

Efforts for PFCs Reduction and Monitoring in Chalco

Prof. & Dr. Wangxing Li

Dr. Jianhong Yang

Zhengzhou Research Institute of Chalco

Zhengzhou, China

Environmental Concerns

The Anode Effect (AE) in aluminium production produces the greenhouse gases CF_4 and C_2F_6 , while

CF_4 is **6500 times** and
 C_2F_6 is **9200 times** equivalent CO_2 emissions

The ultimate goal for aluminium industry is to get close to zero AEF (Anode effect frequency).

Over the last 5 years the aluminium industry in China has made great efforts to reduce the anode effect frequency and duration.

AE Pros and Cons for Aluminium Production

Positive features:

- Cell control (AE caused by alumina depletion)
- "Cleans" the anode surface
- "Cleans " the electrolyte
- " Melts " the bottom sludge

Negative features:

- **Perfluorocarbon** (CF_4 and C_2F_6) emissions
 - Overheating
 - Waste of energy
 - Melting of side ledge
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Needs for Low AE frequency or Getting to Zero AEF

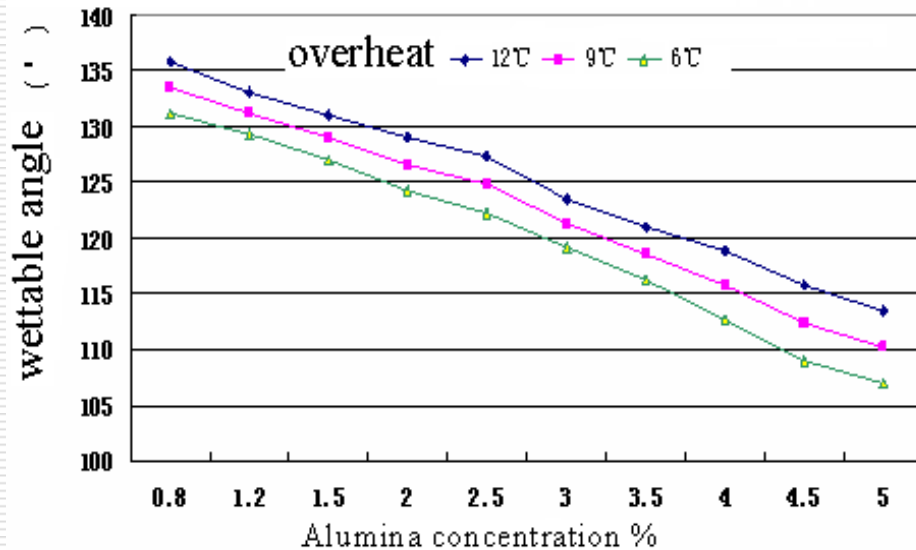
New technology needed

- **To** clean electrolyte and anode surface
- To remove bottom sludge

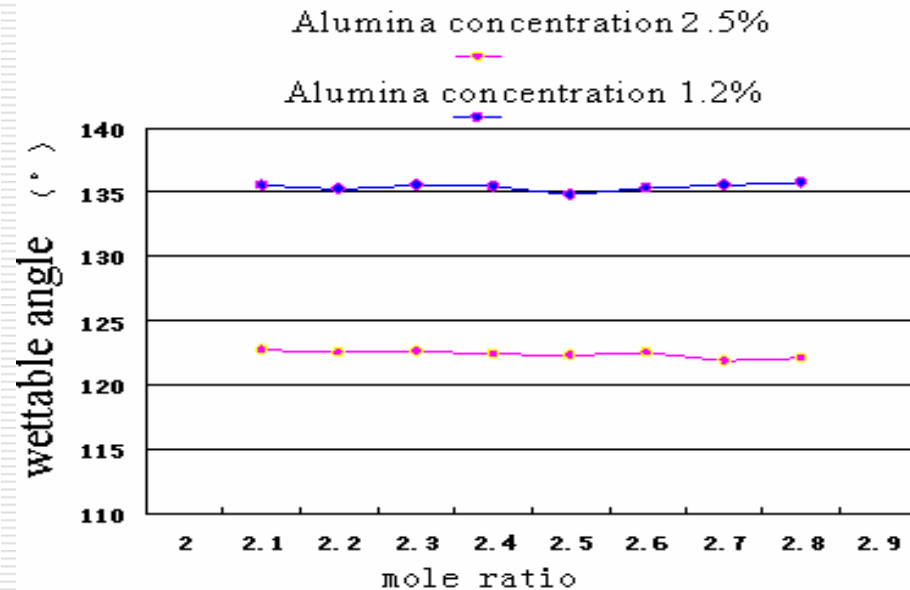
New control model needed

- To control feeding in aluminum reduction cells (cell control used to depend on AE).
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Research on Zero AEF in Zhengzhou Research Institute of Chalco



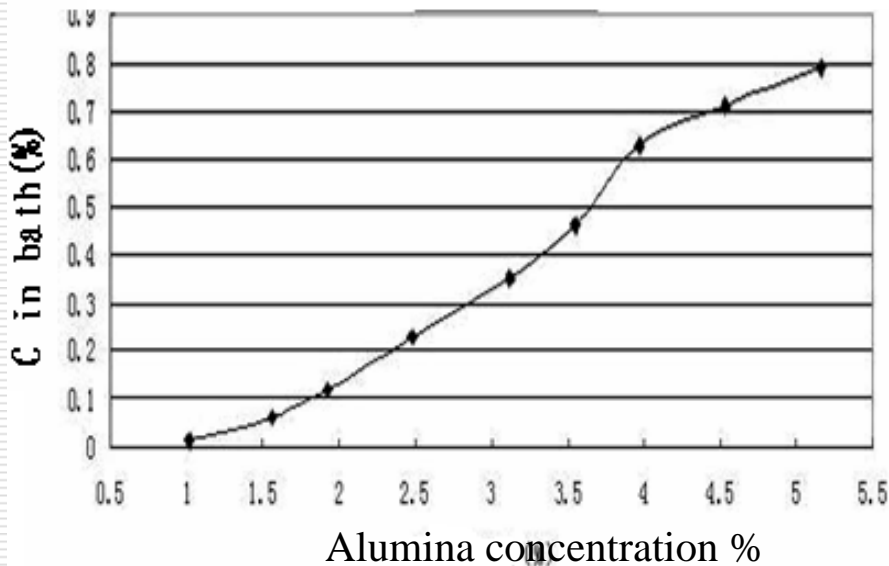
Wettability of Bath to Carbon as function of Al_2O_3 concentration



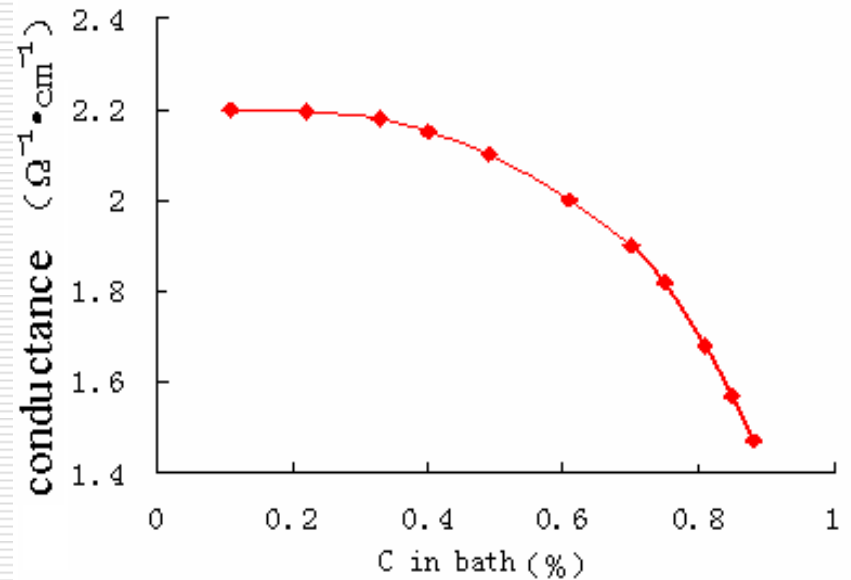
Wettability of Bath to Carbon as function of Bath molar ratio

□ Lower Al_2O_3 conc. is helpful for anode cleaning and separation of carbon-dust from electrolyte

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Carbon content in bath vs Al_2O_3 conc.

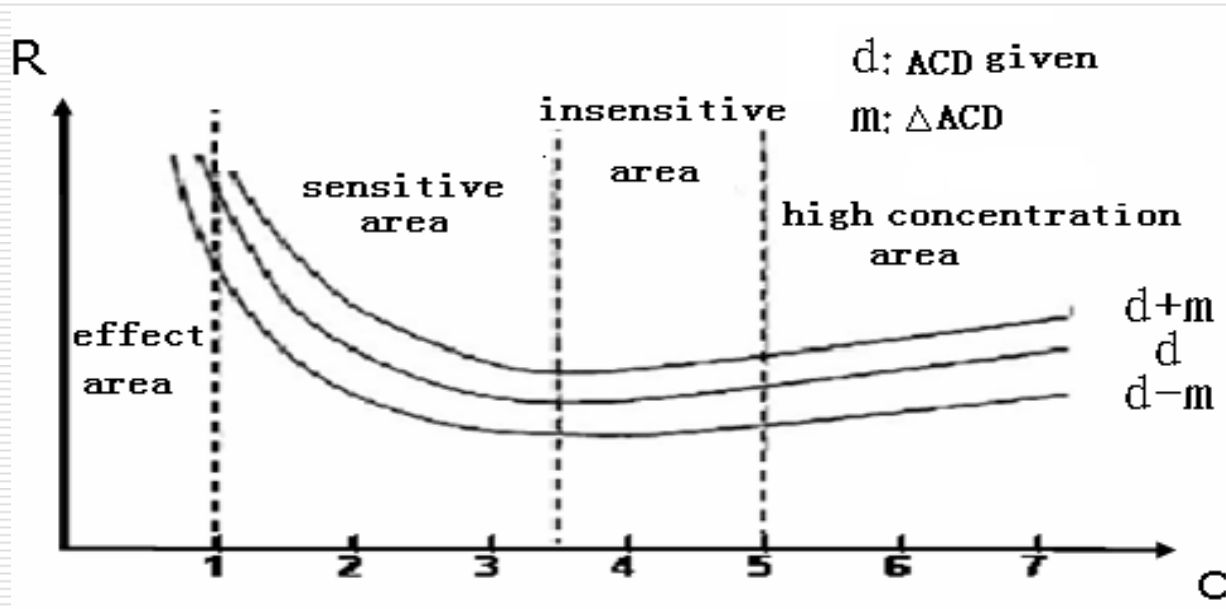


Bath electric conductivity vs carbon-dust content

- ❑ Carbon content in bath increases as alumina conc. increases
- ❑ Bath electric conductivity decreases as carbon in bath increases

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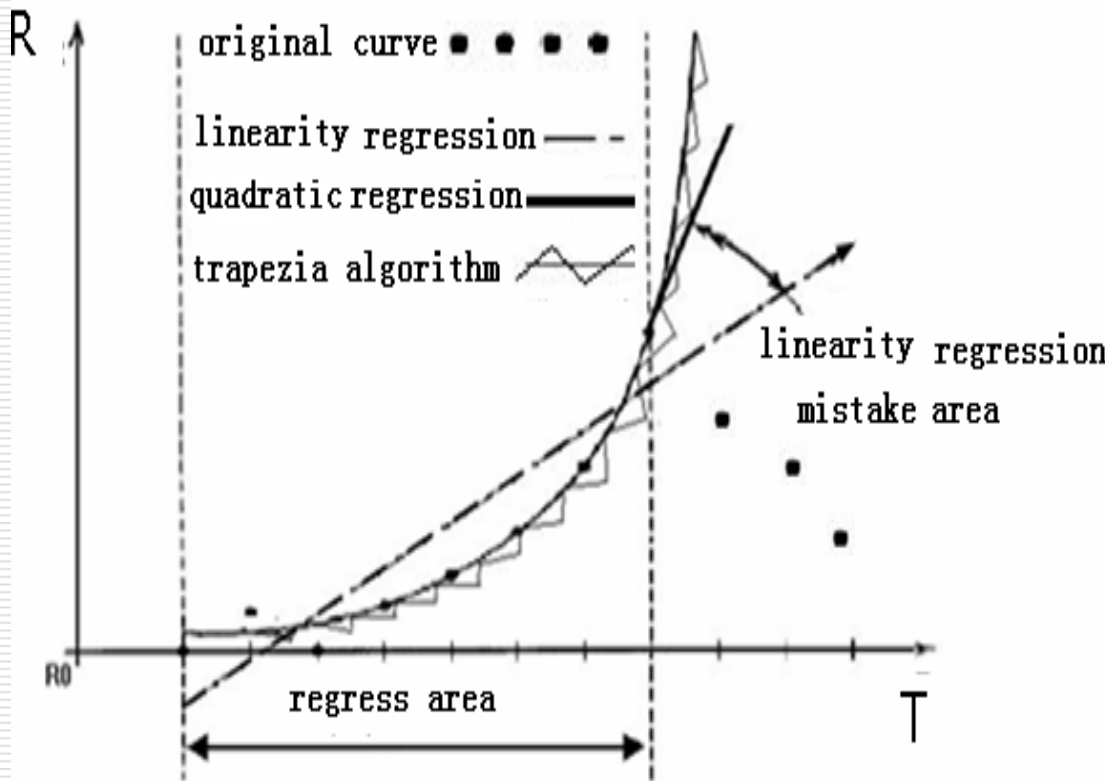
Traditional cell-control model



Relationship between cell resistance with alumina concentration

❑ Expressed by the formula $y=ax+b$, by which it is hard to estimate precisely and rapidly alumina concentration within 1.5-2.5%

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- New cell-control model expressed by $y=ax^2+bx+c$,
- Precise online-estimation of Al_2O_3 conc.

R-T curve in non-saturation zone of alumina

Industry Tests for zero AEF in National Large-scale Trial Base of Aluminum Electrolysis



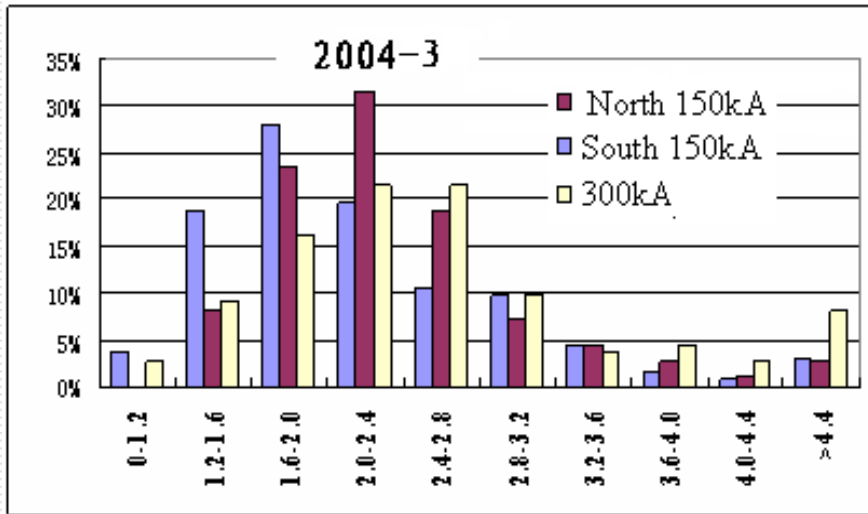
Three 300 kA and three 150 kA cells were chosen for the near-zero AE tests in 2004

Industry Tests for zero AEF in National Large-scale Trial Base of Aluminum Electrolysis

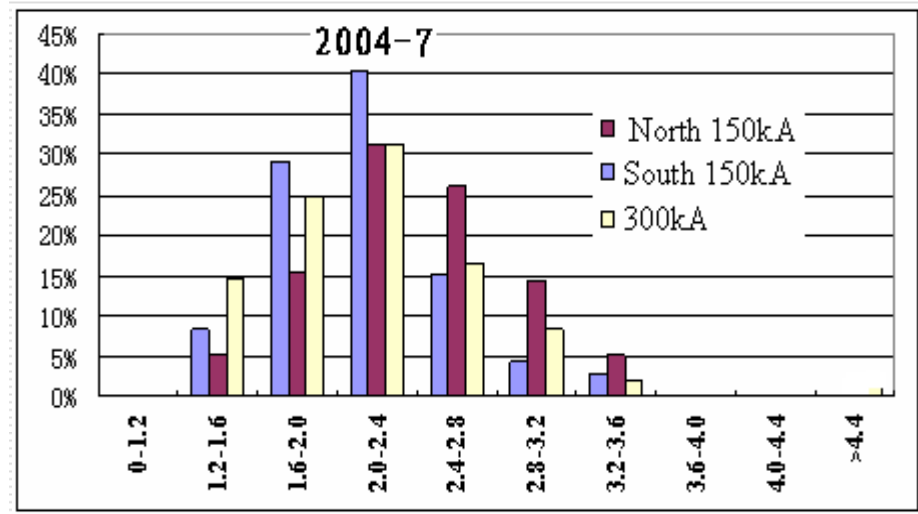
Overheat, °C	5	8	12
Average alumina concentration when AE occurs, %	1.23	1.11	0.96
AE number	50	50	50

- ❑ Critical alumina concentration is lower when overheat is higher.
- ❑ Hard to control AE when Al_2O_3 conc. lower than 1.2 percent,

Industry Tests for zero AEF in the National Large-scale Trial Base of Aluminum Electrolysis



Alumina conc. before application of new control system



Alumina conc. after application of new control system

- New cell-control system based on online-estimation of Al_2O_3 conc.
- Alumina conc. was controlled well in low & narrow range

Industry Tests for zero AEF in the National Large-scale Trial Base of Aluminum Electrolysis

Determination of control-range of Al_2O_3 concentration

Average Al_2O_3 Conc., %	AE status	Sludge status	Average Al_2O_3 Conc., %	Accidental AE	Sludge status
1.30	hardly control Easily occur	clean	2.50	In control No AE	clean
1.50	In control No AE	clean	2.70	In control No AE	less
1.80	In control No AE	clean	3.00	hardly occur	much
2.00	In control No AE	clean	3.30	hardly occur	much
2.20	In control No AE	clean	3.60	hardly occur	much

□ When Al_2O_3 conc. was within 1.5-2.5%, AE could be controlled and no sludge was formed.

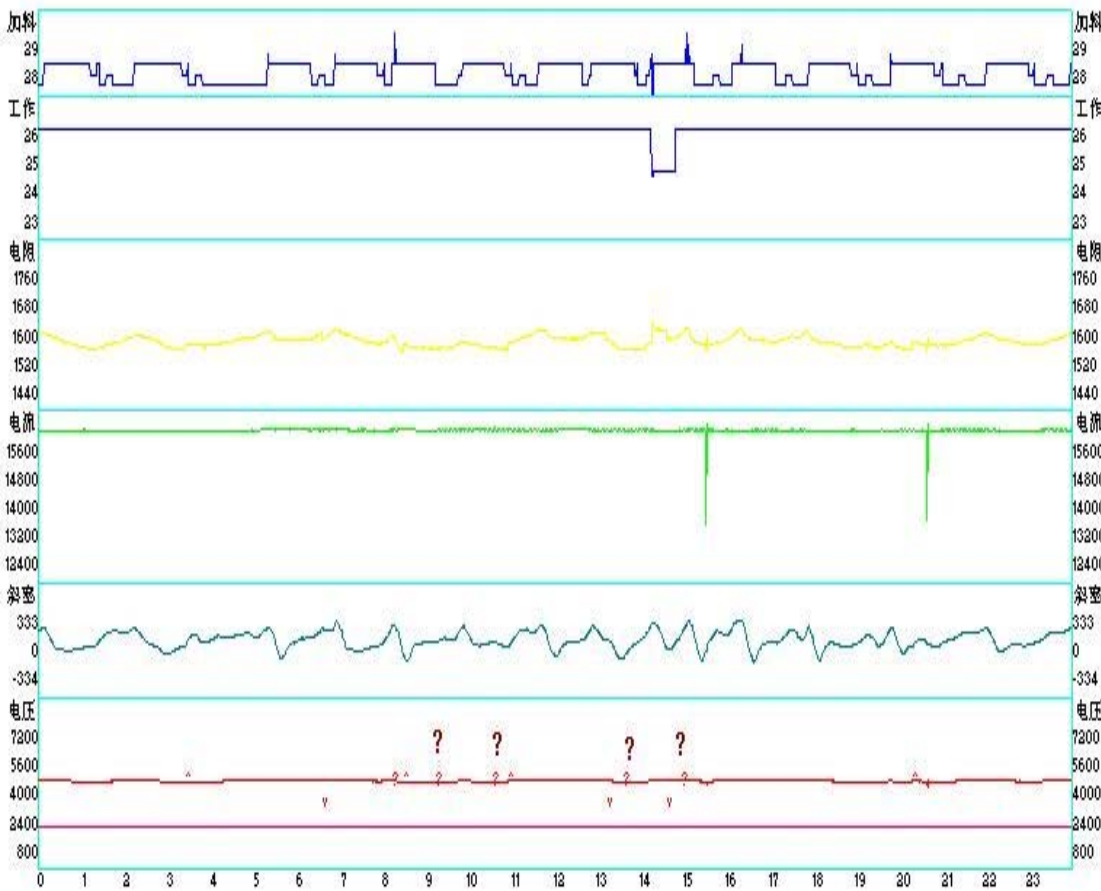
Industry Tests for zero AEF in the National Large-scale Trial Base of Aluminum Electrolysis

Enrichment of carbon dust in bath

Days of non-AE	C, %	Days of non-AE	C, %
2	0.007	94	0.011
48	0.020	156	0.010
81	0.017	254	0.009

□ When Al_2O_3 conc. was within 1.5-2.5%, no carbon dust enrichment in bath and near-zero AE production could be realized

Industry Tests for zero AEF in the National Large-scale Trial Base of Aluminum Electrolysis



Signal for abnormal status of cells.

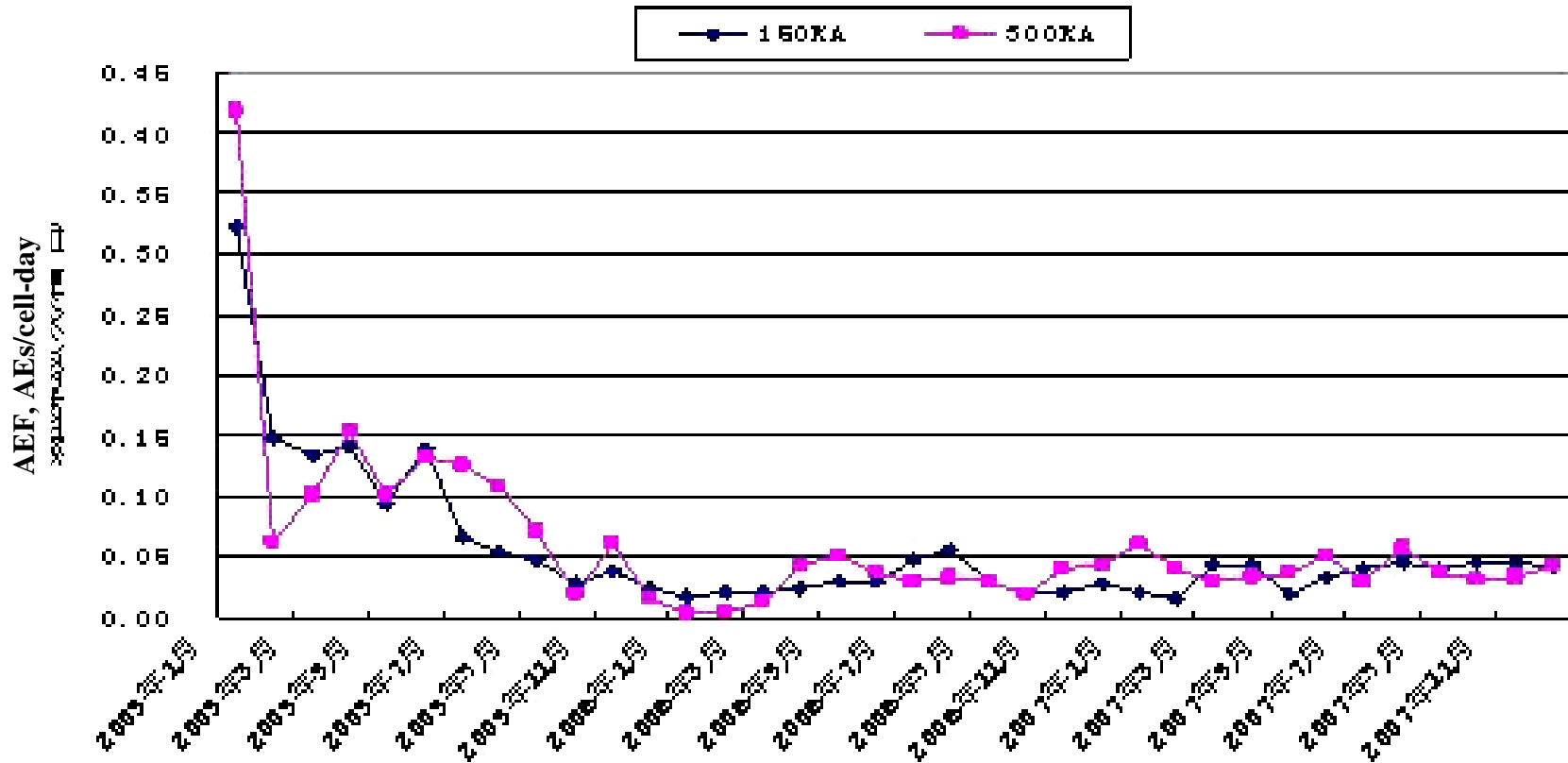
- ❑ Accidental AE is usually resulted from poor bath circulation and mechanical trouble at low Al_2O_3 conc. range
- ❑ Forecast technology for accidental AE depends on precise online-estimation of Al_2O_3 conc.

Industry Tests for zero AEF in the National Large-scale Trial Base of Aluminum Electrolysis

Cell number	Test period	AE number	AEF, time/cell-day
150kA-6#	Eight months	0	0.0000
150kA-7#	Eight months	1	0.0041
150kA-8#	Eight months	1	0.0041
300kA-5#	Eight months	1	0.0041
300kA-6#	Eight months	1	0.0041
300kA-9#	Eight months	2	0.0082
Average		1.0	0.0041

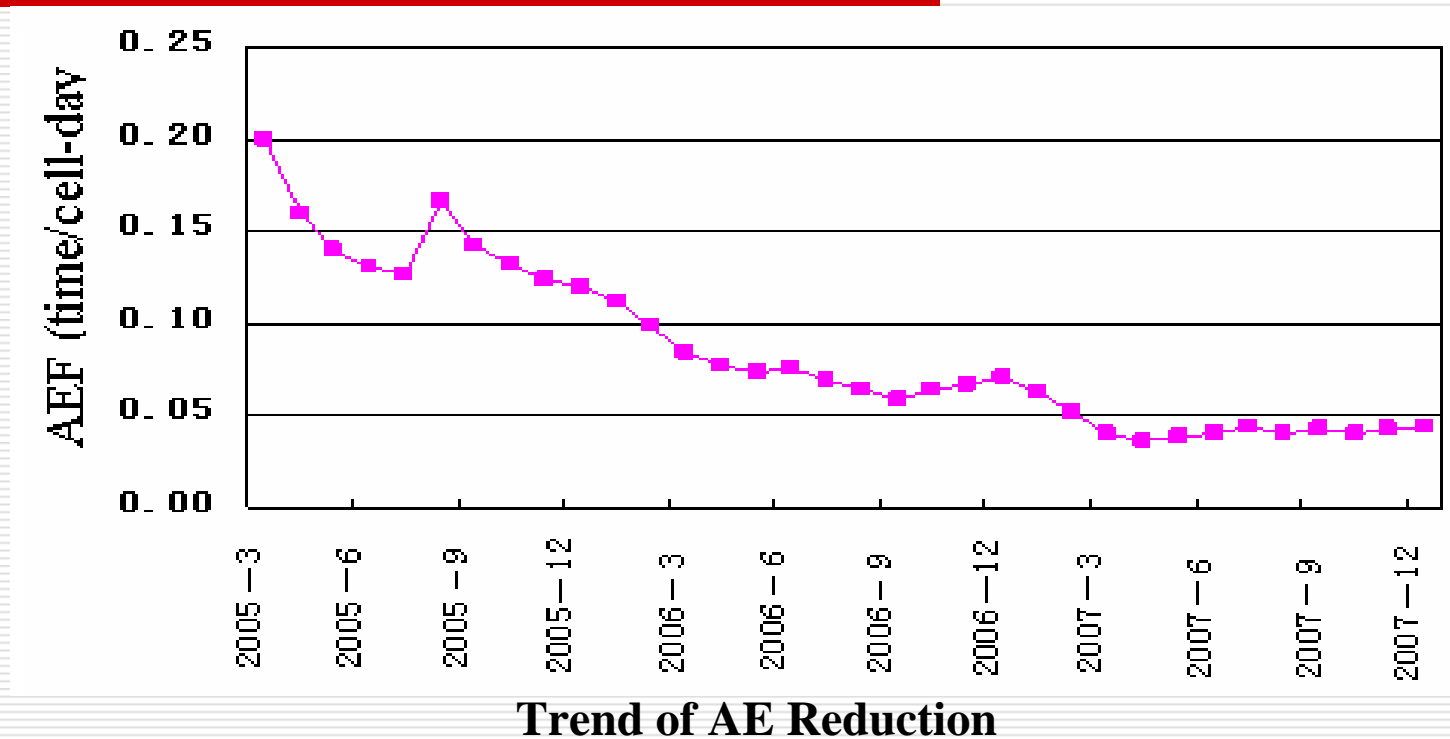
□ During the industry tests in eight months, six cells were running well, carbon dust separated normally, and no sludge formed.

Industry application of zero AEF tech in the National Large-scale Trial Base of Aluminum Electrolysis



Average AEF less than 0.03 times/cell-day in 2005~2007

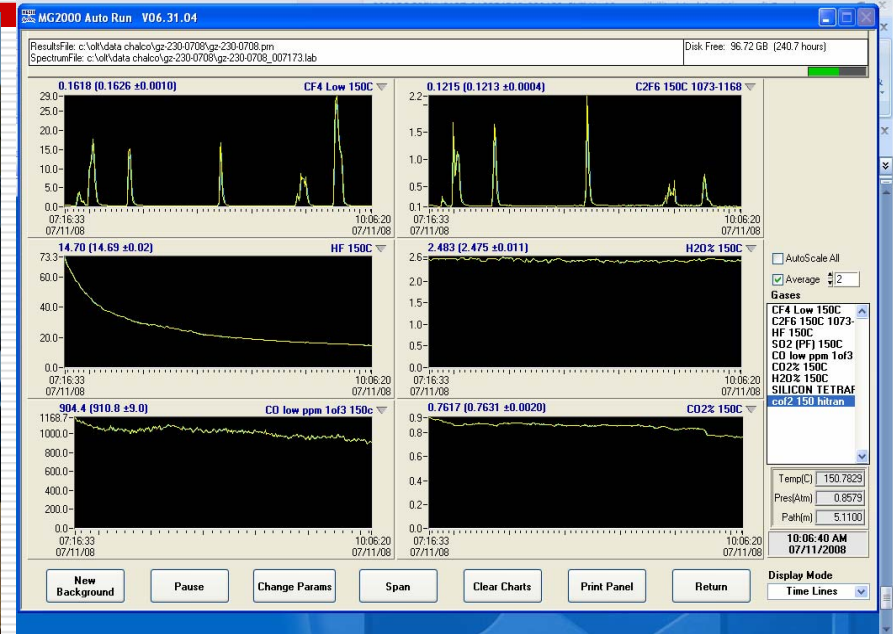
Industrial application of zero AE tech in Qinghai branch of Chalco



□ Near-zero AEF tech was applied in Qinghai branch. It was a great success.

PFC measurement by Zhengzhou Research Institute of Chalco

Fourier Transform Infrared Spectrometer



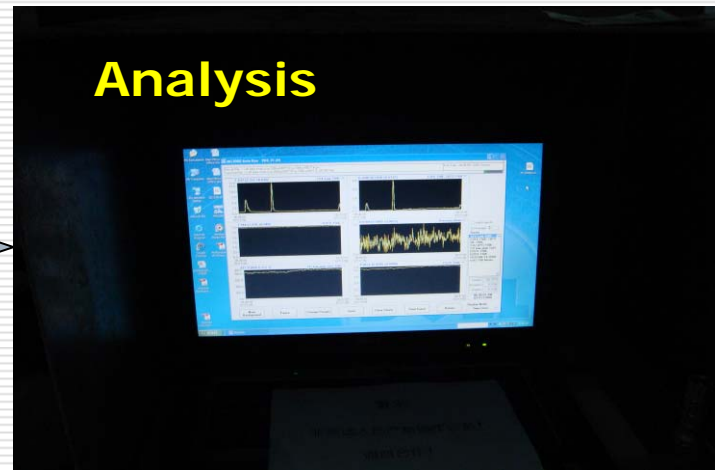
- Exhaust-gas passed continuously through FTIR sample chamber
- PFC conc. was recorded on a computer at intervals of 1 – 60 seconds

Communication with the famous expert Jerry Marks of IAI

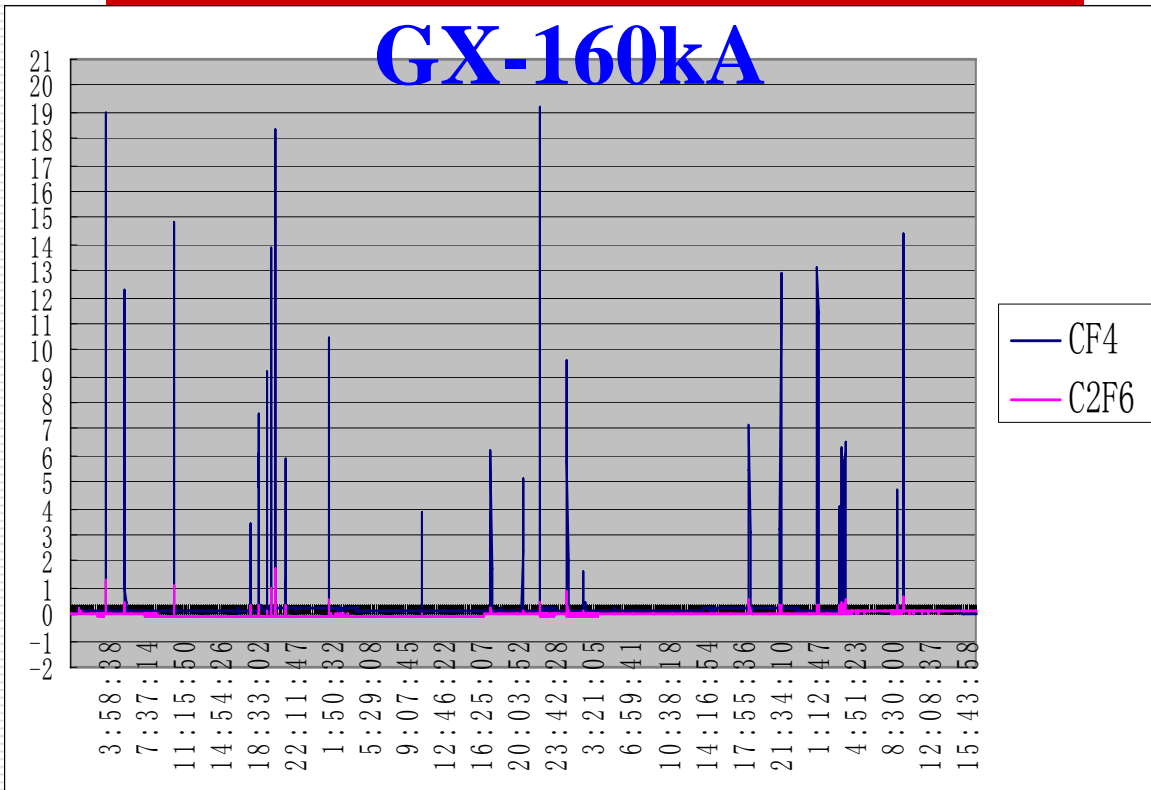
- Jerry Marks, expert of IAI and scientist of US EPA, visited us on Oct 6th 2008, we had good discussion on PFCs monitoring tech.



PFCs Measurements



PFCs Measurements



Continuous run 86 hours

Measurement cell number: 68; AEF: 0.1 time/cell-day ; AE-duration: 120(s)

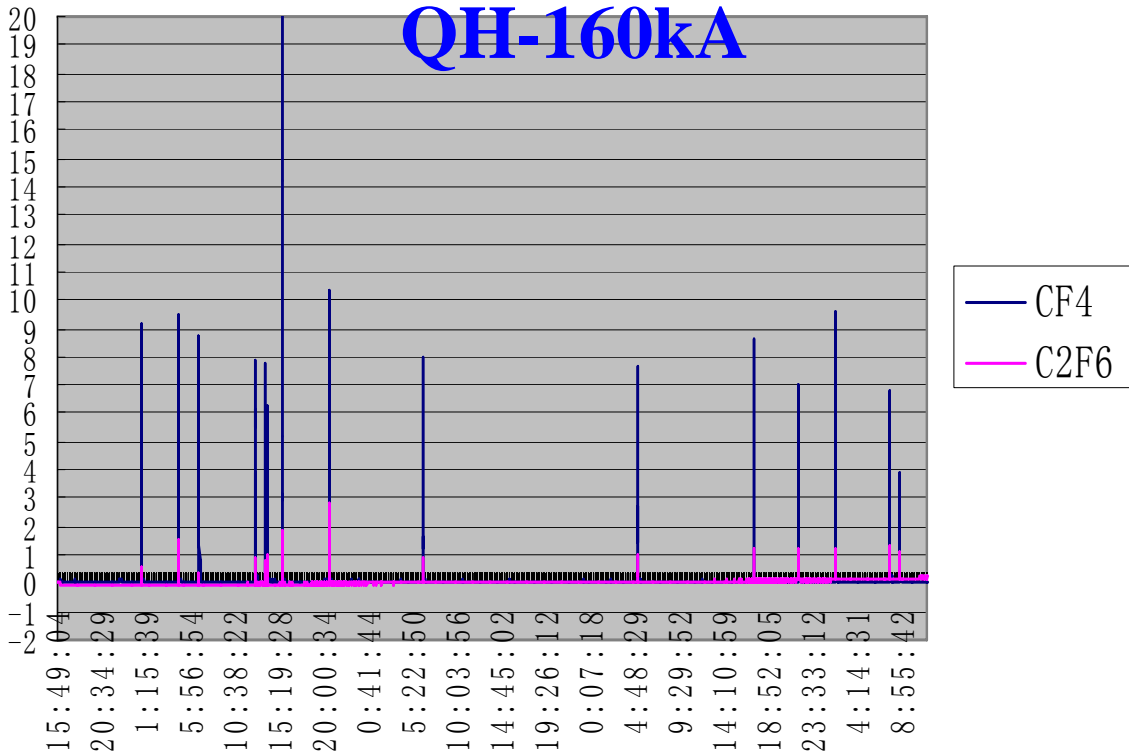
● **Technology on zero AE have been applied.**

● **No CF₄ continuous emission.**

● **Total PFC emission: 0.43 t CO₂-eq/t-Al.**

PFCs Measurements

QH-160kA



Continuous run 90 hours

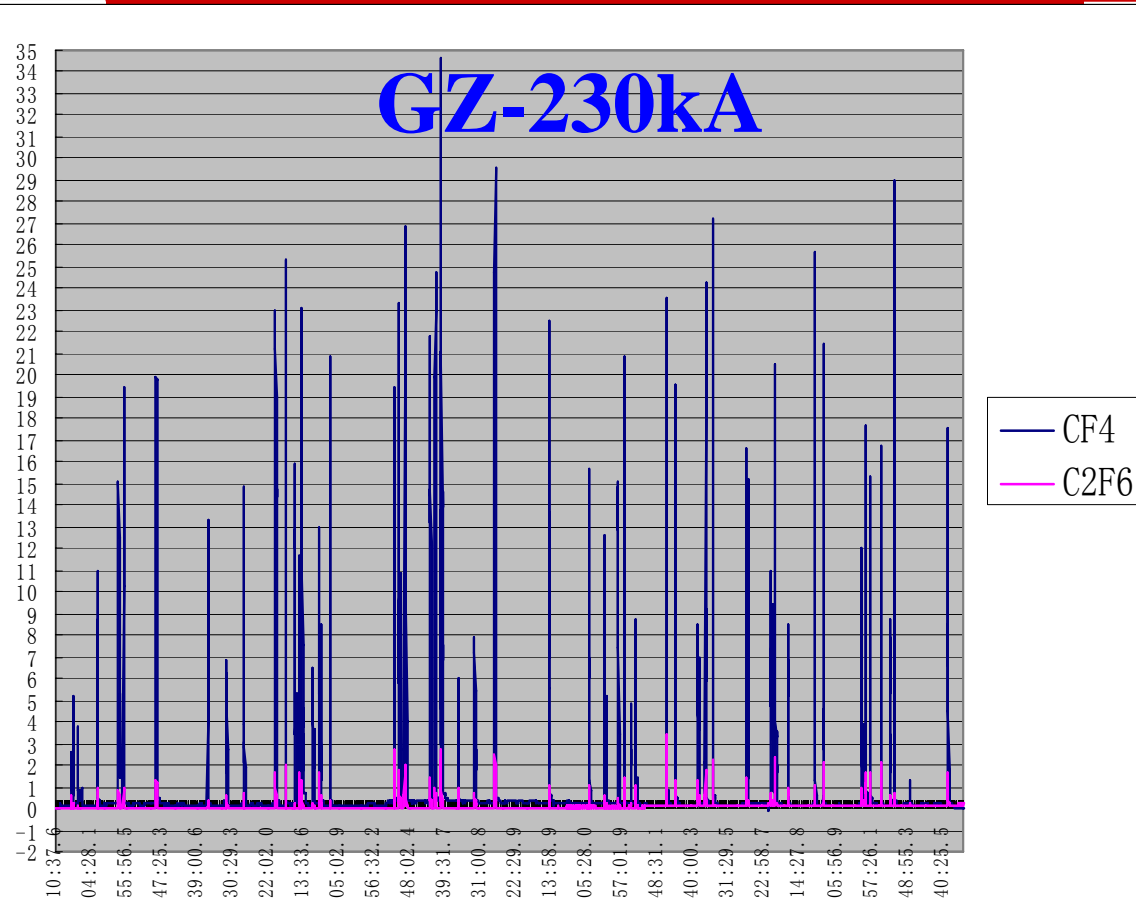
● Technology on zero AE have been applied.

● No CF₄ continuous emission.

● Total PFC emission: 0.65 t CO₂-eq/t-Al.

Measurement cell number: 39; AEF: 0.1 time/cell-day ; AE-duration: 193(s)

PFCs Measurements



Continuous run 72 hours

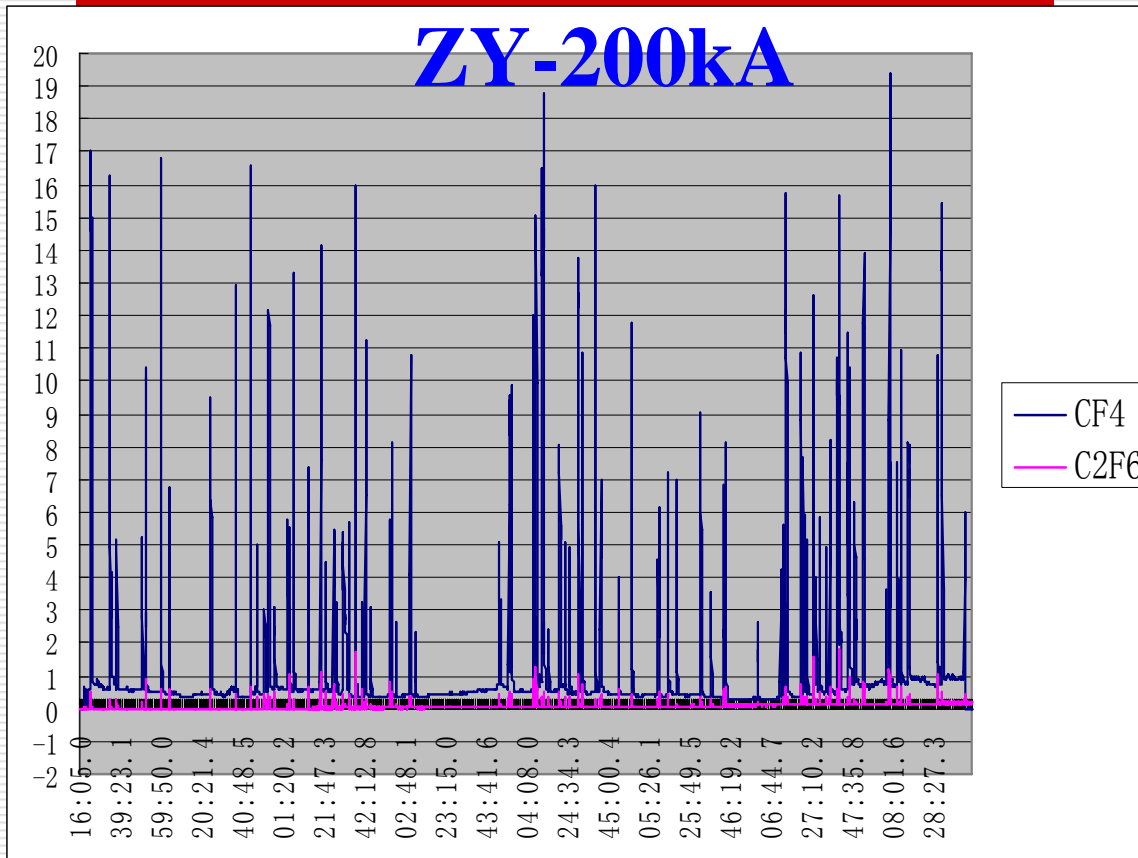
Measurement cell number: 36; AEF: 0.54 time/cell-day; AE-duration: 422(s)

- Suffered from ice rain disaster three months ago.

- No CF_4 continuous emission.

- Total PFC emission: 2.66t $\text{CO}_2\text{-eq/t-Al}$.

PFCs Measurements

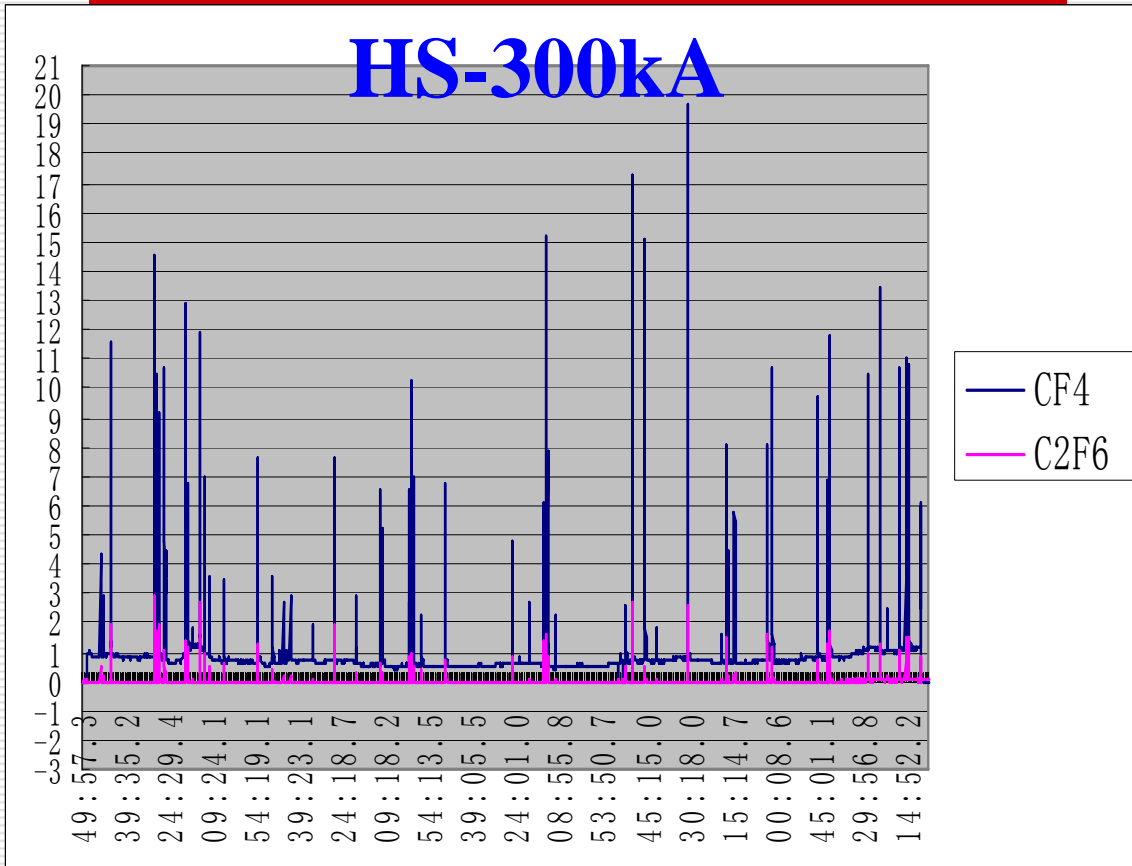


Continuous run 72 hours

- Suffered from ice rain disaster three months ago.
- CF_4 continuous emission can be seen clearly. Non-AE-PFC emission: 1.20 t CO_2 -eq/t-Al
- Total PFC emission: 2.79 t CO_2 -eq/t-Al.

Measurement cell number: 95; AEF: 0.28 time/cell-day; AE-duration: 276(s)

PFCs Measurements

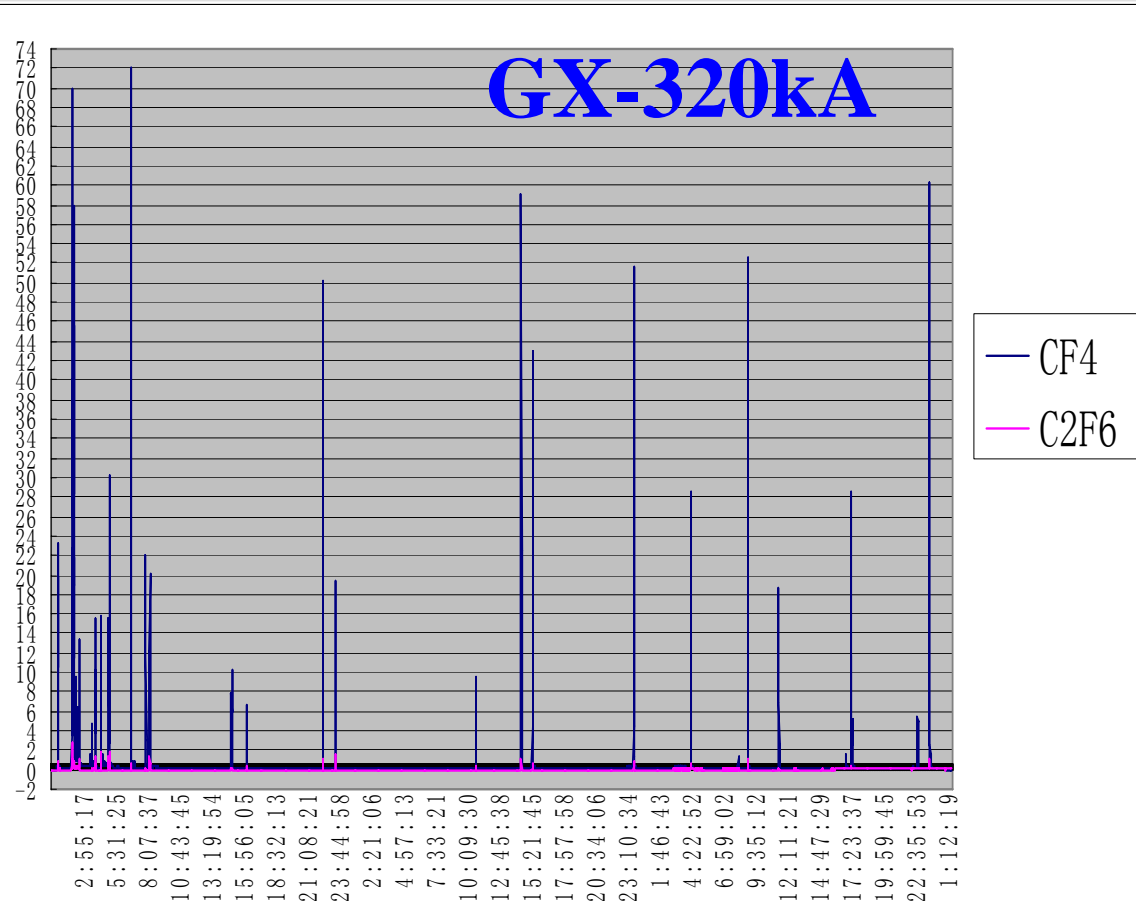


Continuous run 72 hours

- Technology on zero AE wasn't applied.
- CF4 continuous emission can be seen clearly. Non-AE-PFC emission: 2.02 t CO₂-eq/t-Al
- Total PFC emission: 2.53 t CO₂-eq/t-Al.

Measurement cell number: 45; AEF: 0.39 time/cell-day ; AE-duration: 101(s)

PFCs Measurements

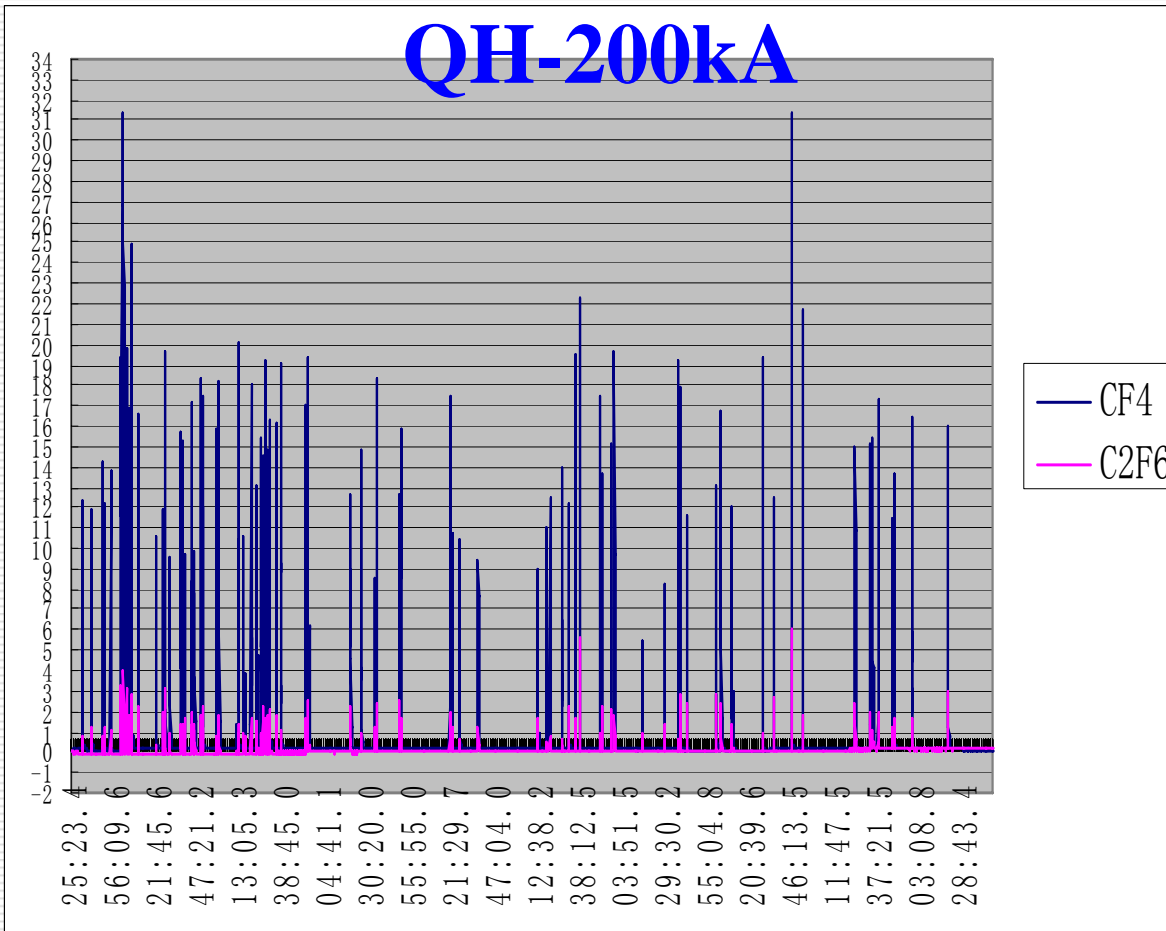


Continuous run 72 hours

- Technology on zero AE wasn't applied.
- No CF_4 continuous emission.
- Total PFC emission: 1.18t $\text{CO}_2\text{-eq/t-Al}$.

Measurement cell number: 13; AEF: 0.66 time/cell-day; AE-duration: 102(s)

PFCs Measurements



Continuous run 73 hours

- Technology on zero AE wasn't applied.
- No CF₄ continuous emission.
- Total PFC emission: 1.64 t CO₂-eq/t-Al.

Measurement cell number: 53; AEF: 0.37 time/1cell-day ; AE-duration: 92(s)

Comparison of PFCs Emission Level

Overseas and indoors emission level	AEF(Tim e/cell-day)	Avg-AE-duration(s)	PFC emission, tCO ₂ -eq/t-Al
The global emission in 2007			0.7
IAI Reduction target in 2010			0.88
GX-160 measured emission	0.10	120	0.43 (minimum)
GX-320 measured emission	0.66	102	1.18
GZ-230 measured emission	0.54	422	2.66
ZY-200 measured emission	0.28	276	2.79 (maximum)
HS-300 measured emission	0.39	101	2.53
QH-200measured emission	0.36	92	1.24
QH-160 measured emission	0.10	193	0.65

□ PFCs emission has reached a lower level in some Chinese smelters in contrast to the international average level

□ There is still a great room for some other Chinese smelters to reduce PFCs

CF₄ and C₂F₆ Emission

Potlines	GX-160	GX-320	GZ-230	ZY-200	HS-300	QH-200	QH-160
Avg-AE-voltage	14	11	18	23.5	13.8		
AE-duration	120	102	422	276	101	92	193
AE-CF ₄ emission rate kg/t-Al	0.0638	0.1047	0.2085	0.3711	0.3881	0.1988	0.0645
AE-C ₂ F ₆ emission rate kg/t-Al	0.0014	0.0031	0.0297	0.0408	0.0009	0.0375	0.0246
CF ₄ / C ₂ F ₆ (mass ratio)	45.571	33.774	7.020	9.243	431.22	5.30	2.62

□ C₂F₆ emission increases rapidly with Avg-AE-voltage increasing

New Discovery of Continuous CF₄ Emissions

Non-AE CF₄ emission level

Potlines	A	B	C	D	E	F	G
AE-CF ₄ emission rate kg/t-Al	0.0227	0.070	0.162	0.199	0.0628	0.135	0.0249
Non-AE-CF ₄ emission rate kg/t-Al	0.0244	0.0271	0.0241	0.152	0.292	0.0262	0.00224
The ratio of AE-CF ₄ , %	48.2	72.1	87.0	56.7	17.7	83.7	91.7
The ratio of non-AE-CF ₄ , %	51.8	27.9	13.0	43.3	82.3	16.3	8.3

□ Non-AE-CF₄ emission is more than estimated emission, WHY?

Possible reasons for non-AE-CF₄ Emission in China

□ Non-AE-CF₄ due to AE-quenching method

AE quenching is usually performed manually in China. Cell cover removed from cells will introduce anode gases inside potroom. Gases in potroom are purged by fans into sampling pipe. So non-AE-CF₄ could be monitored during measurement.

□ Non-AE-CF₄ due to low flow of CF₄

CF₄ easily settles down low in air due to higher molecule weight. So non-AE CF₄ could more likely be monitored in smelters which are located in valleys.

□ Un-regular Anode Effect

Summary

- Zero AEF has been developed in Zhengzhou Research Institute of Chalco.
 - After application of the tech, PFCs in some smelters of Chalco have reached a pretty low level, although others still have a great room to further reduce PFCs.
 - Tier 3 method (facility specific measurements) should be more often used for monitoring of PFCs.
 - Further efforts are needed to find out reasons for continuous CF_4 emission.
 - Technique for fast AE-quenching methodology needs to be developed.
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The End

Thank you!
