Effects of Anode Quality and Lithium Potassium Fluoride Contents on the Amount of Carbon Dust During Aluminum Electrolysis Process with High Potassium Electrolyte System

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Abstract

In this paper, operation superheat of cells, amount of carbon dust, and carbon content in electrolyte were tracked and analyzed for a long time during a period when carbon anode blocks of varying qualities were being used in an aluminum smelter. Electrolyte composition adjustment test was carried out to track and analyse the variations of carbon dust amount and superheat with the variations of KF and LiF content. The results showed that high-quality anodes could significantly reduce the amount of carbon dust and the content of carbon in bath. Reducing the content of KF in electrolyte could improve the superheat and reduce the amount of carbon dust significantly. Anode quality, LiF and KF content in electrolyte, superheat, and carbon content in anode covering materials are important factors affecting the amount of carbon dust produced in the aluminum electrolysis process.

Keywords

Amount of carbon dust • Anode quality • KF and LiF contents • Superheat

Introduction

In aluminum reduction process, some carbon particles will fall off from anodes and enter the electrolyte melt to form carbon dust due to the anodes' selective oxidation, uneven combustion, electrolyte erosion, and other reasons [1–3].

Carbon dust has a negative impact on aluminum electrolysis process and also brings economic burden to aluminum smelters [4–6]. Carbon dust was listed in the "Chinese national list of hazardous waste" in 2016, characterized by "Toxicity" and identified by code 321-025-48. So, it's very important for aluminum smelters to reduce the carbon dust amount in the production process.

The amount of carbon dust varies greatly among different aluminum smelters in China, ranging from a few kilograms per tonne of aluminum to more than 20 kg per tonne of aluminum. In this paper, the effect of anode quality, KF, and LiF content on the amount of carbon dust was studied through a long time tracking analysis in an aluminum smelter with high potassium electrolyte system in China.

Conditions and Methods

Industrial tests were carried out in an aluminum electrolysis potroom comprised of 36 cells running at 400 kA. The follow-up analysis and electrolyte component adjustment test described in this paper were mainly carried out on the last 18 cells in the aluminum electrolysis potroom, namely cells numbered 2619 through 2636. Before the beginning of the tests, the average KF content of electrolyte was about 4.6%, and the average LiF content was about 1.5%. It belonged to the high KF and low LiF content electrolyte system (generally, the content of both KF and LiF is limited to 3%, and it's considered to be on the "high side" if this threshold is exceeded).

From September 26, 2018 to November 7, 2019 (i.e., a total of 59 weeks), the variation of carbon dust amount, superheat, and carbon content in electrolyte were continuously analyzed during the period when five different types of carbon blocks with varying qualities were used in this aluminum electrolysis potroom.

Table 1 shows physical property requirements from the "Chinese standard of prebaked anode for aluminum

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Table 1 Standard of prebaked anode for aluminum electrolysis in non-ferrous industry (YS/T285-2012) [7]

Grade	Apparent density, [g/cm^3]	True density, [g/cm^3]	Compressive strength, [MPa]	Reactivity residual rate of CO$_2$, [%]	Bending strength, [MPa]	Resistivity, [μΩ·m]	Coefficient of thermal expansion, [10^{-6}/K]	Ash content, [%]
TY-1	≥ 1.55	≥ 2.04	≥ 35.0	≥ 83	≥ 8	≤ 57	≤ 4.5	≤ 0.5
TY-2	≥ 1.52	≥ 2.02	≥ 32.0	≥ 73	≥ 8	≤ 62	≤ 5.0	≤ 0.7

electrolysis in non-ferrous industry (YS/T285-2012)". The five kinds of anodes were ranked into different quality grades by comparing anode sample results regarding both vanadium content and the criteria described in Table 1: (highest quality) B > E > A > D > C (lowest quality).

It is important to note that, in China, "Qualification Rate of First-Grade Anode" is a parameter usually employed to express the quality of an anode. It refers to the fraction of tested samples that meets or exceeds all the requirements of "TY-1" grade, as defined by said YS/T285-2012 standard (see Table 1).

The amount of carbon dust was measured by centralized weighing, and the weekly average value of carbon dust per tonne of aluminum was used as the evaluation basis of carbon dust variation. The carbon dust of all the 18 cells was daily accumulated in a storage box and was weighed with the crane scale which has an accuracy of ±5 kg. The total daily amount of carbon dust was divided by the total amount of aluminum produced by the 18 cells per day to obtain the amount of carbon dust per tonne of aluminum. Weekly averages were then calculated.

The electrolyte samples were taken every week on Tuesday and Friday. There were 36 electrolyte samples for the 18 cells every week. A certain mass was taken out from each sample and then mixed to form a mixed sample. Liquidus temperature, carbon content, and KF and LiFcontent in the electrolyte were all obtained by analyzing the mixed samples, which were taken as the weekly average values of the 18 cells.

The Chinese Non-ferrous industry standard of "Determination of Carbon Content in Aluminum Electrolyte by Infrared Absorption Spectrometry (YS/T1035-2015)" was adopted to determine the carbon content in the electrolyte. The liquidus temperature was measured by the step cooling curve method, and the average bath temperature of the 18 cells sampled twice a week was taken as the operating temperature. The difference between the operating temperature and the liquidus temperature was regarded as the superheat of the 18 cells. KF and LiF contents in electrolytes were determined based on the Chinese Non-ferrous industry standard "Chemical Analysis Methods for Aluminum Electrolytes Part 3: Determination of Sodium, Calcium, Magnesium, Potassium and Lithium Elements—Inductively Coupled Plasma Atomic Emission Spectrometry (YS/T 739.3-201x)".

From February 2 to July 25, 2019 (week 20 to week 44), three cells (namely, 2620, 2621, and 2622) were selected for the electrolyte component adjustment test. In order to reduce the content of KF, solid electrolytes with low content of KF and high content of LiF (KF = 2.49% and LiF = 5.59%) were continuously added to the three cells. During this period, KF and LiF contents in electrolyte, superheat, and carbon content were continuously tracked and analyzed. The electrolyte sampling method was the same as that mentioned above. Sampling twice a week, and after the samples were treated separately, a certain mass was taken out from each sample and then mixed to form a mixed sample. The analysis and measurement of superheat and KF and LiF content in electrolyte were the same as those described above. The amount of carbon dust was also measured by centralized weighing, and the weekly average amount of carbon dust per

Table 2 Physical and chemical indexes of the five kinds of prebaked carbon anodes

	A	B	C	D	E
Manufacturer	Factory 1	Factory 1	Factory 2	Factory 3	Factory 1
Testing period	2018.Sep.26–2018.Oct.20	2018.Oct.21–2019.Mar.14	2019.Mar.15–2019.Jul.11	2019.Jul.12–2019.Aug.29	2019.Aug.30–2019.Nov.07
anode type	Normal anode	High-quality anode	Normal anode	Normal anode	Normal anode
Qualification rate of first-grade anode (%)	60	90	20	45	60
Vanadium content (ppm)	280	128	350	300	180

tonne of aluminum was used as the evaluation basis for carbon dust variation.

Experiments

Tracking Experiment Results

Figure 1 shows the variation curves of the weekly average amount of carbon dust per tonne of aluminum and superheat of the 18 cells during the usage of five different anode types.

Figure 2 shows the variation curves of the weekly average superheat and carbon content in the electrolyte of the 18 cells during the usage of five different anode types.

Anode A was used during the first 4 weeks, from September 26th to October 20th, 2018. The overall average amount of carbon dust was about 16.5 kg/t-Al. The average carbon content of electrolyte was about 0.345%. The superheat was low (about 1.2 °C) and was measured in the second week. The service life cycle of anode A was 35 days.

Anode B was employed from the 5th to 25th week (October 21st, 2018, to March 14th, 2019). At the beginning of this period, the superheat gradually increased its highest registered value of 7.4 °C due to a reduction of the aluminum level. Then, the weekly average carbon dust per tonne of aluminum decreased to 8.3 kg/t-Al and the carbon content of electrolyte decreased to 0.055%. Then the aluminum level was gradually increased back to the normal range, and the superheat gradually stabilized at about 3 °C. The amount of carbon dust stabilized at about 13 kg/t-Al, and the carbon content in bath stabilized at about 0.122%. During the operation of anode B, the first two anode life cycles lasted 35 days and the last two anode life cycles, 36 days.

However, it should be noted that when the superheat reached a high level (for example, 7.4 °C in the 8th week), the 18 cells were generally in the state of "Hot Cell", the anode stubs were washed by electrolyte melt, and a large amount of electrolyte melt was taken out, as shown in Fig. 3.

Anode C was used from the 26th to 42nd week (March 15th to July 11th, 2019). With the gradual replacement of anode B by anode C, the amount of carbon dust increased significantly, reaching a maximum of about 25 kg/t-Al. The carbon content of electrolyte increased to an average of

Fig. 1 Temporal evolution of the weekly average amount of carbon dust per tonne of aluminum and superheat for the 18 cells during the usage of the five different anode types

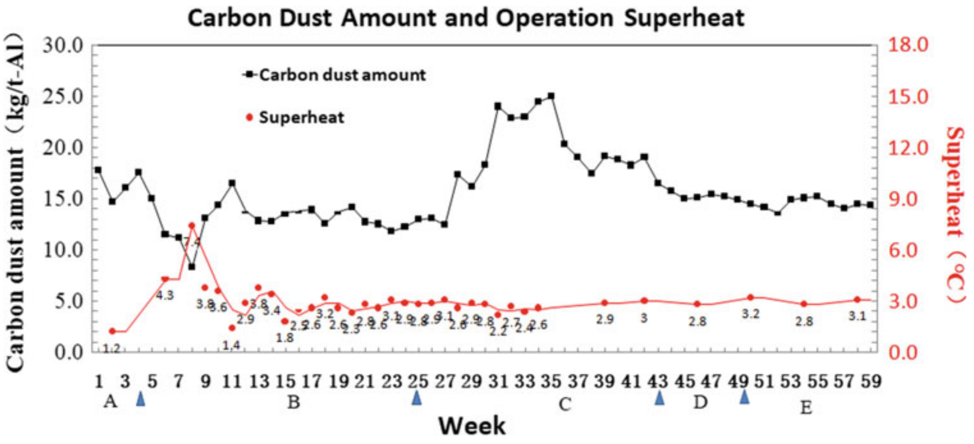


Fig. 2 Temporal evolution of weekly average superheat and carbon content for the 18 cells during the usage of the five different anode types

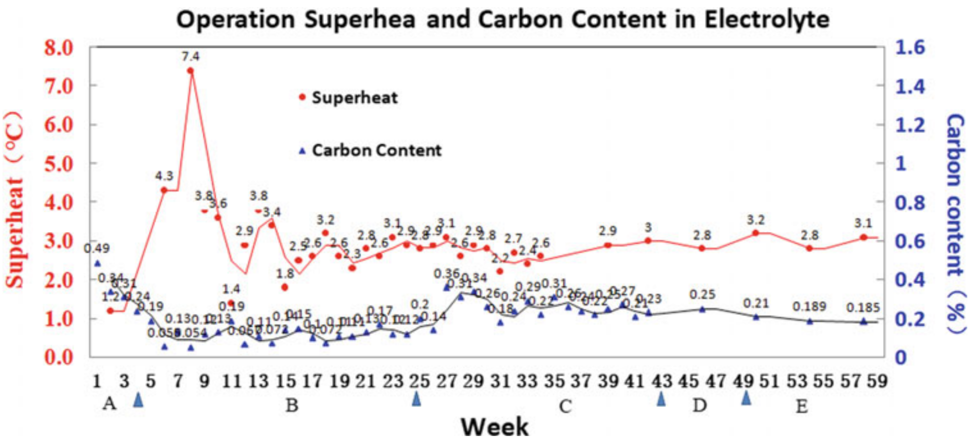


Fig. 3 Characteristics of Hot Cell: anode stubs were washed by electrolyte melt and large amounts of electrolyte melt were removed from the 18 cells

0.26%, and the average superheat was about 2.6 °C. Towards the end of this period, the amount of carbon dust gradually decreased and stabilized at about 20 kg/t-Al, while the carbon content of electrolyte decreased to about 0.24%, and the average superheat was about 3 °C. The service life cycle of anode C was 35 days.

Anode D was employed from the 43rd to 49th week (from July 12th to August 29th, 2019). With the gradual replacement of anode C by anode D, the amount of carbon dust decreased significantly and gradually stabilized at about 15 kg/t-Al, while the average carbon content of electrolyte was about 0.23%. The average superheat was about 3 °C. The service life cycle of anode D was 35 days.

Anode E was used from the 50th to 59th week (August 30th to November 07th, 2019). The amount of carbon dust gradually stabilized at about 14.5 kg/t-Al, while the average carbon content of electrolyte was about 0.187%. The average superheat was about 3 °C. The service life cycle of anode E was 35 days.

Through the tracking and comparative analysis results of the above, the following conclusions could be drawn.

(1) The amount of carbon dust was obviously affected by the quality of anode. High-quality anodes could significantly reduce the amount of carbon dust and carbon content in the electrolyte. Anode B was the highest-quality anode type, and its carbon dust amount and carbon content in electrolyte were significantly lower than other anode types. The second one was anode E, which had a lower carbon dust amount and carbon content in the electrolyte too.

(2) The amount of carbon dust was obviously affected by the superheat. When the superheat was higher, the carbon dust amount decreased, and when the superheat was lower, the carbon dust amount increased. This trend was observed for all anode types. During the testing periods for anode B and C, the amount of carbon dust varied according to the superheat variation.

(3) The carbon content in the electrolyte was affected by both anode quality and superheat. For the same superheat: the higher of anode quality, the lower of carbon content would be. For the same anode quality: the higher of superheat, the lower of carbon content would be.

(4) Lower superheat might be a characteristic of a high KF and low LiF electrolyte system. During the period of anode B was employed, when the superheat reached 7.4 °C , the cells were in the state of "Hot Cell". However, in a pure electrolyte system, superheat between 5 °C to 12 °C is considered to be within the normal range, and the phenomenon of "Hot Cell" is not expected to be observed.

(5) The relatively higher amount of carbon dust might also be a characteristic of a high KF and low LiF electrolyte system. Anode B was the one with the highest quality, its "Qualification Rate of First-GradeAnode"—i.e., the ratio of tested samples meeting or exceeding "TY-1" grade requirements—reached 90%. During its usage period, the superheat increased from 2–3 to 7.4 °C, which led to the "Hot Cell" phenomenon, and the amount of carbon dust only decreased to 8.3 kg/t-Al, which was still on the high side. The amount of carbon dust could not be further reduced only by improving the anode quality and superheat.

Electrolyte Composition Adjustment Test

The curves of superheat versus KF and LiF content adjustment for the three cells are shown in Fig. 4. The comparison curves of the carbon dust amount of the three cells and 18 cells in the same period are shown in Fig. 5.

The electrolyte composition adjustment test could be divided into three stages, as follows.

In the first stage, which lasted for five weeks (February 2nd to March 7th, 2019), high LiF and low KF content solid

Fig. 4 Temporal evolution of superheatand KF and LiF content for the three test cells

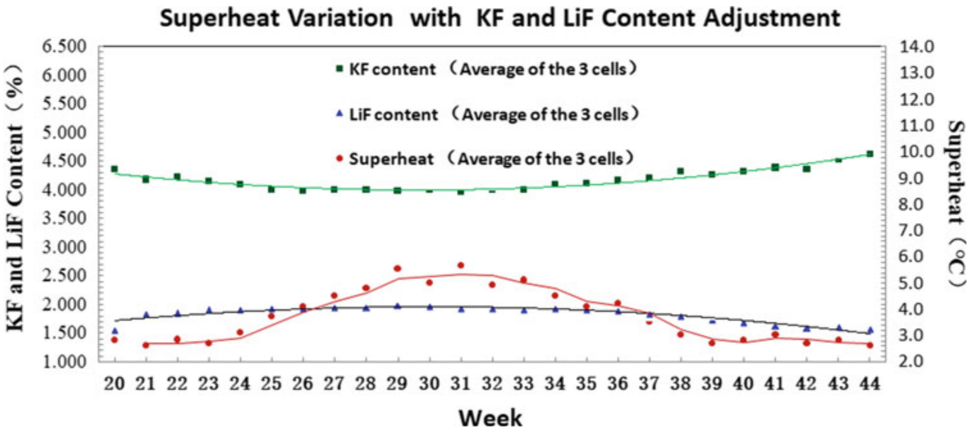
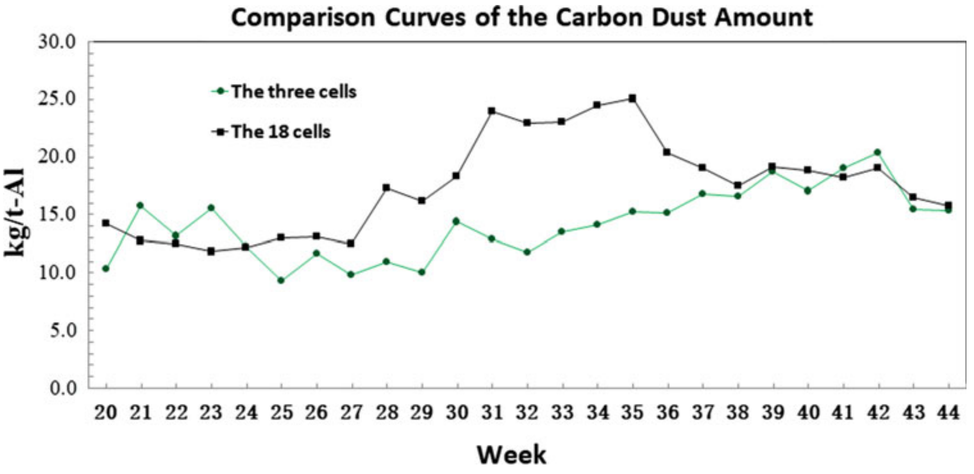


Fig. 5 Temporal evolution of carbon dust amount for both the three test cells and all 18 cells



electrolytes were added to the three cells. As a result, KF content gradually decreased, and LiF content gradually increased. In this stage, the amount of carbon dust and superheat had no significant change.

In the second stage, which lasted for ten weeks (March 8th to May 16th, 2019), high LiF and low KF content solid electrolytes were continuously supplemented. KF content become lower than 4.0%, while LiF content became higher than 1.9% in the three cells. The average carbon dust amount of the three cells had been significantly lower than that of the 18 cells, and the average superheat rose to 4–6 °C.

In the third stage, which lasted 10 weeks (May 17th to July 25th, 2019), the supplement of high LiF and low KF content solid electrolyte decreased and stopped. At this stage, the KF content gradually increased, and LiF content decreased, so that the bath chemistry became comparable to that of the entire potline. As a consequence, the carbon dust amount gradually increased and approached the carbon dust amount of 18 cells. The superheat also gradually recovered to 2–3 °C.

Through the electrolyte component adjustment test, it could be seen that when the KF content was reduced to less than 4% and LiF content was slightly increased to more than 1.9%, the superheat could be significantly improved, and the carbon dust amount could be significantly reduced. During the period from the 29th to 33rd week, when the superheat was about 5 °C, the average amount of carbon dust was 12.5 kg/t-Al. Compared with the18 cells, the amount of carbon dust of the three test cells was reduced to 8.4 kg/t-Al, or a reduction of 40.2%.

Analysis and Discussion

The usage of anodes blocks of varying qualities and the adjustment test of electrolyte components revealed that the amount of carbon dust was not only affected by anode quality, but is also related to the KF and LiF content in the electrolyte and the superheat. Lower superheat and higher amount of carbon dust might be the characteristics of aluminum electrolysis process with a high KF and low LiF content electrolyte system.

Investigation and Comparison with Other Smelters

In order to further understand the influence of electrolyte components on the amount of carbon dust, two other aluminum smelters (identified as “X” and “Y” in this work) were investigated during the experiment. The main process parameters, such as anode conditions, electrolyte components, and carbon dust amount of each smelter are summarized below to enable a comparative analysis, refer to Table 3.

From the results of investigation and analysis, the following could be drawn:

(1) The quality of anode B used in the company was the best, but the amount of carbon dust was much higher than that of X and Y smelters, which proved that anode quality was not the only decisive factor of carbon dust amount.

(2) Compared with the smelters in this paper, smelters X and Y presented a lower KF content in the electrolyte and a higher superheat, which might be an important reason for the lower amount of carbon dust.

(3) With the decrease of KF content in the electrolyte, the amount of carbon dust decreased. The KF content of Y smelter was the lowest, and the amount of carbon dust was also the lowest.

Relationship with Net Anode Consumption

The amount of carbon dust is closely related to the quality of anode [8–12]. The carbon particles in carbon dust mainly come from the “additional consumption” referred to in “net anode consumption”. In 1991, W K Fisher of Swiss Aluminum Company deduced the relationship between net anode consumption and the parameters of the electrolytic process and anode quality [2, 8, 9], as shown in the following formula:

$$N_C = C + \frac{334}{C_E} + 1.2(BT - 960) - 1.7C_{RR} + 9.3A_P + 8\lambda - 1.5A_{RR} \tag{1}$$

where N_C is net anode consumption (400–500), [kg/t-Al]; C is the cell factor (270–310), [-]; C_E is current efficiency (82–95), [%]; BT is the electrolytic cell temperature (945–980), [°C]; C_{RR} is the residual rate of CO_2 reaction (75–90), [%]; A_P is air permeability (0.5–5.0), [10^{-9}m^3/s m^2]; λ is anode

Table 3 Comparison of operating parameters and amount of carbon dust in different smelters

Item	Smelters in this paper	X smelters	Y smelters
Cell name plate (kA)	400	500	500
Line current (kA)	396.5	497.77	488.92
Anode current density (A/cm^2)	0.797	0.761	0.747
Anode size (mm)	1570 × 660 × 650	1770 × 770 × 650	1770 × 770 × 650
Anode slots	Excluded	Excluded	Included
Anode replacement cycle (days)	36	35	34
Anode quality	High-quality anode B	Normal anode	Normal anode
Qualification rate of first-grade anode (%)	90	<60	<60
Vanadium content in anode (ppm)	<130	278–444	320–383
KF content in the electrolyte (%)	4.55	4.01	1.14
LiF content in the electrolyte (%)	1.68	2.62	1.21
Average cell temperature	949 °C	946 °C	954 °C
Superheat of normal cell (°C)	3	7.2	4.2
Carbon dust amount (kg/t-Al)	13	2–4.5	0–3

Note The “Superheat of normal cell” in the table refers to the superheat of the cells in normal operation with unobstructed feeding holes and stable voltage curves thermal conductivity (3.0–6.0), [W/m K]; and A_{RR} is the residual rate of air reaction (60–90), [%].

However, the formula above doesn't reveal the relationship between the carbon dust amount with either the net anode consumption or the parameters of the electrolytic process.

The net anode consumption includes "electrolytic reaction consumption" and "additional consumption". The additional consumption also includes anodic oxidation and carbon particles dropping. However, some of the carbon particles dropped from the anode will be oxidized and burned again after entering the electrolyte melt, and the remaining carbon particles will form carbon dust. So, there is no direct linear relationship between the amount of carbon dust and the net anode consumption.

If the electrolyte has good wettability with carbon, the carbon particles will be "wrapped" by the electrolyte, which is not easy to oxidize and burn, resulting in a large amount of carbon dust. On the contrary, if the electrolyte is not well wetted with carbon, even if a lot of carbon particles are dropped form anode, the carbon particles can be well separated from the electrolyte, being therefore easy to be oxidized and burned, and the final amount of carbon dust will be reduced.

The wettability of electrolyte and carbon depends on the bath composition and the superheat of the electrolyte itself. KF content in a high potassium electrolyte system will significantly increase the wettability between the electrolyte and carbon [2], while low superheat will increase the viscosity of the electrolyte. These might be the underlying reasons why KF content and superheat had a significant effect on the amount of carbon dust in the experiments in this paper.

Other Factors

During our experiments, we noticed that the anode covering materials for the whole smelter were treated in a centralized way and then distributed to each aluminum electrolysis potroom after grinding. That means the anode covering materials of the test cells could not be treated and reused separately.

A total amount of about 18 tonnes of anode covering material was required per day, or about 175 kg/(t-Al day). Many samples of both used and recently ground anode covering materials were analyzed during the testing period of anode B. Table 4 compares the carbon content of both anode cover material groups.

The carbon content of "Covering materials after grinding" was significantly higher than that of the "Covering material above the butts of anode B", which might indirectly indicate that anode B (high-quality anode) had less carbon particles falling.

It was hard to accurately calculate the amount of carbon dust introduced by the covering materials given that the proportion of the original covering materials that melted into the bath was not clear.

Assuming that 50–70% of the covering material would melt into the bath and all would be converted into carbon dust, and the carbon content in the carbon dust was calculated as 25%, the carbon dust increment caused by the carbon content in the covering material was about 5–7 kg/t-Al. Of course, part of the introduced carbon would also be "burned" in electrolyte melt, in such a way that not all of it would form carbon dust.

However, it was certain that high carbon content in covering materials in a high potassium electrolyte system would also increase the amount of carbon dust.

Conclusions

(1) High-quality anodes could significantly reduce the amount of carbon dust and the carbon content in electrolyte, but the amount of carbon dust was also affected by the superheat. For the same superheat, both the carbon dust amount and carbon content decreased with higher anode quality. For the same anode quality, both the carbon dust amount and carbon content decreased

Table 4 Analysis results of carbon content in anode covering materials

Description Sampling date	Covering materials after grinding, [%]	Covering materials above the butts of anode B, [%]
2019.2.12	2.96	–
2019.2.21	1.86	–
2019.3.2	1.76	0.32
2019.3.31	1.35	0.76
Average	1.98	0.54
Difference	1.98 – 0.54 = 1.44	

Note The samples of "Covering materials above the butts of anode B" were formed by mixing equal mass of anode covering material samples collected at different heights above the anode B butts with higher superheat. Conversely, it increased with lower superheat.

(2) Lower superheat and higher amount of carbon dust might be characteristics of aluminum electrolysis process with a high KF and low LiF content electrolyte system.

(3) The results of the electrolyte composition adjustment test and the comparison to other smelters showed that the LiF and KF content in electrolyte had an obvious influence on the carbon dust amount. With the decreasing content of KF in the electrolyte, the carbon dust amount was significantly reduced. Increasing the LiF content in the electrolyte could significantly improve the superheat, which had the benefit of reducing the carbon dust amount.

(4) The carbon content of covering materials itself would also be an important factor affecting the amount of carbon dust produced in the electrolysis process.

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