

Using SPC Method to Design an Aluminum Fluoride Addition Strategy for Aluminium Electrolysis

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Abstract

A 400 kA aluminum reduction potline suffers from extensive cathode damage due to defects in the refractories materials. The aluminum level was raised in order to reduce a further damage of the pots. However, it caused increased heat dissipation from the sidewall, which increased the energy consumption and formed long ledge toe that caused frequent cathode problems such as cracking. An optimization plan was carried out on six test pots over a year which included, among other measures, a new cryolite ratio (CR) and bath temperature control regime. These were necessary as reduction of CR and bath temperatures variations were a precondition for pot performance optimization. A new AlF_3 feeding strategy which is based on Statistical Process Control (SPC) method, was implemented on the test pots and compared to a group of reference pots. This strategy aimed to reduce the variations of AlF_3 feed leading to a reduction of variations in cryolite ratio (CR), and the bath temperature. After 4 months of operation, the variation of AlF_3 additions was reduced by 35 % and thereby reducing variation in CR by 37 % and bath temperature variations by 14 % compared to a group of reference pots. This control method ensured a more stable operation which allows optimization of metal level and voltage.

Keywords: Bath chemistry control; SPC method; aluminium fluoride feeding strategy.

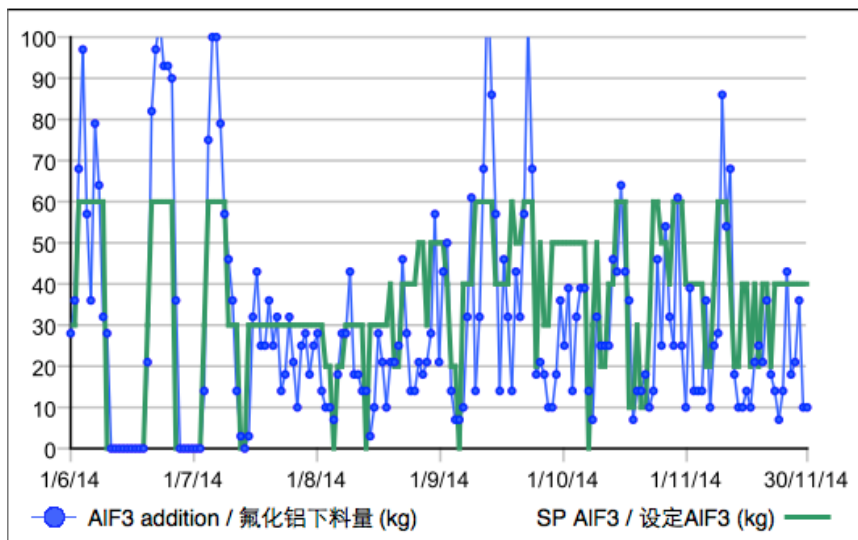
1. Introduction

A 400 kA series electrolytic cells potline suffers from extensive cathode damage due to defects in refractories materials. The cathode damage is mostly transverse cracks in the carbon block upper surface, which leads to high concentrations of Fe and Si in the molten aluminium metal. Most of the pots that were built during the initiation of the potline show signs of cathode damage, hence they all carry the risk of cathode damage. In order to reduce further damage of the pots, the metal level on all pots had been previously raised to 30 – 34 cm. This reduces the cathode temperature and reduced pot failure. However, operating at high metal level leads to many disadvantages: (1) higher energy consumption as more heat is dissipated out from the sidewall and extra voltage is needed to compensate for that heat loss and (2) reduced bath level due to the need to accommodate higher metal level in the cavity. This leads to a decrease of alumina dissolution in the bath and increase of sludge, resulting in an increase of cathode voltage drop (CVD).

A project was done, aimed to optimize the performance of six test pots by reducing metal level and voltage to optimum levels without reducing CE or causing further damage to the cathodes [1]. One of the preconditions for metal level and voltage optimization was stable pots operation. In this smelter, one of the main causes of pot instability is the automatic control system that controls the AlF_3 feeding, causing a wide variation in bath chemistry, CR and bath temperature. Hence a new strategy was required to address this issue. This paper focuses on the work and strategy done to stabilize AlF_3 feed in order to reduce the variations of CR and bath temperature.

2. Original AlF_3 Control Strategy

The AlF_3 additions at this Chinese smelter are controlled by an automatic system based on a complex “online intelligent optimization” process [2] aimed to control superheat using (according to the manufacturer claims) a variety of process inputs such as: bath temperature, alumina concentration, noise, resistance and it does not require human intervention. However, this system operation leads to significant daily fluctuation in AlF_3 feed, resulting in severe fluctuations in bath chemistry, CR and bath temperature as can be seen in Figure 1. The fluctuations in actual AlF_3 feed over 6 months on a single pot caused by the automatic AlF_3 control strategies can be seen in the top graph in Figure 1, which resulted in fluctuations in CR and bath temperature (bottom graph), leading to unstable pot condition.



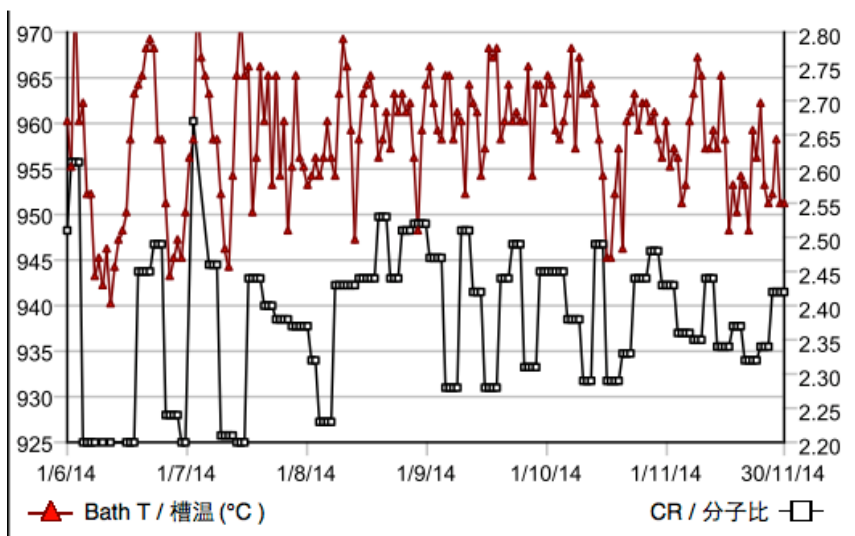


Figure 1. Fluctuations in the actual AlF_3 feed (top graph) over 6 months on pot 1049 using original AlF_3 control strategies, resulting in fluctuations of CR and bath temperature (bottom graph).

In addition, the automatic system does not offer manual adjustment by process engineers to compensate for the variations caused by the automatic operation. The smelter engineers and operators can only control the “set point AlF_3 ” parameter, not the actual feed. This leads to daily AlF_3 feed fluctuations from 0 kg to 100 kg from one day to the next (illustrated in Figure 1). The histogram in Figure 2 shows the extremely large distribution in CR, ranging from 2.1 to 2.8, with a standard deviation ± 0.10 .

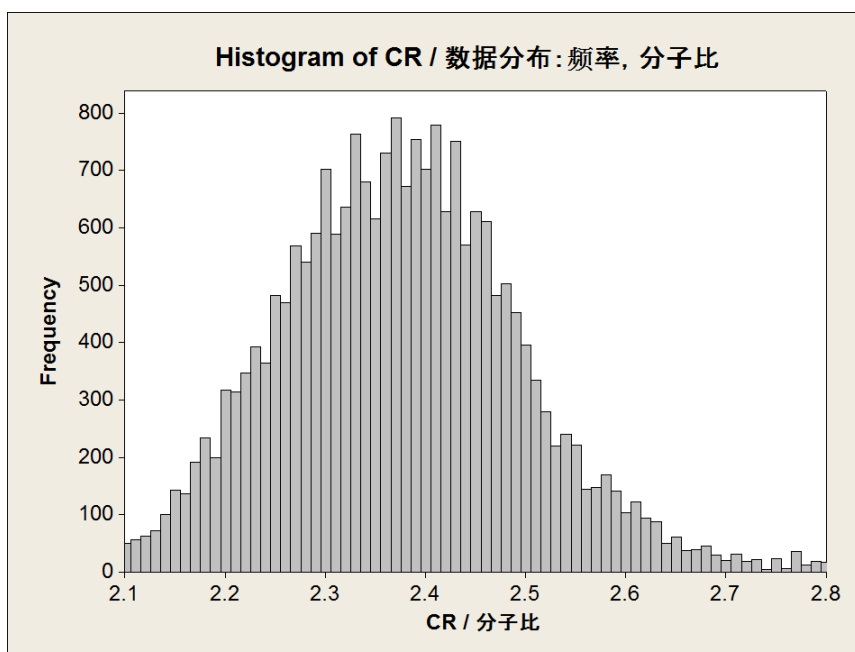


Figure 2. Histogram showing very wide CR distribution on a potline over four months (March - June 2015), using the original AlF_3 control strategy.

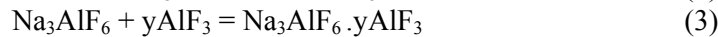
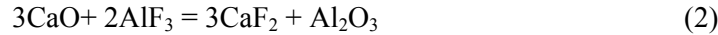
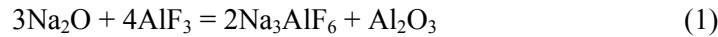
This type of “online intelligent optimization” control of AlF_3 addition is not effective on pots where the temperature change/trend is due to energy variations rather than bath chemistry variations. Events such as anode spikes, anode effects (AE), increased noise or changes to anode

set modifier can directly affect the bath temperature and change the heat balance of the pot. If the root cause for the bath temperature trend is not due to change in bath chemistry, adjusting AlF_3 feeding will bring even more problems. A good example that illustrates this problem is a high bath temperature due to anode spike scenario. The system will try to reduce the temperature by increasing AlF_3 feed, however, it will cause a reduction in liquidus temperature and a further increase of the superheat. If the spike is not removed, this trend will continue, and finally will cause the pot to be out of control.

3. AlF_3 Feed Control and Fluoride Balance in Reduction Pot

Aluminium reduction process is a dynamic process, where, among other parameters, maintaining stable bath chemistry (stable CR) is the prerequisite to ensure a highly efficient production process. During the reduction process, fluoride ions are being consumed and hence they need to be replenished. In the pot, the main function of AlF_3 addition is to maintain fluoride balance in the electrolyte. A good AlF_3 control strategy should consist of stable AlF_3 input which requires: 1) stable daily AlF_3 additions where possible based on a long-term AlF_3 target, 2) corrections of AlF_3 feed from the long-term target only if required due to bath chemistry changes. A long-term nominal AlF_3 demand should be specific to each individual pot, and in order to set an accurate target, the theory behind fluoride balance (generation vs. emission) should be considered.

AlF_3 consumption and losses occur via several mechanisms [3] as illustrated in Figure 3. The main mechanism of AlF_3 consumption is due to the reaction with impurities in the raw material – alumina – to form fluoride species. When alumina purity is low, it contains higher levels of impurities such as sodium oxide, calcium oxide, lithium, magnesium, potassium, and other alkali metal oxides (which is common in alumina that is sourced from China). These compounds react with the fluoride ions to form fluorinated species such as cryolite NaAlF_6 , NaAlF_4 , CaF_2 , LiF , MgF_2 and KF . The amount required for reaction can be predicted from the concentration of the oxide impurities, according to the following reactions (Equations 1 to 3):



Where y is the proportion of excess AlF_3 based on its target concentration.

The second mechanism of fluoride consumption is via gaseous HF and particulate fluorides emissions from the pot. Gaseous HF is generated from the reaction of fluoride ions with moisture in the air, surface water or hydroxyl ions in the alumina during the electrolysis process; this gaseous HF is emitted out of the pot [5]. Particulate fluorides are generated from the vaporization and condensation of bath species and from entrainment of bath particles and liquid bath droplets in the pot gases [6]. The emission of these fluoride species are partially captured by the anode cover, which returns back to the pot when the cover melts or collapses; HF is mainly captured by gas treatment center (GTC), and returns to the pot with the fluorinated alumina when alumina is added to the cell. However, some of the fluoride ions still manage to escape as gaseous HF and NaAlF_4 through holes in the cover and gaps in the pot hooding into the potroom area (known as fugitive roof emissions) or escape from the GTC into the stack. Hence the better the integrity of the anode cover and the more efficient the operation of the GTC, fewer fluorides are lost.

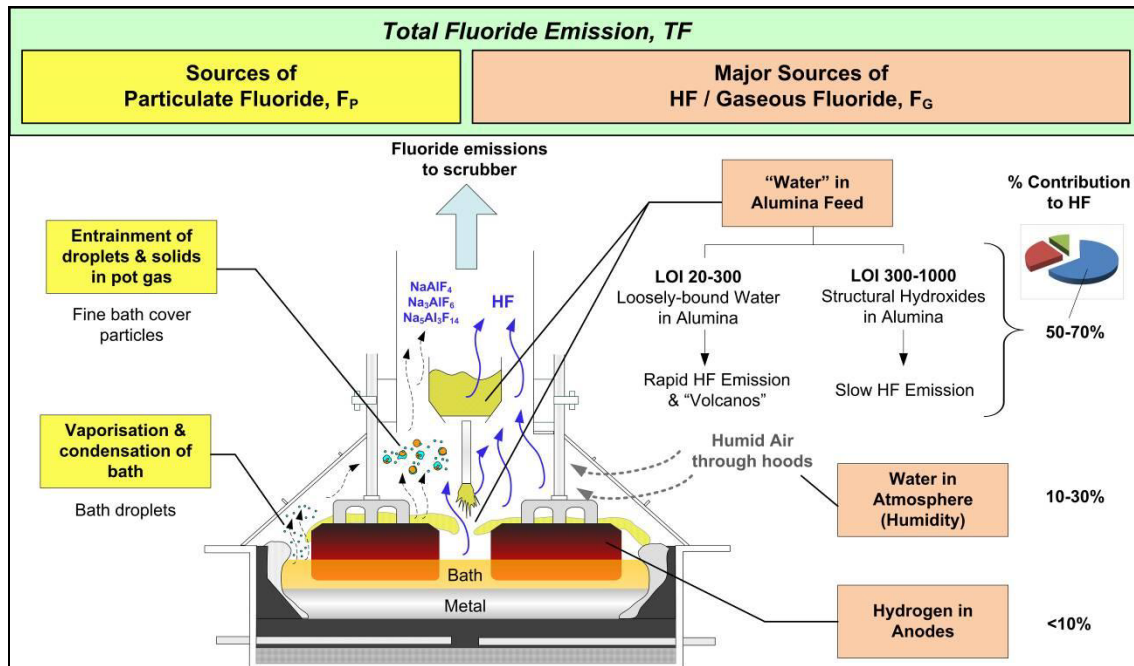


Figure 3. The different pathways for both particulate and gaseous fluoride emissions to escape a pot. Reproduced from the FEMG [6].

The third mechanism of AlF_3 consumption is via cathode sodium adsorption which relates to pot age. Hyland et al. [3] shows that due to the adsorption of sodium in the cathode, the sodium (coming from the raw material) concentration in the bath will be correspondingly reduced, and the demand for the aluminum fluoride to neutralize it will be reduced. Hence the consumption of AlF_3 is related to pot age - as the amount of adsorbed sodium gradually reduces with the increase in pot age, the need for AlF_3 is increased. When the cathode reaches the saturation point for sodium intake, the AlF_3 demand is due only to the first two mechanisms (neutralizing impurities in alumina and replacing fluoride emission losses). Different cathode materials have different adsorption ability to sodium; anthracitic cathode material has a greater level of absorption than that of the graphitic cathode material [4].

Figure 4 shows the combination of all three mechanisms of AlF_3 consumption in electrolytic cells. The blue line in Figure 4 is the actual potline AlF_3 consumption (30-day average values); and the red dotted line is the long-term AlF_3 demand, which is based on demand due to mechanism 1 (the consumption of sodium calcium alkali metal), and mechanism 2 (fluoride losses). The influence of pot age (mechanism 3) is shown by the blue line, with zero AlF_3 additions for new pots when the cathode is adsorbing sodium, and increasing as the pot ages until finally, it reaches the long-term demand, when the cathode is saturated with sodium.

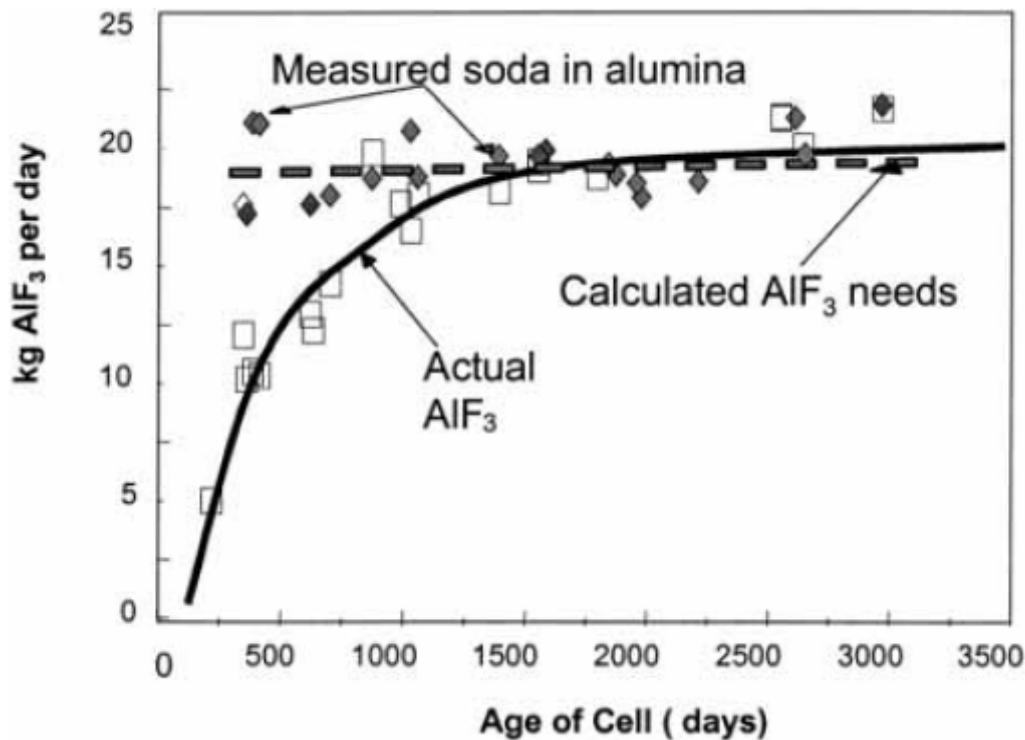


Figure 4. Actual historical AlF_3 (kg/day) added to cells in one potline (using 30-day averages) with pot age (days) in blue. The red line shows the long-term AlF_3 demand, due to soda in alumina and other factors. This figure is reproduced from Hyland et al, 2000 [3].

3.1. New statistical process control (SPC) method to control AlF_3 feed

The use of the original AlF_3 control system resulted in large variations in daily aluminum fluoride additions, CR and bath temperature, leading to unstable pots condition. Hence a new strategy was required to control AlF_3 which should be based on: 1) stable daily AlF_3 additions where possible that is based on long-term AlF_3 demand; 2) corrections of AlF_3 feed from this long-term target only if it is required. This should be determined on the basis of a statistical process control (SPC) analysis of the CR trend, i.e. test whether CR is statistically out of control, or whether it is just due to normal variation. This SPC method is a completely different strategy compared to the automatic system which is actually based on pot resistance and perhaps bath temperature.

The principle of the new system is maintaining long-term stability of AlF_3 addition, to achieve stable CR and bath temperature by using long-term AlF_3 feed target individually for each pot with SPC control on the corrections from target CR trend. The long term AlF_3 addition target is set for the pot according to different pot conditions (in terms of pot age and feed moving average). The corrections are needed to bring CR back to target hence an adjustment value is calculated for each day. In order to minimize CR variations, this adjustment should be as small as possible. The actual AlF_3 feed can be represented by the following equation:

$$\text{AlF}_3 \text{ addition} = \text{AlF}_3 \text{ setpoint} + \text{AlF}_3 \text{ adjustment} \quad (4)$$

where,

- $\text{AlF}_3 \text{ addition}$ is scheduled AlF_3 feed per pot (kg/day)
- $\text{AlF}_3 \text{ setpoint}$ is the set long-term target amount of AlF_3 addition for each individual pot; this set value can be based on pot age (e.g. AlF_3 model based on pot age) and a long-term

feeding history (e.g., a 90-day moving average). Using these statistical analyses method, different pots are given their own CR target.

- AIF_3 adjustment is a value calculated through the SPC analysis of whether or not CR is abnormal. When statistical analysis shows that CR has a clear increasing or decreasing trend or when CR deviates from normal patterns (according to the statistical Nelson rules as shown in Table 1 [7]), then a correction (AIF_3 adjustment) is calculated and AIF_3 addition is adjusted.

If the long term AIF_3 feed requirement (AIF_3 setpoint) is accurate, then AIF_3 adjustment will be minimized. Under this condition, if CR does not deviate from the target, then AIF_3 addition = AIF_3 setpoint, i.e. AIF_3 additions remain constant.

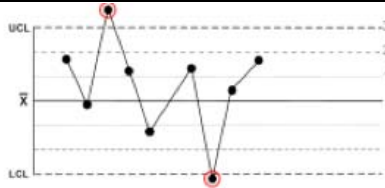
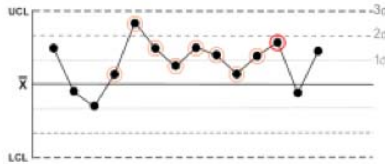
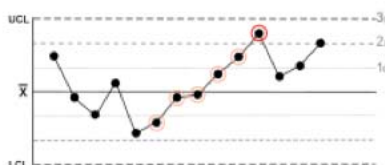
Statistical process control (SPC) method on CR trends can verify if the CR trend is under control or its deviation from the target is statistically significant. Having a long term AIF_3 target can also help to easily identify the root cause of variation in CR and whether it is due to changes in raw material properties or a particular trend within a period of time.

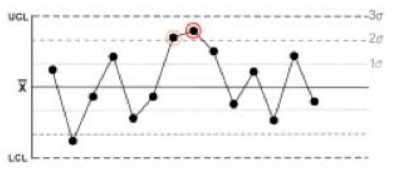
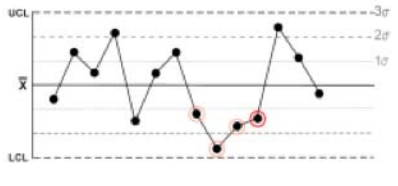
According to the new AIF_3 feed control, a statistical analysis is carried out on 9 historical CR data points, these data points are analyzed using five statistical rules to identify if the CR changes are statistically significant. The process is considered out of control if the following rules are met:

- 1) One point is outside of 3 standard variations,
- 2) 9 sample points (or more) are consistently on one side of the mean, but does not exceed the control bands ($\pm 3\sigma$),
- 3) 6 sample points (or more) continue to increase or decrease,
- 4) 2 points out of 3 are outside of 2 standard deviations on the same side. The 3rd point can be on either side of the mean;
- 5) 4 points (or more) out of 5 are outside of 1 standard deviation on the same side. The 5th point can be on either side of the mean.

If one or more of these rules are met, it indicates that CR is out of control and an adjustment is required on the AIF_3 addition. This adjustment value can be obtained through converting the deviation of CR from CR target to the amount of AIF_3 required.

Table 1: SPC rules to distinguish out of control data [7].

Rule #	Description	Example	Type of problem
1	One point is more than 3 standard deviations from the mean		Shows that one sample point (2 is shown in this example) is severely out of control (outside of control limits $\pm 3\sigma$)
2	Nine (or more) points in a row are on the same side of the mean.		Shows long term deviation
3	Six (or more) points in a row are continually increasing (or decreasing).		Trend exist

5	Two (or three) out of three points in a row are more than 2 standard deviations from the mean in the same direction.		This is a moderate trend of moderate loss of control. The 3 rd point can be on either side of the mean
6	Four (or five) out of five points in a row are more than 1 standard deviation from the mean in the same direction		This shows a strong trend of minor loss of control. The 5 th point can be on either side of the mean

An example of the daily AIF₃ scheduler output is shown below in Figure 5, which indicates the target AIF₃ feed and CR for each pot, historical CR values (past 9 data points), the SPC test outcome, the amount of AIF₃ correction needed from long term pot target (in kg) and the final scheduled AIF₃ (right-most column) for each pot.

AIF ₃ Scheduler 计划氟化铝量																	Date 日期												
Pot 槽号	Nominal AIF ₃ Actual (kg) 氟化铝量目标值 (公斤)	CR Target 分子比目标值	Date of Newest Data Point 最新的数据点的日期	Past CR Data Observations 历史分子比数据									SPC Rules 异常检测						AIF ₃ Correction (kg) 氟化铝修正量 (公斤)	Scheduled AIF ₃ Addition (kg) 计划氟化铝量 (公斤)									
				9	8	7	6	5	4	3	2	1	1	2	3	5	6	SPC test for CR 异常检测结果											
1129	34	2.4	22/9/2015	2.43	2.39	2.40	2.50	2.51	2.55	2.49	2.46	2.48									H	HIGH 异常偏高	12	46					
1130	34	2.4	22/9/2015	2.40	2.46	2.38	2.32	2.32	2.37	2.36	2.39	2.39													NORMAL 正常	0	34		
1131																													
1132	34	2.4	22/9/2015	2.12	2.41	2.41	2.44	2.48	2.48	2.47	2.45	2.47													H	HIGH 异常偏高	10	44	
1133	34	2.4	22/9/2015	2.20	2.31	2.35	2.26	2.31	2.33	2.34	2.33	2.40													L	LOW 异常偏低	-7	27	
1134																													
1135	34	2.4	22/9/2015	2.41	2.46	2.45	2.35	2.32	2.29	2.34	2.31	2.40															NORMAL 正常	0	34
1136	34	2.4	22/9/2015	2.45	2.40	2.46	2.20	2.30	2.33	2.43	2.45	2.53															NORMAL 正常	0	34

Figure 5. AIF₃ scheduler based on long-term target and SPC corrections.

4. Results

The new AIF₃ addition strategy was implemented on a 6 test pots at a 400KA smelter for a period of 4 months. The influence of the new strategy could clearly be seen on AIF₃ feed, CR and bath temperature trends when comparing one test pot trends to a reference pot trends as shown in Figure 6. The bath temperature and CR (top graphs) and AIF₃ addition (bottom graphs) trends of a test pot are shown on Figure 6 (left), while the reference pots trends for the same time period are shown on Figure 6 (right). It can be seen that the test pot's AIF₃ feed has less variation compared to the reference pot, which reduced CR and bath temperature variation compared to their trends on the reference pot.

Furthermore, when an external factor (e.g. AIF₃ density change, shown in Figure 6) occurs on both pots, the long term AIF₃ feed target on the test pot made it much easier to identify the change in CR trends while in the reference pot it is much harder to notice the change due to the constant variations in AIF₃ and CR.

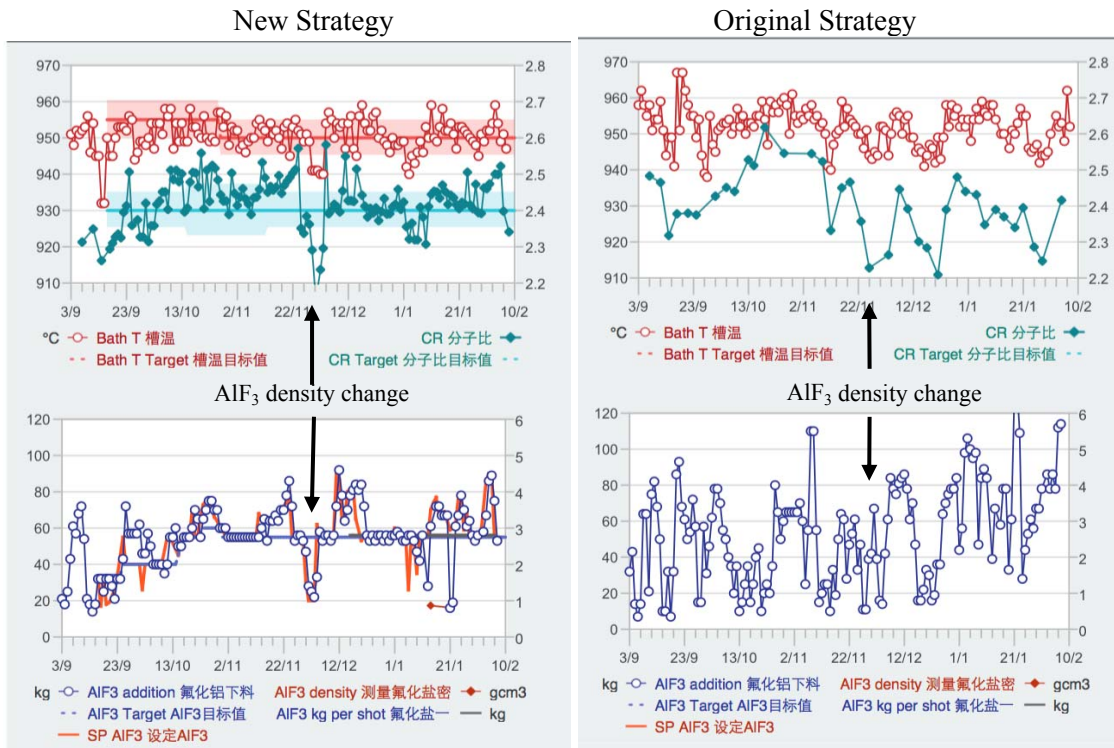


Figure 6. Bath temperature and CR (top graphs) and AIF₃ addition (bottom graphs) trends, for a test pot with the new AIF₃ addition strategy (left) and a reference pot with the original strategy (right). The impact of an external factor (AIF₃ density change), which affected both pots, is seen clearly on the test pot CR trends but not so clearly on the reference pot (marked in arrow).

The impact of the new AIF₃ feed strategy on the entire test pots group can be seen when comparing the AIF₃ feed, CR and bath temperature performance of the test pots to the 6 reference pots. The standard deviations of AIF₃ feed, CR and bath temperature of the test pots and reference pots over 4 months period is listed in Table 2. The new strategy implemented on the test pots led to 35 % less variation on AIF₃ feed on the test pots compared to the reference pots; standard deviation for CR is $\sigma \pm 0.123$ for reference pots and $\sigma \pm 0.077$ for test pots, meaning 37 % less variation of CR on the test pots compared to the reference pots; Standard deviation for bath temperature is $\sigma \pm 6.51$ °C for reference pots and $\sigma \pm 5.57$ °C for test pots, resulting in 14 % less variations in bath temperature on the test pots compared to the reference pots.

Table 2. Standard deviation in process parameters on test and reference pots over 4 months.

Parameter	Test Pots	Reference Pots	Reduction in variation in Test vs. Reference pots
AIF ₃ – σ	± 18.59 kg	± 28.39 kg	- 35 %
CR – σ	± 0.077	± 0.123	- 37 %
T – σ	± 5.573 °C	± 6.511 °C	- 14 %

These results can be seen more visually in histograms of AIF₃ addition, CR, and bath temperature shown in Figure 7, Figure 8, and Figure 9, respectively.

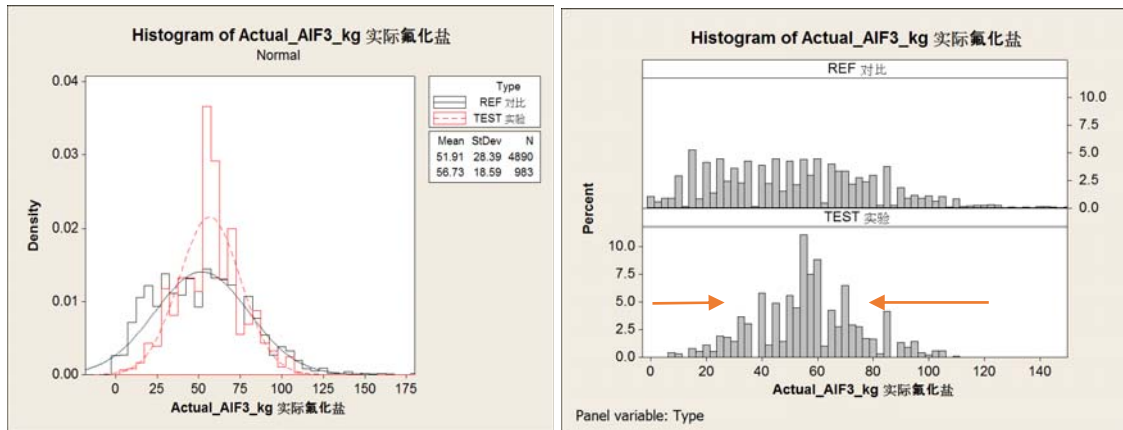


Figure 7. Histograms showing distribution of actual AIF₃ addition and standard deviation for test pots and reference pots.

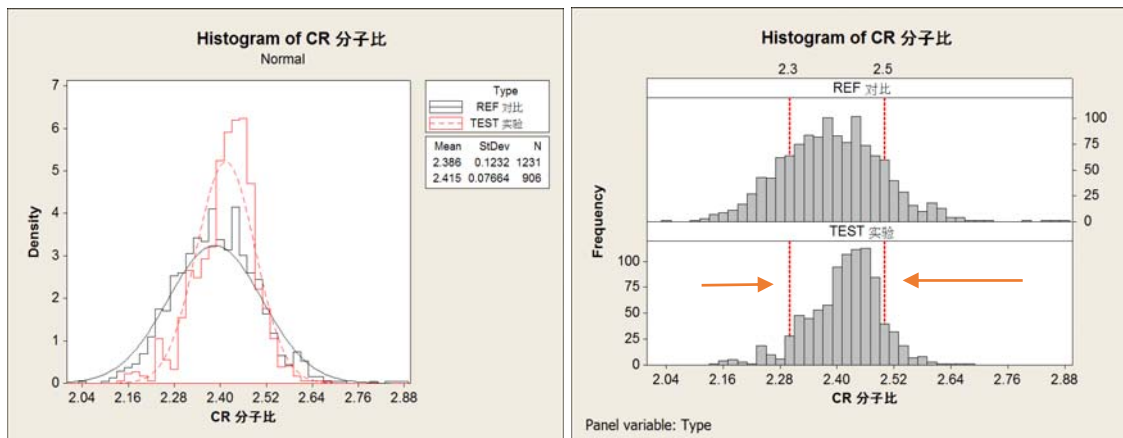


Figure 8. Histograms of CR showing standard deviation for test pots and reference pots.

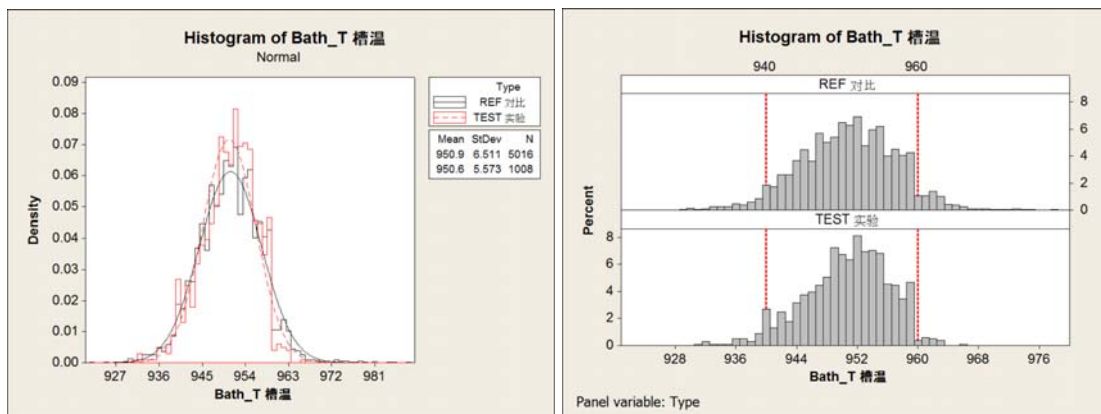


Figure 9. Histograms of bath temperature showing standard deviation for test pots and reference pots.

The new strategy has less effect on the bath temperature compared to CR due to the additional factors that affect bath temperature such as noise level, and energy input variations (from spikes, AE, etc.).

5. Discussion

The new AlF_3 addition and control strategy reduces variation on the inputs to the process (AlF_3 feed) that leads to reduction of variation on process outputs (CR and bath temperature) with the benefits of more stable pots operation overall. However, there is an additional benefit of having stable inputs and outputs – the ability to easily and rapidly identify the impact of external factors on the outputs. This leads to easier root-cause assessment of any variation in parameters trends and allows removing them which open the way to continuous improvement. The new AlF_3 feed strategy allows the smelter to clearly see, study and manage or remove most causes of variation in CR or bath temperature. An example of this process is illustrated in Figure 10.

- A. Previous Condition – when the input AlF_3 feed varies and unstable, the output will also be unstable CR and bath chemistry; hence the output trend is consistent with the input.
- B. Target Condition – when the input is stable AlF_3 additions, the output will also be stable CR and bath chemistry; again the input and output trend lines are consistent.
- C. Target Condition + External Input – when the input AlF_3 additions is stable, but at the same time there is a change in external factor input, then the output will be unstable CR and bath chemistry; here the AlF_3 input trend is not consistent with the output, highlighting the presence of another external input.

A case study of how this strategy works was shown previously in Figure 6. By stabilizing the AlF_3 additions, the impact of the automatic control system itself on the process was removed, which results in stable AlF_3 feed and hence stable outputs (CR and bath chemistry). This also allows for identification of other external variables that impacted CR and bath temperature but could not be easily identified previously, in this case, changes in AlF_3 density.

The impact of the change in AlF_3 density can clearly be seen on CR trends on the test pot, which led to significant drop of CR below target (Figure 6, left chart). However, this change which also impacted the reference pots was not obvious on the reference pot's CR trend (Figure 6, right chart) due to the large variation derived from the large AlF_3 feed fluctuations.

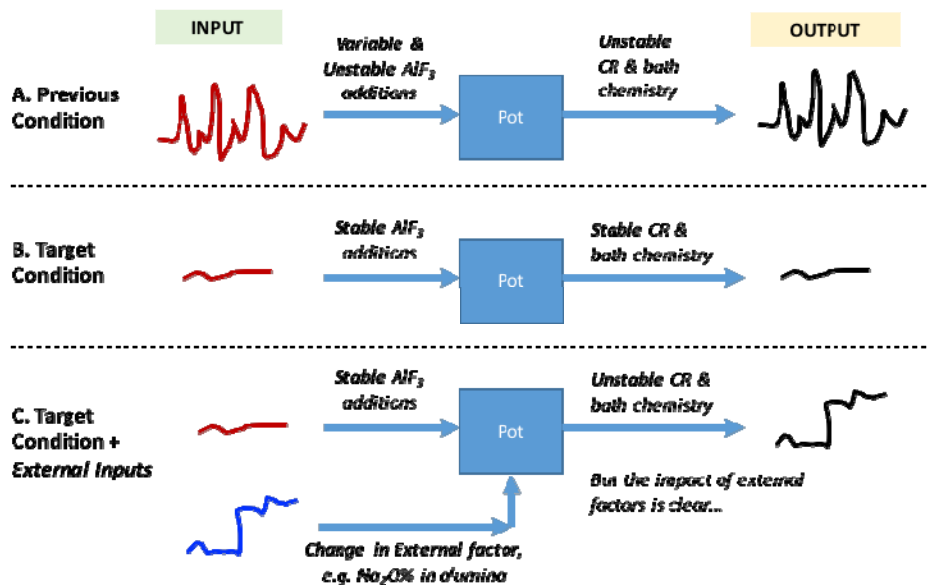


Figure 10. Diagram illustrating how stable process outputs (such as CR, bath chemistry and temperature) is dependent on stable process inputs (AlF_3 additions) using three scenarios: [A] unstable process inputs, [B] stable process inputs, and [C] stable inputs + external factors.

The change in raw materials suppliers in the smelter led to change in raw materials quality which impacted the pots performance. AlF_3 density changed several times during the test period. The changes in density were very significant as can be seen in Figure 11, a change of almost 100% occur during Nov 2015 when the density changed from ~ 1.5 to $\sim 0.78 \text{ g/cm}^3$ and again from February to March 2016. These changes were easily identified on CR trend on the test pots which allowed the smelter team to be aware of the change early and implement a system to reduce the impact of these changes on the pots performance. Once a new shipment of AlF_3 arrived, the team measured AlF_3 density directly from the pots feeders; once the new material reached the feeders, the AlF_3 feed settings were changed to adjust for the new AlF_3 shot weight. This reduces the impact of the new density on pot performance. In addition, the stable CR trend offers an indication of whether the adjustment was done correctly and on time. Any sharp change in CR meant the AlF_3 settings change was not done in a timely manner.

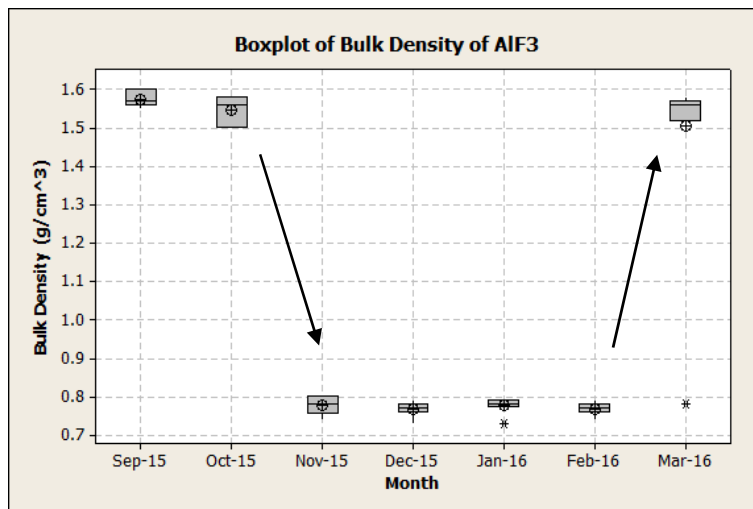


Figure 11. Boxplot of bulk density (g/cm^3) of AlF_3 supplied every month to the smelter, showing two major changes in AlF_3 density.

The changes in raw material supplier also affected alumina quality with a change in impurity levels. The change in impurity levels had an impact on AlF_3 long term requirement over the course of the project as can be seen in Figure 12 which shows a monthly average of AlF_3 feed over 14 months. It can be seen that there was a large increase in the monthly average AlF_3 feed requirement over the 14 month period, from a minimum of 25 kg in April 2015 to maximum 75 kg during February 2016. Due to these alumina supplier changes, the AlF_3 set point has to be reviewed frequently and adjusted in order to maintain CR on target.

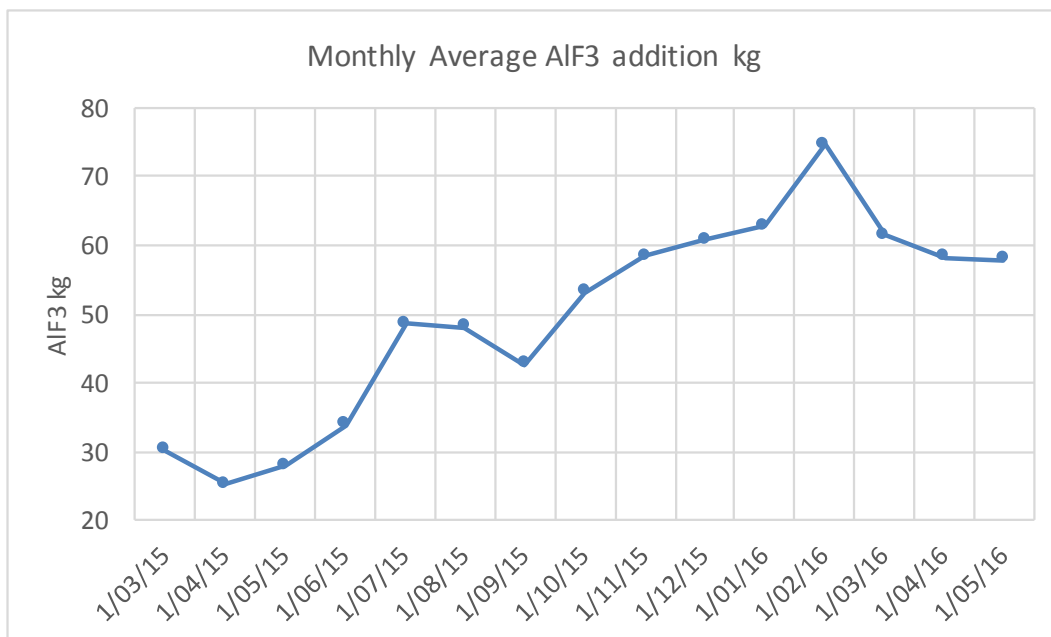


Figure 12 – Monthly average of actual AlF₃ additions over 14 months for test pots.

6. Conclusions

A new AlF₃ feeding strategy, which is based on long term feed target and correction using SPC of CR trends, was used as part of a project that aims to optimize damaged cathode pots metal level and energy consumption. This new fluoride feeding strategy aimed to minimize the variation of AlF₃ feed and hence reduce variations of CR and bath temperature trends.

The new strategy was implemented on 6 test pots and compared to a group of 6 reference pots over 4 months. During the test period, the test pots AlF₃ addition variation was reduced by 35 %, CR variation was reduced by 37 %, and bath temperature variation is reduced by 14 %. This strategy ensured stable operation of the pots, which was a precondition for metal level and energy consumption optimization without a reduction in current efficiency or causing further damage to the cathodes.

This AlF₃ feeding strategy had an additional benefit on top of the stable AlF₃ and CR control, which was the ability to identify the impact of external factors on pot performance. This led to the ability to study and better manage external factors affecting bath chemistry and material balance and opened the way to a process of continuous improvement.

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