

OPERATING PARAMETERS OF ALUMINUM ELECTROLYSIS IN A KF-AIF₃ BASED ELECTROLYTE

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Abstract

Sustained, stable operation of low-temperature, potassium-cryolite-based aluminum electrolysis in 20 and 100 ampere cells fitted with vertical metal anodes and wetted cathodes was performed. The current efficiency, the amount of consumed alumina, and the amount of aluminum produced during electrolysis were calculated based on the measured amount of oxygen evolved on the anode. The purity of the recovered aluminum was analyzed throughout electrolysis. The cell voltage anomalies caused by the presence of sodium fluoride in the electrolyte were studied using a quasi-reference electrode.

Introduction

Efforts in replacing consumable carbon anodes with inert anodes in conventional Hall-Heroult technology have been unsuccessful for a number of reasons, but anode life and materials stability issues dominate work in this area. High operating temperatures of about 950°C in current conventional practice are a significant factor affecting anode and materials stability. The use of potassium-cryolite-based electrolytes (KF-AIF₃) allows for the operation of cells at temperatures as low as 700°C, 200-250 Celsius degrees below current operating temperatures, due to the relatively high solubility of alumina in these electrolytes at low temperatures. Over the past 10 years, low-temperature electrolysis in cells with potassium-cryolite-based electrolytes fitted with inert anodes has been demonstrated in several laboratories [1-6].

It has previously been shown at Argonne National Laboratory that an aluminum bronze anode and a TiB₂-based cathode could be used in aluminum electrolysis in a KF-AIF₃ electrolyte with a cryolite ratio, $CR = N_{KF}/N_{AIF_3}$, of 1.3 at 700°C [1]. Electrolysis was performed in 10, 20 and 100 A cells with anode current densities of about 0.45 A/cm². Current efficiencies of about 85% were reached and purity of aluminum product was better than 99.5% at times. However, sodium, present as sodium fluoride in the electrolyte, is introduced to the electrolytic cell as an impurity in the alumina feed and can build up over time. The presence of NaF above 2 wt% in the electrolyte was determined to likely have a detrimental effect on anode wear and consequently negatively impacted the operating parameters [2].

Research by Wang [3, 4] has been done on electrolysis in potassium-based electrolytes in cells with cermet anodes. The work suggested that electrolysis was more stable in the KF-NaF-AIF₃ (KF:NaF=1:1) electrolyte with CR=1.5 at 800°C because

high unstable fluctuated voltage (5.96-19.6 V) was observed in cells operated at 700°C. Voltage fluctuation was explained by the formation of cathode encrustation.

According to Zaikov [5, 6], aluminum electrolysis in cells with KF-AIF₃ electrolytes with CR=1.3 and cermet or metal anodes was complicated by salt passivation on the electrodes due to a change in the electrolyte composition. Increasing the CR to 1.5 and temperature to 800°C, as well as modification of the bath composition, allowed for stable aluminum electrolysis in an NaF(12wt%)-KF(30)-LiF(3)-AIF₃(55) electrolyte.

The research by Wang and Zaikov [3-6] suggests that aluminum electrolysis in potassium-cryolite-based electrolytes is more viable with increasing either temperature or CR. Unfortunately the main advantage of low temperature electrolysis – improved materials stability – disappears.

Thus, the purpose of the present work was to determine appropriate operating parameters, using a modified technique, for sustained low-temperature electrolysis in a cell fitted with vertical metal anodes and wetted cathodes in potassium-cryolite-based electrolytes, and to study the effect of NaF on the process conditions and the purity of recovered aluminum metal.

Experimental

Set Up

Electrolysis tests were performed in cells fitted with vertical electrodes. The 20 and 100 ampere electrolysis cell designs had the same configuration. The crucible containing pre-weighed salts was placed into the alumina furnace tube and sealed with a metal cap. Electrical leads were threaded into the electrodes to ensure reliable electrical contact. The cathode leads were made of stainless steel and the anode leads were aluminum bronze. The electrodes were completely immersed in the molten electrolyte, suspended by leads encased in alumina tubes. A DC power supply (TDK-Lambda GENESYS™ 40-250) provided a constant electrical current during electrolysis. Nitrogen gas flow into the furnace was maintained at 1.1 L/min. To monitor pressure inside the cell, a pressure gauge was installed on the metal cap.

The outlet gas was scrubbed by passing through a glass wool scrubber, a jar with a sodium hydroxide solution, and a column with desiccant before it was analyzed for its oxygen content. Oxygen content was determined with an oxygen sensor (Cambridge Sensotec Ltd. Rapidox 2000 Oxygen Analyzer), which was calibrated with two nitrogen-oxygen gas mixtures whose oxygen concentrations defined the upper and lower limits of a range of the oxygen content of the outlet gas.

Alumina was added throughout the electrolysis process to replace the alumina consumed by the primary reaction. An automatic feeding system was developed to deliver desired amounts of alumina at specified intervals.

In some tests, the electrolysis cell was equipped with a Mo quasi-reference electrode to help identify the origin and extent of voltage anomalies. The potential between the reference electrode and the anode (E_A) and the potential between the reference electrode and the cathode (E_C) were monitored during electrolysis.

Before, during, and after electrolysis, samples of electrolyte were collected by means of electrolyte freezing on an alumina rod or by suction into an alumina tube. Concentrations of aluminum, potassium, and sodium, as well as concentrations of possible impurities in the electrolyte were determined by Inductively Coupled Plasma spectroscopy (ICP). The oxygen content in the electrolyte samples was analyzed by a LECO RO600 Oxygen Determinator.

In a series of experiments, an aluminum metal heel was added to the cell before electrolysis to allow aluminum samples to be taken during the early stages of electrolysis. Impurities in the produced aluminum metal were determined by ICP.

The cell voltage, current and operating temperature as well as the cathode and anode potential data were monitored by a National Instruments data acquisition unit and recorded once every second by the Labview computer program. The outlet gas oxygen content was recorded every 30 seconds using the Rapidox software.

Electrolyte

The electrolyte with a cryolite ratio of 1.3 was prepared by mixing appropriate amounts of aluminum fluoride and potassium fluoride. In some tests, sodium fluoride (2 or 4 wt%) was added as well, but the CR was maintained at 1.3, where CR was calculated as $CR = (N_{KF} + N_{NaF}) / N_{AlF_3}$. For the 20 A tests, the electrolyte was prepared in a cell just prior to electrolysis. For the 100 A tests, the electrolyte was prepared beforehand and stored in a dry cabinet.

Potassium fluoride and sodium fluoride (Aldrich), with a purity of 99%, were used to prepare the electrolyte. Since KF is hygroscopic, it was delivered from the supplier in small batches and stored in a dry cabinet. The oxygen content in KF was determined before each experiment and the KF was found to have less than 0.3 wt% oxygen.

Smelter-grade alumina and aluminum fluoride supplied by Noranda were analyzed for impurities using ICP and LECO. The alumina contained approximately 0.3 wt% sodium and the aluminum fluoride contained approximately 4.5 wt% Al_2O_3 and approximately 0.6 wt% of other oxide impurities. This was taken into account for electrolyte preparation. Prior to the electrolysis testing, the alumina powder was dried at 400°C in an open cell for 4-6 hours, and then kept above 100°C in a thermo cabinet.

Samples of the molten electrolyte were taken before electrolysis began and again before any alumina was added to the melt. In general, the amount of oxygen in the electrolyte was approximately 2.5-2.7 wt% just after melting. Oxygen may have been introduced into the melt from the moisture in the KF and from the oxygen containing impurities in AlF_3 , the main component of which is aluminum oxide.

For electrolysis testing, the electrodes were usually lowered into the melt and then energized. After electrolysis, the electrodes

were removed from the melt prior to electrolyte solidification. Both 20 and 100 A tests were carried out in a cell fitted with a central inert anode and two wetted cathodes at an anode current density of 0.45 A/cm² in a temperature range 700-800°C. The anode-cathode distance was 2 cm. The duration of experiments varied from 24 to 100 hours. The molten KF- AlF_3 system with CR=1.3 was used as the base electrolyte composition.

It was important to know how the electrolyte cryolite ratio was changing during the course of electrolysis. Calculated and measured values for concentrations of KF, NaF and AlF_3 in electrolyte samples were compared. The theoretical change in electrolyte composition was calculated considering the mass of each sample and the amount of added and consumed alumina at the time each sample was taken. Consumed alumina was estimated from the current efficiency during electrolysis as determined by real-time oxygen analysis in the outlet gas. The measured and calculated values of KF, NaF, and AlF_3 concentration (and consequently the CR of electrolyte) did not change significantly during electrolysis testing and were within 5% of each other.

Electrolyte samples taken during electrolysis were analyzed for the presence of impurities that could be caused by corrosion of the anode. Results indicated that the amount of Cu, Fe, Ni, and Mn in the electrolyte was less than 0.05 wt% at the beginning, during and at the end of electrolysis.

The alumina concentration in the electrolyte was checked throughout each experiment. It was found that the alumina content in the electrolytes being studied over all composition and temperature ranges was close to saturation, and stabilized near 4.5-5.5 wt% (Figure 1). Over the range of test conditions, the effect of temperature and composition on alumina solubility was observed: a temperature increase of 30 Celsius degrees results in a change in alumina concentration in the electrolyte KF- AlF_3 (CR=1.3) from 4.4 to 5.4 wt%, on average (Figure 1: Exp.E-29 and E-26); an increase of NaF concentration at a constant temperature results in an alumina solubility decrease (Figure 1: Exp.EAL-19 and E-9); or CR change from 1.3 to 1.1 sharply decreases the alumina solubility (Figure 1: Exp.EAL-14). (E-## and EAL-## represent experiment numbers).

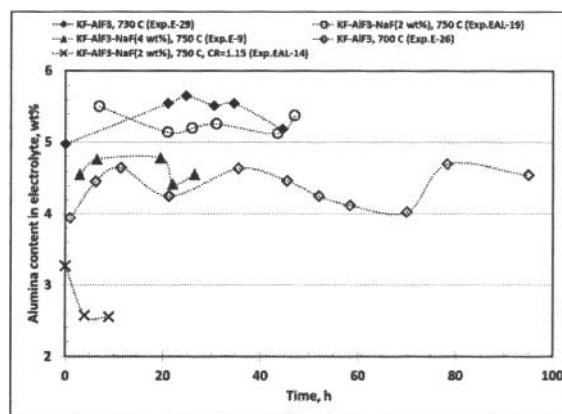


Figure 1. Alumina content in the electrolytes during electrolysis

No significant electrolyte evaporation was noted during tests at 700°C, but electrolyte evaporation did increase as the temperature increased. A white substance that condensed on the cold parts in

the furnace was analyzed by Scanning Electron Microscopy (SEM). It was determined that the condensate consisted of potassium aluminum tetrafluoride (KAlF_4). Furthermore, translucent crystals forming on and covering the anode surface as is remained suspended above the electrolyte at the conclusion of electrolysis testing were also analyzed by SEM and confirmed that the basic component of the potassium cryolite, with low molar ratio, is KAlF_4 .

Results and Discussion

Operating Parameters of 20 and 100 Ampere Electrolysis

A typical plot of voltage, current, temperature and oxygen content in outlet gas versus duration of electrolysis is shown in Figure 2 (Exp.EAL-24). This electrolysis test was performed in a 20 A cell with a KF-AlF_3 electrolyte at 700°C . The voltage was stable (3.3 V) with a maximum voltage oscillation of 5 mV. The oxygen level reached 4% during the first hour, then dropped to 2%, and then stabilized around 4.5–5% by the third hour of the test. The cathode potential slightly increased while the anode potential slightly decreased confirming the smooth course of electrolysis.

Usually, at the beginning of each test, the set temperature was manually adjusted to the desired value. Once adjusted, the set temperature was not altered in order to determine the rise in temperature during the test. In conditions when the electrolysis process is stable and consistent, an increase in operating temperature decreases cell voltage and enhances oxygen content in the outlet gas.

The values of voltage in 20 A tests were within the 3.3–3.8 V range with maximum voltage oscillation of 20 mV. For comparison, a baseline test using the same cell design but fitted with a graphite anode and two graphite cathodes was performed. At the beginning of electrolysis, the voltage was 3.0 V, but increased to 4.0 V by the 17th hour. After electrolysis, it was discovered that the anode was completely consumed, as expected.

During the 100 A tests, voltage was relatively stable with some minor fluctuation during the course of electrolysis (Figure 3).

In order to determine the reason for the voltage changes, which might occur during electrolysis, two Mo quasi-reference electrodes were used. Sometimes, especially during tests lasting several days, Mo electrodes were replaced with new electrodes. This typically did not cause any appreciable changes to the voltage readings. To show an example of voltage anomalies, an electrolysis plot in the $\text{KF-AlF}_3\text{-NaF}$ (4 wt%) melt is presented in Figure 4. E_{cathode} and E_{anode} potentials can help determine which process has more impact on the cell voltage. During the first two hours, the voltage and E_{cathode} changes were similar, which indicated that the voltage anomalies could be attributed to the cathode process. Then, by the 22nd hour, the correlation between voltage and E_{anode} was observed. The cell voltage increase was likely connected to changes at the anode.

The high level of oxygen present in the outlet gas stream during the first 60 minutes of electrolysis was observed in almost all experiments. Typically, the maximum concentrations detected were 4–5%. Considering the amount of oxygen-containing impurities analyzed in the raw salts, which were used for electrolyte preparation, and the amount of oxygen evolving during the first hour of each test, it was postulated that this elevated level of oxygen in the outlet gas flow was due to the purification of all

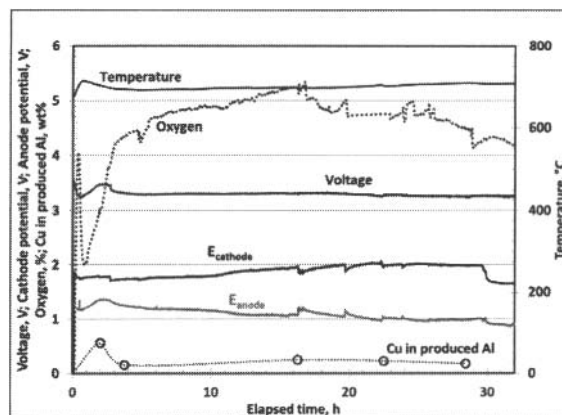


Figure 2. Plot of electrolysis in KF-AlF_3 (20 A) (Exp.EAL-24)

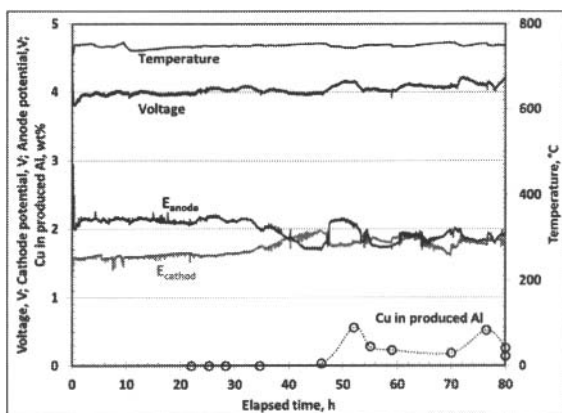


Figure 3. Plot of electrolysis in KF-AlF_3 (100 A) (Exp.100E-37)

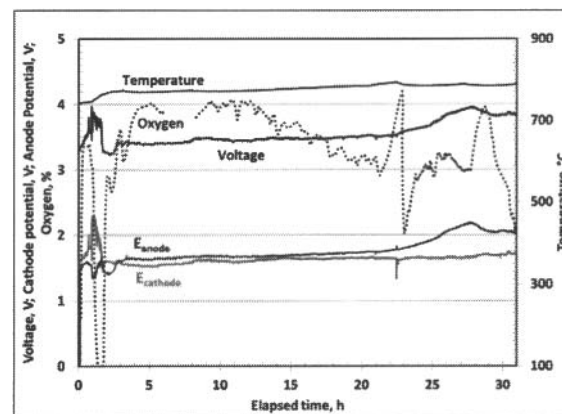


Figure 4. Plot of electrolysis in $\text{KF-AlF}_3\text{-NaF}$ (4 wt%) (20 A) (Exp.EAL-21)

the oxygen-containing impurities in the electrolyte during the early stage of electrolysis [7]. Determining the amount of oxygen being evolved during electrolysis is difficult because even small changes in the gas flow rate lead to fluctuations in the measurements. For this reason, the gas flow rate and pressure in the cell were carefully controlled. When flow rates or pressures were fluctuating, inconsistent oxygen values were observed even when the cell voltage was stable. For example, during electrolysis

(Figure 5) the oxygen concentration in the outlet gas slowly increased and reached 4.4% by the 11th hour, then unexpectedly dropped and recovered again by the 20th hour. At that time, the cell voltage was stable and neither E_{anode} nor E_{cathode} indicated any abnormalities.

Sodium Fluoride

It is known [8] that even small additions of NaF to the KF-AlF₃ melt with the molar ratio of $N_{\text{KF}}/N_{\text{AlF}_3} < 1.7$ ($CR < 1.7$) significantly increases the temperature of primary crystallization. To establish the liquidus temperature of the electrolytes being studied, the melt temperature was measured in the test cell at the beginning and/or after electrolysis by recording the electrolyte temperature during cooling. Liquidus temperatures as determined by cooling curves are listed in Table 1. It should be mentioned that the liquidus temperatures obtained in experiment E-5 before and after electrolysis are similar, suggesting that the electrolyte composition did not change significantly during the electrolysis test.

Table 1. Liquidus temperatures of electrolytes

Electrolyte	CR	$T_{\text{liq.}}^{\circ}\text{C}$	Comments
KF-AlF ₃ + NaF(2 wt%) (Exp.E-5)	1.4	705	Before electrolysis
		699	After electrolysis
KF-AlF ₃ (Exp.E-8)	1.3	630	Before electrolysis
KF-AlF ₃ + NaF(4 wt%) (Exp.E-7)	1.3	656	Before electrolysis
KF-AlF ₃ + NaF(4wt%) (Exp.E-9)	1.3	662	Before electrolysis

According to the liquidus values, it seemed that despite of the presence of sodium in the potassium-cryolite-based electrolyte with a low CR, there is still an opportunity to perform electrolysis at 700°C in the potassium-cryolite system with 2-4 wt% of NaF. To test this, electrolysis in the KF-AlF₃ electrolyte containing 4 wt% of sodium fluoride was performed at 700°C. In this test the voltage increased to 8.5 V by the fifth hour while oxygen decreased to near zero by the first hour. Even the interruption of the test, which at times has allowed the electrolysis process to recover, did not help to improve electrolysis. After the experiment was completed, it was discovered that the cathode was covered with a thick layer of grey deposit, but the anode looked normal.

A similar course of electrolysis during the first two hours was observed in the next experiment with the same composition of electrolyte and temperature 700°C (Figure 6). But after increasing the temperature to 750°C, the process recovered. The oxygen content in the outlet gas flow occasionally reached 6%. The voltage was around 3.6 V, but large voltage oscillations were observed. However, current efficiency of this test was 83%.

As was mentioned above, using the quasi-reference electrode in a test with the KF-AlF₃-NaF(4 wt%) electrolyte (Figure 4) allowed for the understanding that the processes occurring on the cathode were responsible for the voltage behavior. An increase in temperature minimized the amplitude of voltage oscillation. The oxygen emission stopped after the first hour of electrolysis and resumed after an increase in temperature.

The same course of electrolysis had been observed in the test with KF-AlF₃-NaF(2 wt%) electrolyte. A voltage oscillation with an

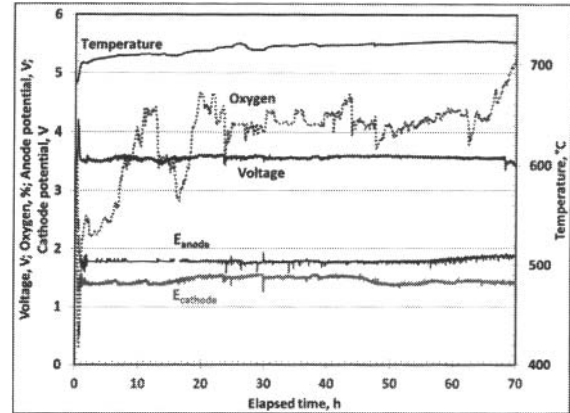


Figure 5. Plot of electrolysis in KF-AlF₃ (20 A) (Exp.EAL-25)

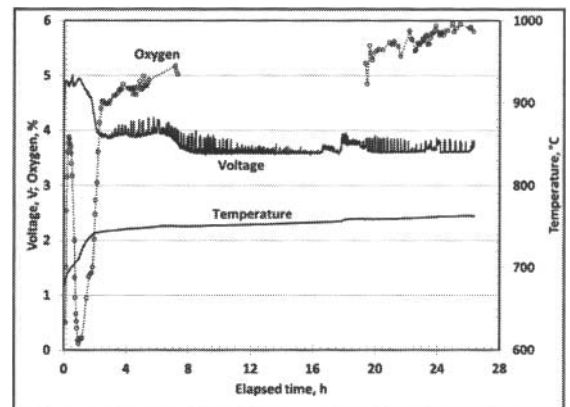


Figure 6. Plot of electrolysis in KF-AlF₃-NaF(4 wt%) (20 A) (Exp.E-9)

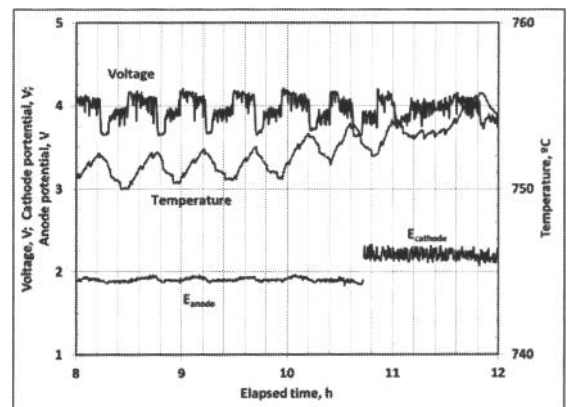


Figure 7. Plot of electrolysis in KF-AlF₃-NaF(2 wt%) (20 A) (Exp.EAL-19)

amplitude of 250 mV occurred at 750°C at the beginning of electrolysis. This noticeable oscillation of voltage continued until the temperature was increased 5-7 Celsius degrees. The enhanced plot of electrolysis between 8th and 12th hours is shown in Figure 7. It can be seen that the voltage and temperature changes aligned with each other. It is possible to assume that the KF content increased near the cathode surface as a result of aluminum

depletion that led to a local rise of CR. This in turn resulted in electrolyte freezing on the cathode surface. The voltage increased and consequently the temperature increased as well. The temperature rise initiated the dissolution of the cathode deposit and renewal of the surface for the aluminum deposition.

Thus, it can be concluded that small amounts of sodium in the potassium cryolite bath did not have a significant effect on the cell voltage value or on the oxygen content in the outlet gas. Only the operating temperature needs to be adjusted to take the NaF content in the electrolyte into account.

Current Efficiency

Current efficiency (CE) was calculated based on both the amount of oxygen generated and the quantity of aluminum produced.

The determination of oxygen concentration generated on the anode allows current efficiency estimates to take place during electrolysis. As an example, the calculated current efficiency during electrolysis in KF-AlF₃ electrolyte at temperature 730°C is shown in Figure 8. In this test, currents of 20, 15 and 10 amperes were applied. The current efficiency rises with increasing current density, as expected. At a current of 20 A, the CE reached 85%. The average CE in this test, calculated on measured oxygen, was 66%. The inconsistent oxygen evolution resulted in a change of CE during electrolysis. The CE calculations based on the amount of generated oxygen and on the produced aluminum metal for some experiments are given in Table II.

Based on the value of CE calculated, in accordance with evolved oxygen, the amount of consumed alumina can be estimated directly, during electrolysis. According to these calculations the frequency of automatic alumina feeding was corrected during the test, otherwise undissolved alumina would collect on the bottom of the cell and would inhibit the formation of an adequate coalesced aluminum metal product.

Moreover, it is also possible to estimate the amount of aluminum being produced at any time throughout electrolysis. This was used to determine the amount of impurities accumulated in the aluminum metal produced at the time of each metal sampling.

Cathode

Due to their good wetting properties, cathodes made of TiB₂ or composite TiB₂-C seem to be the most suitable for performing low-temperature electrolysis in a potassium cryolite bath. However, thermal stability is essential, since TiB₂-C cathodes often crack during electrolysis. Technology for TiB₂-C cathode manufacture needs to be improved.

Anode

After each test, the aluminum bronze anode was covered by a thin, flaky oxide layer. Pieces of this layer were always found on top of the frozen electrolyte – rather than deep inside it – suggesting that the oxide layer did not begin spalling until after electrolysis was stopped and the electrodes were raised out of the electrolyte melt. Significant anode corrosion was not observed, as suggested from the low impurity levels in the product aluminum. Nevertheless, aluminum metal droplets were sometimes found embedded on the anode, damaging its surface. In order to avoid

Table II. Current efficiency, based on the oxygen evolved and aluminum produced (20 A tests)

Description of test	CE based on oxygen, % (Avg/Max)	CE based on Al, %	Al, g expected	Al, g produced
KF-AlF ₃ , 700°C, 24 h, (Exp.E-8)	65/92	75	110	120
KF-AlF ₃ -NaF(4wt%), 750°C, 24 h, (Exp.E-9)	65/84	83	114	133
KF-AlF ₃ , 700 °C, 47 h, (Exp.EAL-11)	55/76	50	160	154
KF-AlF ₃ , 750°C, 47 h, (Exp.EAL-12)	55/82	50	170	160
KF-AlF ₃ , 730°C, 74 h, (Exp.EAL-22) *	66/85	76	318	295
KF-AlF ₃ , 700°C, 96 h, (Exp.EAL-26)	55/80	54	360	346

*In Exp.EAL-22 applied current changed during test.

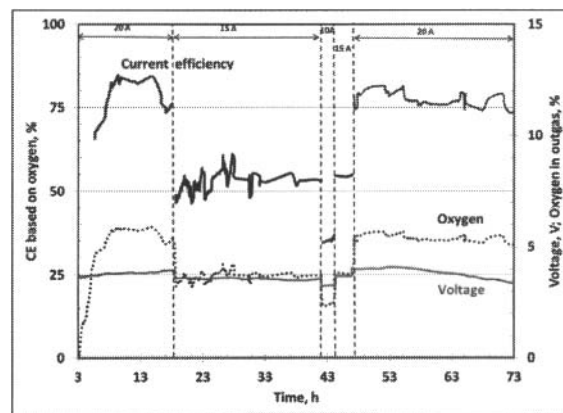


Figure 8. Current efficiency based on oxygen evolved during electrolysis at current 20, 15 and 10 A in KF-AlF₃ electrolyte (T=730°C) (Exp.EAL-22)

such a phenomenon, research is focused on improving cell fluid dynamics.

The thickness of the anode layer versus time is shown in Figure 9. It should be mentioned that no correlation was found between the anode layer thickness and the electrolyte composition (NaF presence) as well as between the anode layer thickness and the operating temperature (700-770°C range). The thickness of the anode layer increased during the first ~50 hours of electrolysis and then stabilized around 0.6-0.7 mm. All tests were performed in cells fitted with vertical electrodes: one aluminum bronze anode and two wetting cathodes, at the anode current density of 0.45 A/cm² and anode-to-cathode distance (ACD) of 2 cm.

It was noticed that the pre-oxidized state of the anode surface prior to electrolysis affects the course of electrolysis, as it has been pointed out in some articles [9, 10]. For the experiments described, the surface of aluminum bronze anode was not specially treated.

Aluminum purity

Usually, the copper impurities in aluminum metal were in a range of 0.3-0.9 wt% in 20 and 100 A tests with duration up to 100 hours. No correlation was found between purity of produced aluminum and the operating temperature (in a range of 700-770°C). The most important factor for producing metal of high purity is stability of electrolysis. The minimum level of copper content in aluminum metal produced that was achieved in a 100 A cell test for 100 hours was 0.1-0.2 wt% (Figure 3). It is recognized that even in 100 A tests, the purity level in the aluminum can vary due to circumstances associated with cell operation that would not occur at higher amperages over longer times.

To determine the purity of aluminum metal being instantaneously produced during electrolysis, pure aluminum metal was added to the cell prior to electrolysis. The amount of aluminum produced at the time of each sampling was calculated according to the CE based on oxygen content in the outlet gas. It can be seen in Figure 10 that aluminum produced at the beginning of electrolysis contains the most copper impurity. However, if the electrodes are energized prior to being immersed into the electrolyte, the aluminum produced in the early stages of electrolysis does not contain impurities (Figure 10, Exp.EAL-23). After some time, however, the instantaneous concentration of copper impurity becomes relatively constant if electrolysis is stable (Figure 2). If the anode behaves abnormally, whether planned or unplanned, it is natural to expect aluminum metal quality deterioration.

Conclusion

Sustained operation of the low-temperature, potassium-cryolite-based aluminum electrolysis process in 20 and 100 ampere cells fitted with vertical metal anodes and wetted cathodes was performed. Aluminum bronze anodes covered by a protective oxide layer can be effectively used as inert anodes during long-term testing. Stable electrolysis is the basis for success in producing aluminum metal of commercial purity. The cell voltage anomalies caused by the NaF presence in the potassium cryolite can be avoided by careful control of operating parameters.

References

1. Yang J., Hryn J., Davis B., Roy A., Krumdick G., Pomykala J. *Light metals* 2004, p. 321
2. Yang J., Hryn J., Krumdick G. *Light metals* 2006, p. 421
3. Wang J., Lai Y., Tian Z., Liu Y. *Light metals* 2007, p. 525;
4. Wang J., Lai Y., Tian Z., Liu Y. *J.Cent. South Univ. Technol.* 2007, p. 768
5. Zaikov Y., Chramov A., Kovrov V., Krukovsky V., Apisarov A., Tkacheva O., Chemezov O., Shurov N. *Light metals* 2008, p. 505
6. Frolov A., Gusev A., Zaikov Y., Kataev A., Shurov N., Chuikin A., Redkin A. *Light metals* 2009, p. 1129
7. Tkacheva O., Spangenberg J., Davis B., Hryn J. *Proceedings of the 9th International Symposium on Molten Salts Chemistry and Technology (MS 9)*, Trondheim, Norway, 2011, 5-9 June
8. Apisarov A., Dedyukhin A., Redkin A., Tkacheva O., Nikolaeva E., Zaikov Y., Tinghaev P. *Light metals* 2009, p. 401
9. Chapman V., Welch B., Skyllas-Kazacos M. *Electrochimica Acta* 2011, 56, p. 1227
10. Glucina M., Hyland M. *Corr. Sci.* 2006, 48, p. 2457

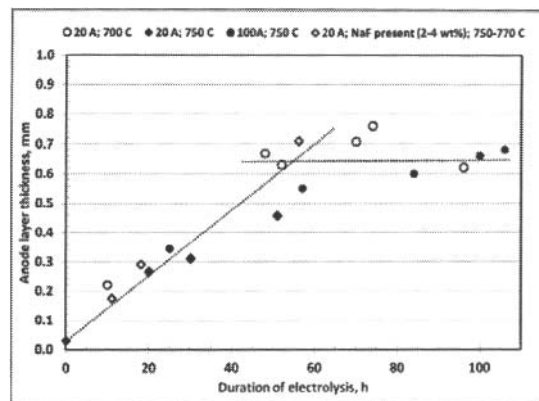


Figure 9. Thickness of anode layer measured after electrolysis

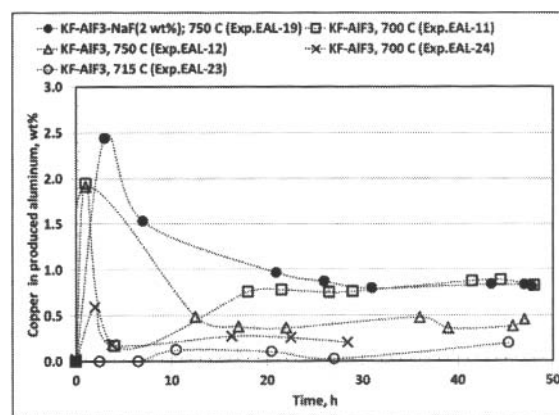


Figure 10. Instantaneous content of copper in aluminum metal produced during electrolysis in 20 A cell

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+ This paper is dedicated to the memory of our co-author, colleague, and friend, Tom Alcorn (+2011).