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Managing the Electrolysis Process by Integrating In Situ Measurements of the Bath's Properties

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Control of the bath's composition and temperature is crucial to the stability, energy consumption and material efficiency of the aluminium electrolysis process. The traditional approach involves periodic measurement of the bath's composition with x-ray diffraction, as well as the bath's temperature. The sampling and corrective measures applied to the cell can take 8–12 h. Since the relationship between the excess AlF_3 in the bath and the temperature is difficult to manage, the electrolysis process involves a time lapse. With the integration of in situ measurements of the bath's properties in the electrolysis cell, optimization of the primary aluminium reduction process was achieved. Increased measurement frequencies and the integration of in situ measurements into the electrolysis process reduced the instability of the process, resulting in energy savings and increased current efficiency of 96.4%.

INTRODUCTION

Due to the energy intensity of the Hall–Heróult electrolysis process, it is crucial to optimize the process control. The regulation of the temperature and the composition of the bath is crucial for both the stability and efficiency of the process. The basic parameters on which the regulation of the bath's composition and temperature depend are the excess AlF_3 in the bath, the bath temperature, the cathode voltage drop (CVD), the age of the pot, the anode changing and the anode effect. Additional corrective actions are determined by the operator, together with additional resistance.[1] Some of the control parameters are dynamically measured, while parameters like the bath temperature, the excess AlF_3 and the CVD have to be periodically measured manually. The bath temperature is usually measured once a day, or at least once a week, while the excess AlF_3 is typically measured a few times per week.[2,3] The bath temperature is usually measured using a type K thermocouple. The most common method for determining the bath's composition is x-ray diffraction (XRD). Bath sampling and preparation of the sample for XRD (grinding, compacting) are time consuming (8–12 h), and as a result there

is a time gap between obtaining the measurement results for the temperature and the bath's composition, which means a delay in action.

The aluminium industry strives to reduce power consumption and improve current efficiency, which requires correct and better process control, and accurate results available in a short time. Electrolysis control is based on the dynamic adjustment of the resistance following the actual technological parameters. Based on the bath's composition and temperature, the regulation algorithms calculate the additions of AlF_3 as a function of the deviation from the target bath's acidity and/or the target temperature and the cell voltage.[4,5] The goal of thermal regulation of the electrolysis process is to achieve stable cells and a high current efficiency at low ACD.[6–8] Novel approaches can measure the temperature, the excess AlF_3, the concentration of CaF_2 and Al_2O_3, the bath ratio and superheat at the same time, directly in the aluminium reduction cell.[9–11] The measurement is based on differential thermal analysis (DTA), observing the cooling curves of the bath and a reference cup. The chemical composition of the bath can be determined based on the difference between those two curves. At the same time, the temperature is also measured. The

results are available in a few minutes and can be wirelessly transferred to the process-control computer.

In this work, the improved in situ measurements of the bath's properties were made with the goal of optimizing the aluminium reduction process, with a positive impact on current efficiency and energy consumption. The work examines the impact of in situ measurements of the temperature and the excess AlF_3, on the instability, resistivity and current efficiency of the electrolysis process.

METHODS

The experiment was conducted on a 160-type AP18 electrolysis cells over a period of 38 months. To compare the measurement accuracy of the STARprobe[TM] and the XRD, the bath composition results from 20 electrolysis cells were analyzed simultaneously for 34 days.

The bath's temperature and composition were measured separately every 72 h. Bath samples were taken with special thongs, cooled, and crushed to a particle size below 63 μm. The bath's composition was determined with Panalytical Cubix3. To prepare 3.0-g samples, 0.3 g of the Wax-C micropowder binder was added. The samples were pressed at 1.8 bars for 15 s. The XRD analysis was made in the $30.8°2$–$28.35°2$ Θ range. The temperature was measured with a type-K thermocouple. The results of the temperature measurement in the control system after 1 h, and the results of the bath chemistry analysis after 8–12 h, were inserted.

The in situ measurements were made with the commercial STARprobe[TM] device. The frequency of the measurements was increased to 32 h. Measurements were made during the same shift as the tapping of the metal. Measurements were made using a special probe, which was submerged 5–7 cm into the bath at the tapping hole. Before submerging the probe into the bath, carbon dust was skimmed
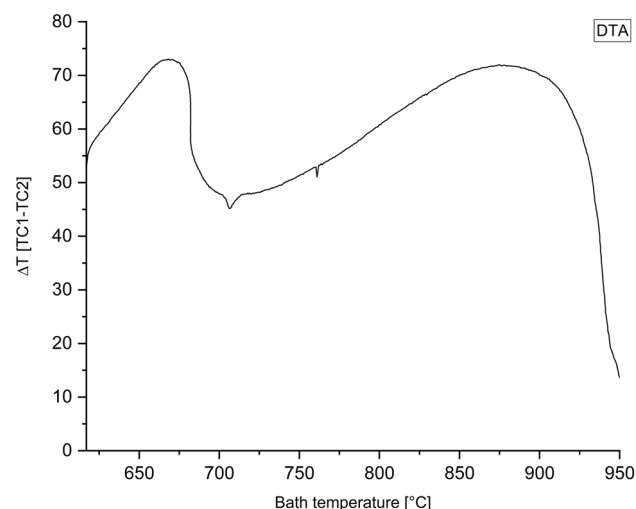
from the bath. When the temperature of the bath sample and the reference cup were equalized, the probe was taken out of the bath. The software logic was based on the DTA. The cooling curves of the reference cup and the sample cup were observed (Fig. 1). The software calculated the bath composition based on DTA analysis. The temperature was measured at the same time as the bath's composition. Information about the excess AlF_3, the CaF_2, the Al_2O_3, the bath ratio, the temperature and the superheat temperature was derived from the measurements. This reduced the time required to take corrective action in the control system to 3–4 min.

RESULTS AND DISCUSSION

The number of measurements with XRD and the in situ measurements at a certain excess AlF_3 are represented in Fig. 2. Comparing the results of the in situ measurements and the XRD analysis for 20 cells shows a large deviation for the samples where the AlF_3 excess was outside the 11–14 wt.% range. The difference between the test results was between 0.43 wt.% and 2.55 wt.%. The average XRD analysis result was 1.34 wt.% higher compared to the in situ measurement. In samples with the highest concentration of the AlF_3, the XRD analysis measured the chiolite peak at $30.8°2$ Θ. When the sample of the bath was cooled, the excess AlF_3 crystalizes as chiolite; therefore, the AlF_3 is directly connected with the intensity of the chiolite peak. During rapid solidification, CaF_2 contributes to the formation of $NaCaAlF_6$ and $NaCa_3AlF_2F_{14}$. Almost the same situation was observed in samples with low AlF_3 excess, where the peaks were measured at $28.35°2$ Θ.

Long-term periodic measurements of the temperature and excess AlF_3 were used as a reference to control the use of the in situ method. As illustrated in Fig. 3, the concentration of the AlF_3 changes the bath's liquidus temperature. The use of in situ
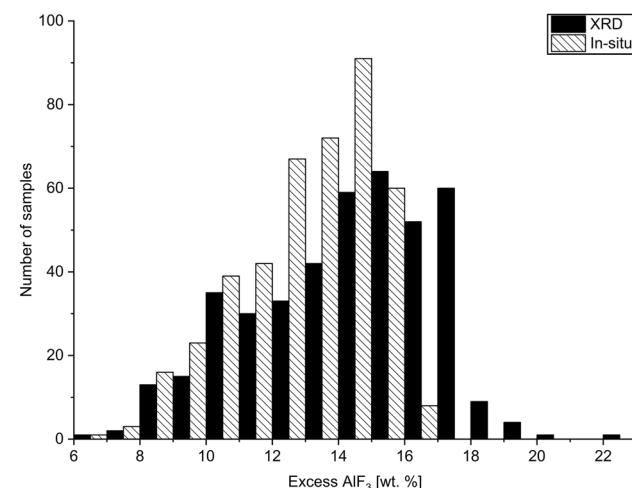

Fig. 1. Principle of the in situ measurement with STARprobe[TM].

Fig. 2. In situ versus XRD analysis of excess AlF_3 in the bath.
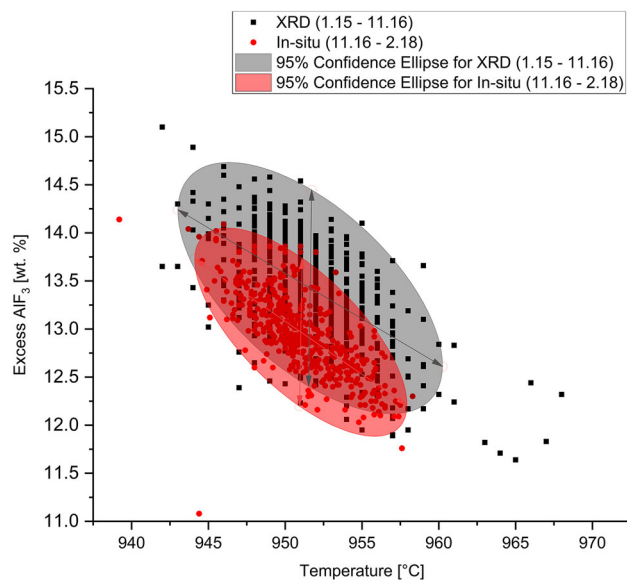
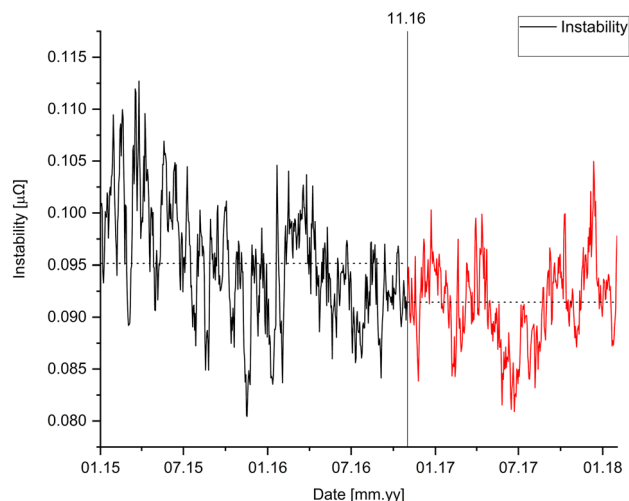Fig. 3. Bath temperature versus excess AlF₃ in the 1.15–2.18 period.

Fig. 4. Average instability before and after the integration of in situ measurements.

Fig. 5. Average target resistance before and after the integration of the in situ measurements.

measurements between 11.16 and 2.18 reduced the oscillations of the bath temperature and the composition. The average bath temperature over a period of 15 months was reduced by 0.6°C to 951.0°C, compared to the average temperature of 951.6°C in the previous period, when XRD measurements were made between 1.15 and 11.16 (23 months). The decrease is directly connected with better control of the excess AlF₃. The deviation between the maximum and minimum excess AlF₃ was reduced by 11.6%. The average value of the excess AlF₃ was reduced from 13.42 wt.% to 12.96 wt.%. Two major effects were found to contribute to the better stability of the bath temperature and the composition: an increase in the frequency of simultaneous measurements and more accurate measurements of the bath's composition.

The bath's composition and temperature have a major impact on the alumina solubility. Higher concentrations of AlF₃ can cause the freezing of the alumina sludge onto the cathode, resulting in the cell's magneto-hydrodynamic instability.[12] Input parameters of temperature and excess AlF₃ in the bath affects the pseudo-resistance of the cell, which impacts the cell's ACD. Optimal regulation of the cell's resistance and additions of AlF₃ have to ensure that the working point is at the optimal position, normally at a superheat temperature of 5–12°C. The superheat temperature represents the difference between the bath temperature and the liquidus temperature.[13] Resistance instability is an indicator of the stability of the reduction process. Resistance instability represents the average value between the cell's maximum and minimum calculated resistance over a 32-h period. Figure 4 presents the resistance instability in the 1.15–11.16 period, when in situ measurements were not used,
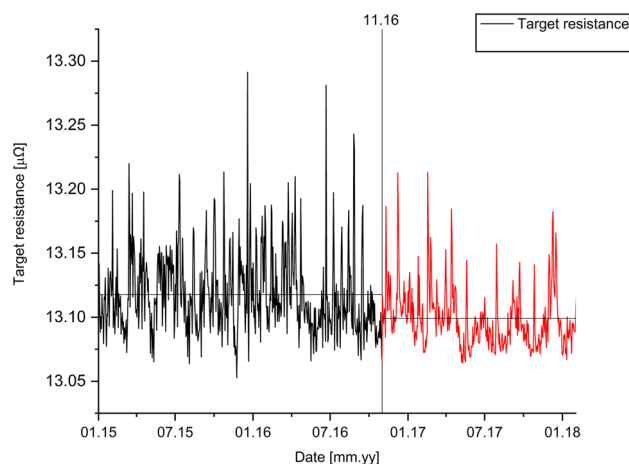
and the 11.16–2.18 period, when in situ measurements were integrated. The stability of the process after the introduction of in situ measurements has improved. The average resistance instability was decreased by 0.004 μΩ (4.21%), and the period deviation of the resistance difference was reduced by 18.75%. Instability was reduced by decreasing the temperature and the AlF₃ excess.

The impacts of the improved stability of the process, the bath's composition and the temperature are shown in Fig. 5 as the target resistance. The target resistance is the sum of the static cell resistance, the resistance given for an anode change, the additional resistance given in the case of instability, the cathode resistance, and the bath-composition resistance, which is given at the discretion of the operator. The 37.4% deviation in the target resistance was reduced, and the average target resistance could be lowered by 0.019 μΩ, while maintaining the gains in cell stability. For a
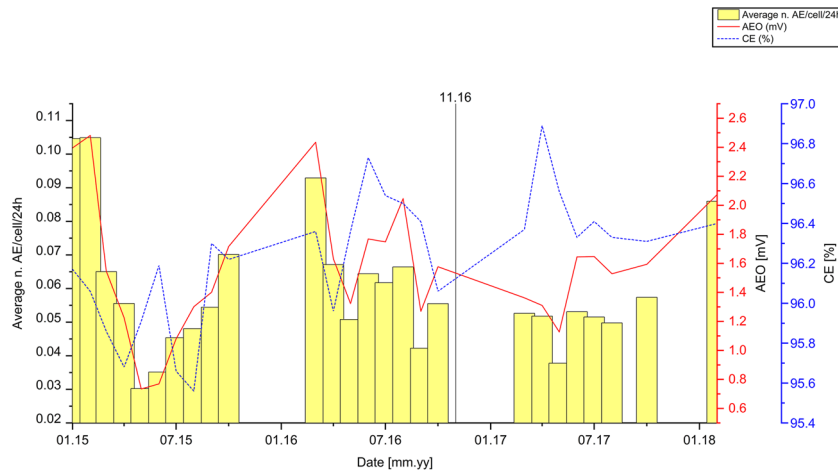
Fig. 6. Current efficiency, AE and AEO, before and after the integration of the in situ measurements.

potline operating at 186.560 kA DC, this would mean cutting its specific energy consumption by 11.56 kWh/t Al.

The best indicator of the potline's performance in the electrolysis process is the current efficiency. As illustrated in Fig. 6, the current efficiency was increased by 0.36%, on average. The increased current efficiency can be correlated with better alumina solubility due to better control of the bath's composition and temperature.[14,15] As result of better alumina solubility, average number of anode effect in 24 h per cell decreased for 0.00631, while the average anode effect overvoltage decreased by 0.14574 mV.

CONCLUSION

We observed the impact of in situ measurements of the bath's properties on the process efficiency compared to XRD. The bath's composition and temperature, the average instability, the average target resistance and the current efficiency were studied. In situ measurements gave more accurate analysis results. The difference between the XRD and the in situ measurement of the excess AlF_3 can exceed 1.34 wt.% due to the sample preparation for XRD. With an increased analysis frequency, the average bath temperature and the excess AlF_3 were reduced by 0.6°C and 0.46 wt.%, respectively. By using the Hotelling T2 test, it can be concluded that there is a significant difference between the XRD and in situ measurements influencing the bath's composition and temperature control. The improved control of the bath's composition and temperature reduced the instability of the process to 0.091 $\mu\Omega$ and the improved stability resulted in 11.56 kWh/t

Al reduction of specific energy consumption, while the current efficiency increased to 96.38%. This is not only a technological improvement but also contributes to a better working environment, as it allows the workers to measure more cells within a given time, leading to shorter periods of exposure.

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