300 kA Potline

The 300 kA potline includes 278 aluminum reduction cells. PFC sampling location was chosen at a branch of the main duct carrying fumes from 45 cells. Related parameters of the potline are listed in Table I. Fourier transform infrared gas analyzer (Gasmet Technologies Oy) was used to measure PFC concentrations (see reference 2). PFC measurement duration was 71.30 hours. The measured PFC concentration curves before application of PFC restraining technology are plotted in Figure 7.

Table I. Parameters of 300 kA Potline

Parameters	Unit	Value
Aluminum Output Per Cell	t/cell-day	2.27
Line Current	kA	305
Average Cell Voltage	V	4.10
Anode Current Density	A/cm^2	0.75
Current Efficiency	%	92.5

Collecting Efficiency	%	97
Flowrate of the Potline	Nm^3/h	311852

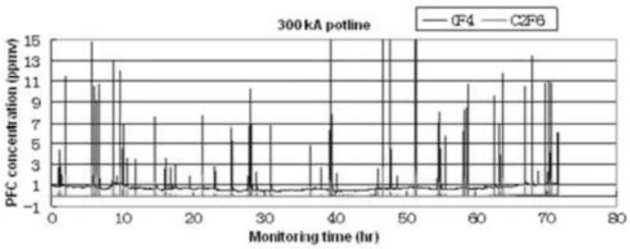

Figure 7a. PFC concentration curve before application of PFC restraining technology

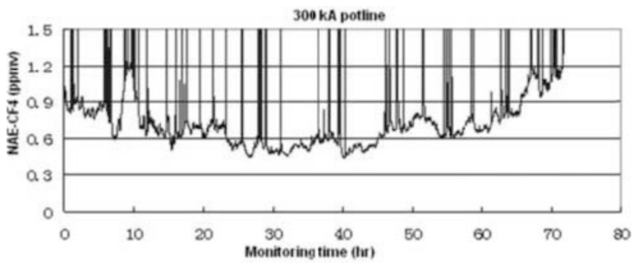

Figure 7b. Measured CF_4 concentration before application of PFC restraining technology

It can be clearly seen from Figure 7 that the 300 kA potline had high anode effect frequency (AEF) and high NAE-CF_4 concentration. The average NAE-CF_4 concentration, excluding anode effect events, was 0.707 ppmv. Because the potline was a newly-started one, it showed poor AE performances early in 2011. PFC restraining technology was implemented at the 300 kA potline between June 2011 and May 2012 and PFC measurement campaign was carried out in June 2012. Measurement duration was 86.07 hours. Measurement results are shown in Figure 8.

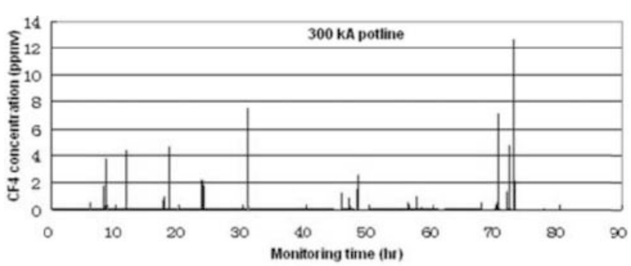

Figure 8a. Measured CF_4 concentration curve after application of PFC restraining technology

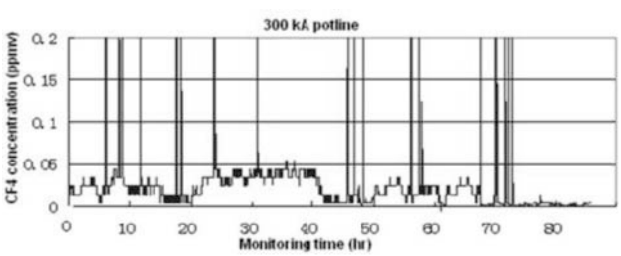

Figure 8b. Measured CF_4 concentration after application of PFC restraining technology

A significant improvement in anode effect performance was achieved after industrial application of PFC restraining technology. AEF of the 300 kA potline has dropped sharply and from 0.31 to 0.055 AEs/cell-day. Average NAE-CF_4 concentration was reduced significantly from 0.707 ppmv to 0.014 ppmv.

<u>Results from 350 kA Potline</u>

The 350 kA potline includes 208 aluminum reduction cells. PFC sampling location was selected at a branch sampling exhaust gases from 49 cells. Related parameters of the potline are listed in Table II. PFC concentration curves before application of PFC restraining technology are plotted in Figure 9. The measurement lasted 72.86 hours.

Table II Related Parameters of 350 kA Potline

Parameters	Unit	Value
Aluminum Output Per Cell	t/cell-day	2.71
Line Current	kA	363
Average Cell Voltage	V	4.17
Anode Current Density	A/cm^2	0.75
Current Efficiency	%	92.6
Collecting Efficiency	%	97
Flowrate of the Potline	Nm^3/h	434080

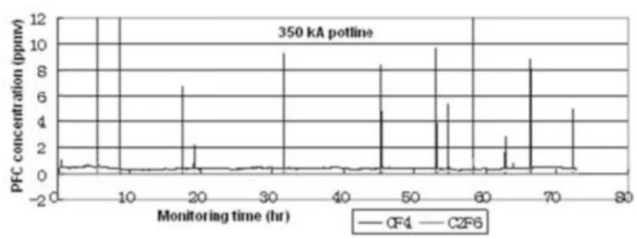

Figure 9a. PFC concentration curve before application of PFC restraining technology

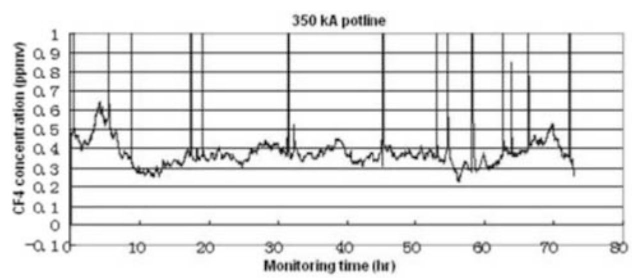

Figure 9b. Baseline CF_4 concentration before application of PFC restraining technology

It can be seen from Figure 9 that both AEF and NAE-CF_4 concentration are lower in the 350 kA potline, the potline has better AE performances compared to the 300 kA potline. The AEF was 0.12 AEs/cell-day and average NAE-CF_4 concentration was 0.374ppmv.

PFC restraining technology was implemented at the 350 kA potline between August 2011 and July 2012. PFC survey was finished in July 2012. PFC measurement duration was 68.67 hours. Results of PFC measurements are shown in Figure 10.

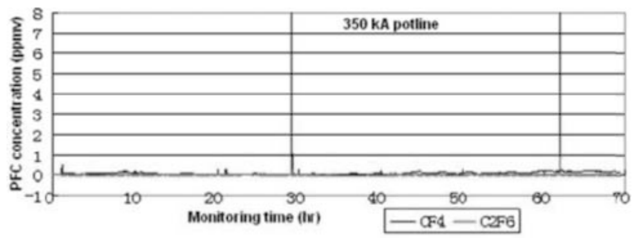

Figure 10a. PFC concentration curve after application of PFC restraining technology

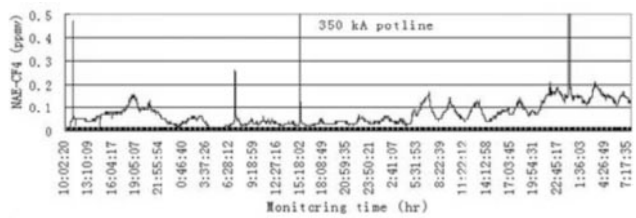

Figure 10b. NAE-CF_4 concentration after application of PFC restraining technology

As can be seen from Figure 10, PFC emissions have reduced significantly after application of PFC restraining technology. AEF of the 350 kA potline was reduced from 0.12 to 0.007 AEs/cell-day. Further attention was given to this potline and AEF was followed. Its monthly AEF was 0.04 AEs/cell-day between July and September this year. NAE-CF_4 generation was depressed substantially. Average NAE-CF_4 concentration has dropped from 0.374 ppmv to 0.070 ppmv.

Conclusions

Mathematical equation for alumina feed control was developed based on anodic current density and cell resistance. An improved feed control algorithm has been designed and implemented.

Small dose feeders have been designed, made and put into industrial tests based on new control technology. Alumina can be added into aluminum reduction cells to maintain alumina concentration within a narrow control band between 2 and 3 % wt.

PFC restraining technology was developed based on new alumina concentration control technology in which alumina concentration pre-estimating was coupled with small dose feeding. Tight alumina concentration control enabled significant reduction in both anode-effect and NAE-PFC emissions.

The effect of PFC reduction on current efficiency was pre-estimated. The increment of Current efficiency due to PFC reduction was about 0.03%. But obvious increasing of CO concentration was observed during anode effects. Further study need to be done in the future..

Acknowledgement

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References

1. Li Wangxing, Chen Xiping, and Chris Bayliss, *On Continuous PFC Emission Unrelated to Anode Effect*s (Light Metals 2011), 309-314.
2. Li Wangxing and Chen Xiping, *Latest Results from PFC Investigation in China* (Light Metals 2012), 619-622.
3. Feng Naixiang, *Aluminium Electrolysis* (Beijing, BJ: Chinese Chemistry Industry Publishing Company, 2006), 51-62.
4. Chen Xiping, Li Wangxing, and Jerry Marks, *PFC Investigation Report in Chinese Smelters* (Zhengzhou Research Institute of Chalco, August 2012), 20-29.
5. *Protocol for Measurement of Tetrafluoromethane (CF_4) and Hexafluoroethane (C_2F_6) Emissions from Primary Aluminum Production.* (U.S. EPA (Washington, D.C.) and IAI (London, U.K.). April 2008)