Potassium Balance and Its Distribution in Commercial Aluminum Reduction Cells—When Potassium-containing Alumina Is Used as the Raw Material for Aluminum Electrolysis

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ABSTRACT

China is short of high grade bauxite for the production of smelting grade alumina. With the massive exploitation of potassium containing bauxite in China, the produced Bayer alumina contains a non-negligible content of potassium oxide. When this kind of alumina is used as the raw material for aluminum electrolysis, the potassium would cause multiple effects to the cell performance. In this paper, the potassium concentrations of fresh alumina, secondary alumina, aluminum fluoride, anode, electrolyte, anode cover, cathode block, carbon lining, silicon carbide block and product aluminum et al. in 160 kA and 200 kA prebaked aluminum reduction cells were tested and a potassium balance model was preliminarily given. Initial results showed that most of the potassium was brought into the cell by the potassium containing impurities in the fresh alumina. The only effective way for potassium removal from the cell was through the carbon residue though nearly 80 wt% of the potassium would stay and enrich in different positions of the cell.

Keywords : Aluminum Electrolysis, Prebaked Aluminum Cell, Potassium Balance, Alumina Impurities
Figure 2. Possible circulation of potassium in an aluminum reduction cell.

Here). A conductivity of about 1.0 S cm\(^{-1}\) is reported at 700 °C in KF-NaF-Al\(_2\)O\(_3\) melts, which has an expected consequence of a doubled ohmic drop in the bath compared to prevailing industrial electrolyte (approximately 2.2 S cm\(^{-1}\) at 960 °C). The most obvious advantages of the K-cryolite systems are that they allow low melting temperatures to be reached and exhibit, at the same temperature, much higher alumina solubility than Na-cryolite system.\(^{11}\) However, on top of an increase of their vapor pressure, the major disadvantage is that the electrical conductivity of the K-cryolite system is much lower than that of the Na-cryolite system.\(^{12,13}\)

In this present paper, according to the discussion in Fig. 2, when the potassium-containing alumina is employed as the raw material for aluminum production, the pathways for potassium introducing into the aluminum reduction cell and the pathways for potassium removal from the cell, as well as the potassium accumulation amount in the 160 kA and 200 kA prebaked cells are analyzed. The potassium distribution in the main components of the cell after 1000 days of operation is also exhibited. The potassium circulation paths, including the circulation with secondary alumina and recycled bath/ anode cover over a period of 75 days is also tested and discussed.

2. Experimental

The potassium circulations in 160 kA and 200 kA prebaked aluminum cells were studied. A test cell was chosen for each of the potlines. The two potlines, 160 kA and 200 kA respectively, share the same quality of fresh alumina and anodes, as well as the mutual dry scrubbing system and anode assembly shop. The removed anode cover and entrained frozen bath from the two potlines during anode changing are mixed. The information of the testing cells is listed in Table 1.

Sampling was made from different positions of the running cells except the samples for cathode block and SiC sidewall. The samples of cathode block and SiC sidewall were collected from overhauled cells in the respective potline with pot life of around 1000 days. The potassium concentration was then determined with an atomic absorption spectrophotometer (Z-2700, Hitachi Limited, Japan).

3. Results and Discussion

The potassium concentrations of the samples are listed in Table 2.

3.1 Pathways for potassium introducing into the cell

Potassium impurities in the fresh alumina came from the potassium-containing mother solution for the Bayer alumina production process. The large amount of alumina consumed during aluminum production caused the variation of the bath composition. Changed bath chemistry may cause a series of operating problems of the cell such as increased superheat, electrical resistivity and vapor pressure of the electrolyte, and possible higher voltage drop of the cathode block, which can be derived from the known information that KF-AlF\(_3\)-Al\(_2\)O\(_3\) melts behaves much lower liquidus temperature, lower vapor pressure, lower electrical conductivity and stronger penetration capacity into the cell lining than that of NaF- AlF\(_3\)-Al\(_2\)O\(_3\) melts.

One of the cell daily operation — AlF\(_3\) addition is aimed to maintain the stability of the bath composition, which would compensate the increased molar ratio of NaF to AlF\(_3\) due to alumina (contains a certain amount of Na\(_2\)O) feeding. The actual amount of alumina and AlF\(_3\) (fluoride supplement) addition during a time period of 75 days was obtained from the operating records.

Potassium-containing carbon anodes may introduce a certain amount of potassium as well. During the electrolysis, the carbon reacts with oxyanions and forms carbon dioxide as well as a small amount of carbon monoxide due to secondary reactions. Meanwhile, the potassium impurities are dissolved into the molten bath as the anode consumes. The net consumption of the carbon anode was derived from the actual production of aluminum and current efficiency through Pearson-Waddington equation.\(^{14}\)

The virgin bath used in a new started cell was the mix of 5 t fresh cryolite and 8 t prevailing bath which was cultivated from other cells. Assumption was made that the prevailing bath had the same potassium concentration as the bath shown in Table 2. Since the fresh cryolite contains negligible potassium, the fresh alumina remains to be the primary potassium medium. The amounts of introduced potassium from various pathways are listed in Table 3.

Table 1. Current status of the testing cells.

| Pot line       | 160 kA prebaked cell | 200 kA prebaked cell |
|---------------|----------------------|----------------------|
| Pot life/d    | 1533                 | 1029                 |
| Operating temperature/°C | 931–941           | 931–947              |
| Superheat/°C  | 6–16                 | 4–20                 |
| Current efficiency/% | 89.0               | 90.2                 |
| Cell voltage/V| 4.02                 | 4.15                 |
| Bath composition | 77.46 wt%Na\(_3\)AlF\(_6\)-6.49 | 78.13 wt%Na\(_3\)AlF\(_6\)-6.69 |
|               | wt%AlF\(_3\)-2.45 wt%Al\(_2\)O\(_3\) | wt%AlF\(_3\)-3.78 wt%Al\(_2\)O\(_3\) |
|               | 3.28 wt%MgF\(_2\)-3.11 | 2.65 wt%MgF\(_2\)-2.36 |
|               | wt%KF-0.85 wt%MgF\(_2\)- | wt%KF-0.68 wt%MgF\(_2\)- |
|               | 6.36 wt%CaF\(_2\)    | 5.71 wt%CaF\(_2\)    |
3.2 Pathways for potassium removal from the cell

There are limited ways for impurities output from the aluminum reduction cell because it does not generate much waste. Basically all of the fluorides including anode cover, entrained bath on residual anodes and bath volatilization are recycled from either anode crushing shop or dry scrubbers. As it is shown in Table 2, the potassium concentration in the product aluminum was only around 6 ppm, which means a very small amount of potassium was discharged through the only and largest amount of cell output.

Carbon residue in the molten bath is generated due to the selective oxidation of the carbon anode by the carbon dioxide and air. The amount of carbon residue is affected by the temperature, electrolyte superheat and quality of the anode. Carbon particles in the bath reduce the electrical conductivity of the electrolyte and the cell current efficiency. Cleaning of the carbon residue is one of the indispensable operations, and rough estimation shows that an amount of 10–20 kg d⁻¹ and 15–25 kg d⁻¹ carbon residue was taken out of each cell for the 200 kA and 160 kA potlines, respectively.

Other special operations to the cell such as changing electrolyte with other cells and cleaning of the bottom sludge barely happened, and the information was not available. The quantities of potassium discharged from the cell through various pathways are listed in Table 4.

3.3 Accumulation of potassium in the cell

As discussed above, the introduced potassium could not be effectively discharged from the cell. Therefore, the potassium containing impurities was accumulated in the cell. The distribution of the potassium in the reduction cell is discussed in this section to

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Table 2. Potassium concentration at different positions of the cell.

| No. | Sample                          | K%/   | Instruction                                      |
|-----|---------------------------------|-------|-------------------------------------------------|
| 1   | Fresh alunina                   | 0.0514| Shown as the average of 4 samples               |
| 2   | Secondary alunina               | 0.0863| Shown as the average of 3 samples               |
| 3   | Anode cover (200 kA)            | 1.2200| Varies a lot due to human operation.             |
| 4   | Anode cover (200 kA)            | 0.6700| Since two potlines share the same anode cover recycling, take an average level as 0.9075 % |
| 5   | Anode cover (160 kA)            | 0.9300|                                                |
| 6   | Anode cover (160 kA)            | 0.8100|                                                |
| 7   | Molten bath (200 kA)            | 2.0900| Shown as the average of 4 samples               |
| 8   | Molten bath (160 kA)            | 1.5900| Carbon residue in the bath is formed due to the selective oxidation of the carbon anode. Varies with size and soak time, take an average as 1.3800 % |
| 9   | Carbon residue (200 kA)         | 1.7500|                                                |
| 10  | Carbon residue (200 kA)         | 1.4500|                                                |
| 11  | Carbon residue (160 kA)         | 0.9500|                                                |
| 12  | Carbon residue (160 kA)         | 1.3700|                                                |
| 13  | Aluminum (200 kA)               | 0.00056| Determined with standard addition method using an atomic absorption spectrophotometer, shown as the average of 2 samples, respectively |
| 14  | Aluminum (160 kA)               | 0.00063|                                                |
| 15  | AlF₃ (fluoride supplement)       | 0.0003| Shown as the average of 2 samples               |
| 16  | New anode                       | 0.0310|                                                |
| 17  | Residual anode (200 kA)         | 0.0120|                                                |
| 18  | Residual anode (160 kA)         | 0.0120|                                                |
| 19  | Cathode block                   | 0.5500| Fully permeated by KF, regarded as uniform distribution in the respective bulk |
| 20  | Side carbon lining              | 0.5600|                                                |
| 21  | SiC sidewall                    | 0.6000|                                                |
| 22  | Extra Li₂CO₃ addition           | <0.001| Neglected due to small amount of addition        |

Table 3. The amount of potassium introduced into the cell from various pathways.

| Potassium introducing pathway | Amount of materials /kg 75 d⁻¹ | Amount of potassium introduced/kg 75 d⁻¹ |
|-------------------------------|-------------------------------|------------------------------------------|
|                               | 200 kA | 160 kA | 200 kA | 160 kA | 200 kA | 160 kA |
| Fresh alunina                 | 225564 | 173201 | 116 | 89 | 116 | 89 |
| AlF₃                          | 2548 | 2370 | 0.008 | 0.007 | 0.008 | 0.007 |
| Carbon anode                  | 41762 | 34908 | 8 | 6 | 8 | 6 |
| Virgin bath at cell start*    | 5t + 8t | 5t + 8t | 167 | 127 | 167 | 127 |

*One time of addition at cell start, not included in the 75 days’ period.

Table 4. The amount of potassium discharged from the cell through various pathways.

| Potassium removal pathway | Amount of materials /kg 75 d⁻¹ | Amount of potassium discharged /kg 75 d⁻¹ |
|---------------------------|-------------------------------|------------------------------------------|
|                           | 200 kA | 160 kA | 200 kA | 160 kA | 200 kA | 160 kA |
| Aluminum tapping           | 106265 | 88825 | 0.64 | 0.62 | 0.64 | 0.62 |
| Removed carbon residue     | 750–1500 | 1125–1875 | 10–21 | 16–31 | 16–31 |
| Overall                    | — | — | 11–22 | 17–32 | 17–32 | 17–32 |
As the potassium is added into the electrolyte with alumina feeding, the free $K^+$ ion is formed in the molten bath. Since the molten electrolyte is the direct acceptor for the potassium containing alumina, at the same time, the sodium cryolite based electrolyte forms a eutectic mixture with the potassium cryolite, the molten bath became the largest storage medium for the potassium as predicted (Table 5). The potassium concentration has reached up to 1.59 wt% and 2.09 wt% for the 160 kA and 200 kA cells, respectively (Table 2). The high potassium concentration in the electrolyte will lead to a lower liquidus temperature of the bath, which means a close attention on the cell superheat should be paid during the electrolysis process will decrease. Due to the cathodic polarization, the $K^+$ in the electrolyte could electro-deposited at the surface of the cathode, then the potassium metal will penetrate into any material that is in contact with the molten bath, and exist as graphite intercalation compounds (GICs) or similar structure.2 These materials have different potassium concentrations because of their chemical and microstructural properties as well as their contact area with the bath. However, the measurement result in Table 2 shows that the K concentration in the product aluminum is in the level of 5–6 ppm (in mass fraction), which means a very slight affect on the purity of the aluminum metal.

The bottom of the anode cover is easily wet by the bath. After a long time of running, the potassium concentration in the anode cover is supposed to be relatively uniform because part of the anode cover is taken away, then crushed, and finally returned periodically during anode changing which is performed every 30–32 days for each anode. From Table 5, the anode cover material seems to be the third largest storage medium for the accumulated potassium in the cell, where cathode block material behaves as the second storage medium for the accumulated potassium. The large amount of potassium in the anode cover (73 kg potassium for 160 kA cell and 100 kg potassium for 200 kA cell as shown in Table 5) suggests that the potassium is easy to spread within the potline. When the anode cover is removed during anode changing which is relatively frequent in the electrolysis process, the removed anode cover from a high potassium content cell will be sent to the crushing room and mixed with removed anode cover from other cells. Then the crushed mixture of anode cover will be re-added into a random cell in the potline during anode changing. This operation will make it easy for the potassium to transport from one cell to the others.

The mass of the molten bath, metal pad, cathode block, side carbon lining and SiC side wall is calculated through the average electrolyte height, aluminum height and geometry of the cells. Different from the molten bath, a large amount of solid electrolyte, or so-called side ledge, acts as a protection layer for the side walls from the corrosion caused by the bath. The chemical composition of the side ledge is different from that of the electrolyte. From equilibrium considerations and the phase diagram, the component of the side ledge should be pure cryolite, though typically there can be 3–5 wt% CaF$_2$, 1–3 wt% Al$_2$O$_3$ and a slight excess of 0.5–6 wt% AlF$_3$ in the actual side ledge. With these compositions, the ledge will have liquidus temperatures of 980–990 °C. In the present paper, the side ledge was assumed to be pure cryolite, in which no potassium exists.

### 3.4 Inner loops for potassium within the potlines

Potassium in the anode cover and molten bath do not remain stationary in the cell. They are transported away from the cell with anode residues or volatilizations in the cell fume. On consideration of the economic benefit and environmental factors, they are then recycled and re-added into the cell in the form of anode cover and secondary alumina. The circulating mass during a time period of 75 days is given in Table 6 to understand the mobility of the potassium content in the cell.

### 3.5 Summary

Figure 3 shows the pie charts of mass balances for potassium in the 200 kA and 160 kA reduction cells. It can be seen that the purity of the product aluminum seemed not affected by the potassium concentration in the liquid bath. And the aluminum tapping was not an effective pathway for potassium getting out of the cell. The removed carbon residue which was taken away from the liquid bath contained relatively high potassium concentration of 1.38 wt% because it was in direct contact with the liquid bath, and the potassium component penetrated fast at high temperature. The amount of carbon residue in 160 kA potline was a bit larger because of its higher superheat. Most of the introduced potassium as 82–91 wt% and 66–82 wt% for 200 kA and 160 kA cells, respectively, was accumulated in the reduction cells.

### Table 5. The total amount of potassium accumulated in different positions of the cell.

| Position           | Amount of materials /t       | Amount of potassium accumulated/kg |
|--------------------|------------------------------|-----------------------------------|
|                    | 200 kA | 160 kA | 200 kA | 160 kA |                       |
| Molten bath        | 6      | 6      | 134    | 100    |                       |
| Metal pad          | 23     | 18     | 0.28   | 0.12   |                       |
| Anode cover        | 11     | 8      | 100    | 73     |                       |
| Cathode block      | 23     | 21     | 129    | 115    |                       |
| Side carbon lining | 4      | 4      | 22     | 20     |                       |
| SiC side wall      | 4      | 4      | 23     | 22     |                       |
| Side ledge         | Neglected, assumed as pure cryolite |               |
| Bottom sludge      | Neglected, too little to account |               |
| Overall            | —      | —      | 408.28 | 330.12 |                       |

### Table 6. The mass of potassium circulating within the potlines during a time period of 75 days.

| Potassium circulating pathway | Amount of materials /kg 75 d$^{-1}$ | Amount of potassium circulated/kg 75 d$^{-1}$ |
|------------------------------|-------------------------------------|-----------------------------------------------|
|                              | 200 kA | 160 kA | 200 kA | 160 kA |                       |
| Anode cover                  | 58500  | 51750  | 531    | 470    |                       |
| Secondary alumina            | 225564 | 173201 | 79     | 60     |                       |
| Overall                      | —      | —      | 610    | 530    |                       |

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determined the service life of the whole cell. It has been reported that aluminum reduction cell, the service life of the cathode block bath after a long time of running (134 kg and 100 kg for the 200 kA and 160 kA cells, respectively). This implies a possibility to remove the potassium fluoride in the bath by dealing with the secondary alumina.

The two cells studied in the present paper suffered from low current efficiency and unstable superheat, which is probably caused by the frequent variation in bath composition and unstable side ledge. The addition of potassium-containing alumina into the electrolyte would definitely alter the bath compositions as well as its liquidus temperature in a certain range, which could indirectly affect the formation of the side ledge and then a serious of cell efficiency would suffer from the abnormalities or unstable operation conditions of the cell.

The bauxite external dependence of China has reached up to nearly 60% by the year 2019, so many Chinese aluminum smelters have been using the potassium containing alumina as the raw material for aluminum electrolysis. A good point is that the purity of the aluminum metal seems slightly affected by the potassium. However, the effects of potassium components in the reduction cell is possible to be relieved to a certain extent by the strict tracking of the bath compositions and operating temperatures as well as the fine control of the alumina feeding. But it is worth noting that the potassium could cause serious damage to the carbon material,2 therefore, the biggest potential risk for the employment of potassium containing alumina is the significant reduction in cell service life. However, under this situation, the average cell life in this certain potline is approximately 1800–2200 days, which is significantly shorter than the industry’s average cell life of 2500–3000 days. At the same time, the potassium in the cell increased the risk for the early failure of the electrolytic cell.

Also, the potassium penetrated easily into the cell SiC sidewall and side carbon lining material, which displayed nearly the same potassium concentration as the cathode block (potassium concentration in the SiC sidewall and side lining is 0.60 wt% and 0.56 wt%, respectively, Table 2). The potassium is also harmful to these materials, the penetration of potassium could cause volume expansion of the material from inside, which leads to breaking up, falling off of the cell construction material or leakage of the cell.

Contrast to the amount of potassium accumulated in the molten bath after a long time of running (134 kg and 100 kg for the 200 kA and 160 kA cells, respectively), the mass of potassium circulated in the dry scrubbing system within 75 days was quite large (79 kg and 60 kg for the 200 kA and 160 kA cells, respectively). This implies a possibility to remove the potassium fluoride in the bath by dealing with the secondary alumina.

4. Conclusions

The potassium balance during a time period of 75 days in 160 kA and 200 kA prebaked reduction cells are calculated, and the distribution of accumulated potassium in the cells are presented in this paper.
It is found that nearly 70–90 wt% of the potassium introduced by the potassium-containing alumina addition was accumulated in the aluminum reduction cell, while approximately 10–30 wt% of the introduced potassium was removed with the removed carbon residue.

The accumulated potassium in the cell was distributed in different positions of the reduction cell: 30–33 wt% presented in the molten bath, 32–35 wt% in the cathode block, 22–24 wt% in the anode cover and 11–13 wt% in the sidewall materials. The total amounts of accumulated potassium were 330 kg and 408 kg for 160 kA and 200 kA cells, respectively, for cells with cell lives of around 1000 days.

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