

Bath Ratio and Temperature Control Enhancement in the Potroom

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Bath chemistry and cell operating temperature in Hall-Héroult aluminum reduction cells must be controlled to achieve optimal current and energy efficiency. The conventional way to control the bath ratio and temperature is to regularly take bath samples for chemistry analysis and measure the bath temperature. These measurements are generally performed separately. Moreover, bath samples have to be sent to a laboratory for analysis, with results available in as much as 24 hours later. Due to the delay in getting the bath sample analysis results, control decisions have to be made primarily relying on old and out of sync information. This leads to an unsteady feedback control loop, where the cell is continuously under or over shooting the targeted optimum conditions, which causes sub-optimal cell performance in terms of both current and energy efficiency.^{1,2}

To address this problem, over the last 10-15 years, Alcoa has worked to develop a new device to measure almost instantly the bath chemistry (or excess AlF_3) and temperature. The Superheat, Temperature, Alumina concentration, and Ratio (STAR) analysis system,^{3,4} known as STARprobe™, provides real-time results that allow potroom operators to make chemical alumina and power adjustments for optimal cell performance. To date, it has been successfully deployed in eight Alcoa smelters.

System Overview

The STARprobe system (or kit) is a portable device that takes real-time measurements of bath properties and consists of four major components (Figure 1): a reusable probe tip (Figure 2); a portable probe stand (lance) that can fit in various smelter operations for direct measurement of the bath; electronics to acquire data and perform analysis, which is wirelessly transmitted to a computer server; and the STARprobe computer program that integrates with a PC tablet.¹ All electronic components comply with stringent requirements for operation in the potroom, where there



Figure 1. STARprobe kit with mobile station and monitoring system (left) and portable stand showing the probe tip, lance, and head ready for measurement (right).³

exists a high magnetic field, high ambient temperature, and a highly dusty environment. This system is mounted on a cart to make it a mobile station with spare probe tips and a battery backup to increase the PC tablet autonomy.

Since the probe tip is reusable, a complete measurement cycle requires only a few steps and can take just under 4 minutes to complete. Furthermore, a single PC tablet can process data from two probe heads simultaneously, allowing the operator to measure two pot cells in parallel. Considering that a probe tip is able to take around 100 measurements, in this way, a trained operator can routinely measure 64 cells in 4 hours with an average of 3 minutes and 45 seconds per measurement.

Once the data is available, the STARprobe system makes use of the well-known Differential Thermal Analysis (DTA) method,⁵ the results of which are displayed on the tablet screen (Figure 3), stored in a file, and transmitted to the level 2 control system in the smelter, using an Alcoa QLC cell controller system.

DTA Method

The STARprobe concept is fairly simple and uses the DTA measurement method, which analyses cooling characteristics of the cryolite melt in

order to determine the bath ratio.¹ When a cryolitic melt is cooled from a liquid state to a solid state, it goes through several phase transformations. Each transformation occurs in a specific temperature region, therefore the bath chemistry ratio is proportional to the amount of heat release.

Based on this method, the probe tip contains two type K thermocouples (Figures 2-3)³ that allow these unique cooling characteristics to be measured and the bath ratio to be determined. The thermocouple on the left records the cooling rate of the bath sample, while the thermocouple on the right records the cooling rate of the metallic mass of the probe. With this probe, the ratio result can be known after only a few steps—insert probe tip into molten bath to equilibrate with bath temperature in the pot cell,

remove probe tip from bath and allow it to cool, and STARprobe analyzes the cooling curve and records the results.



Figure 2. Reusable probe tip.

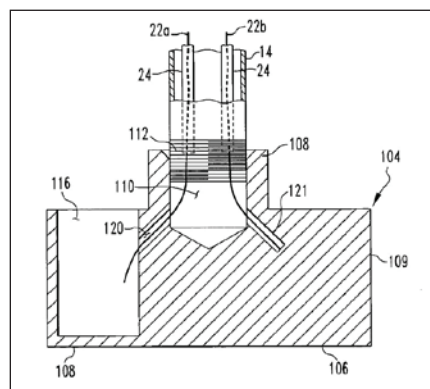


Figure 3. Schematic of the STARprobe tip with two type-K thermocouples.

Figure 4 presents such a pair of DTA curves obtained from a STARprobe measurement. In this case, the cooling rate of the bath sample is slower than the metallic mass of the probe for two reasons. The first and less significant reason is because of the difference of thermal diffusivity between the bath sample (liquid and solid) and the metallic mass of the probe, hence the initial separation of the two curves between 10 and 18 seconds. Second, at the bath sample liquidus temperature, cryolite starts to solidify, which slows the bath sample cooling rate down even further. At the cryolite-alumina phase diagram bath eutectic temperature, the alumina starts to solidify as well. Finally, at a much lower temperature (at the cryolite-AlF₃ phase bath eutectic temperature), the excess AlF₃ finally solidifies.

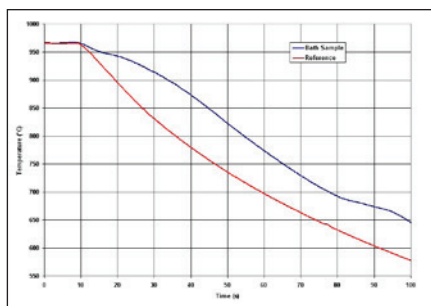


Figure 4. Recorded cooling rate of bath sample and the metallic mass of the probe, which act as reference temperatures in the DTA.

The difference of temperature between the two curves is computed and presented on a second graph (Figure 5). In this case, the sample temperature is selected as an X coordinate. The shape of that curve is independent of the cooling rate, so the bath sample analysis results will not be affected by fluctuation of the ambient conditions.¹ In fact, the shape of the curve depends only on two things, the design of the probe tip and the composition of the bath sample. This means that for a given probe tip design, the shape of the curve uniquely depends on the composition of the bath sample. This is the reason Alcoa was able to come up with a correlation algorithm

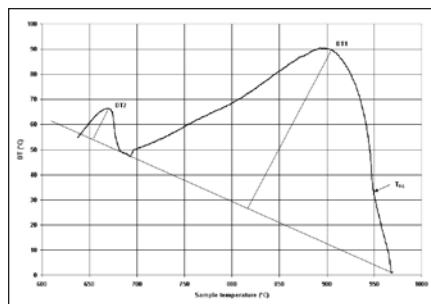


Figure 5. Differential temperature curve and one possible way to perform the DTA analysis.

that could identify the bath composition from the shape of each curve measured. The high temperature maximum is due to the solidification of the cryolite, while the low temperature maximum is mainly due to the solidification of the excess AlF₃. The more AlF₃ in the collected bath sample, the less intense the high temperature peak will be and the more intense the low temperature peak.

Mathematically, this means that the sample bath ratio (or excess AlF₃ concentration) correlates with the ratio of intensity of the two peaks as displayed in the following equation:¹

$$\begin{aligned} \% \text{xs AlF}_3 &= f1[\Delta H \text{AlF}_3 / \text{Na}_5\text{Al}_3\text{F}_{14} / \\ &\quad (\Delta H \text{AlF}_3 / \text{Na}_5\text{Al}_3\text{F}_{14} + \Delta H \text{Na}_3\text{AlF}_6)] \\ &= f2[S2 / (S1 + S2)] \\ &= f3[DT2 / (DT1 + DT2)] \end{aligned}$$

The method used by the correlations algorithm to calculate DT1 and DT2 is not described in Alcoa's published research, as it remains a trade secret. However, even without the latent heat released during the solidification of the bath sample, the reference temperature drifts apart from the sample temperature (Figure 4 illustrates a possible definition of DT1 and DT2 by the author that may or may not be close to Alcoa's correlation algorithm research). For sure, Alcoa's correlation algorithm is fast and the calculated results are comparable to XRD analysis and have been independently verified on many occasions in demonstrations performed in smelters around the world.⁶

Process Control Improvements Achieved by Alcoa

In parallel with the development of the STARprobe, Alcoa developed a new cell controller called QLC that takes full advantage of its bath properties measurement technology. QLC automatically acquires the results of STARprobe measurements in real time and takes the measured cell superheat in consideration in its new STARprobe-based active pot control logic.^{1,7} The gains reported by Alcoa are 0.5% improved current efficiency, 35 mV voltage savings, 5% AlF₃ savings, a one time capital cost saving (X-ray equipment), labor savings for sampling/analysis, and improved understanding by operators, as well as a potential of 100-150 day potlife improvement (still being tested).

The potential for improvement for a given smelter depends on its current level of process efficiency. For example the two cases of current efficiency (CE) improvement reported by Alcoa were from about 94% moving up to about 94.5%;⁷ clearly, a smelter already operating at 95.5% CE should not expect the same level of improvement. Alumar,

one of the Alcoa smelters now using the STARprobe to control its bath ratio and temperature, reported that the technology has proven to be very accurate for ratio (excess AlF₃) measurements and able to replace traditional bath sampling and XRD laboratory analysis.⁸ Alumar also reported the advantages of much faster response time and consequent reaction on chemical additions, faster measurement of bath superheat and alumina concentration, ability to transfer data to pot controllers that are used to modify process control regarding thermal control, and ability to reject bad results and request a recheck measurement immediately. Test groups are pointing to a big potential in terms of voltage reduction as well as reduced aluminum fluoride additions. Also, test groups have shown good levels of superheat with a decreasing trend after starting the STARprobe measurements.

Conclusion

The new STARprobe bath properties measurement device is offering smelters a significant potential to improve process efficiency. While Alcoa is not currently licensing its QLC or its active pot control logic, the company has selected STAS as worldwide distributor for its revolutionary STARprobe technology. For more information, visit: www.stas.com/en/starprobe/html.

References

1. Wang, Xiangwen, Bob Hosler, and Gary Tarcy, "Alcoa STARprobe™," *Light Metals 2011*, pp. 483-489.
2. Dupuis, M., "Excess AlF₃ concentration in bath control logic," National Conference on Advancements in Aluminium Electrolysis, Indian Institute of Metals, Angul Chapter, 2006.
3. Hosler, Bob, Xiangwen Wang, Jay Bruggeman, and Patrick O'Connor, "Molten Cryolytic Bath Probe," U.S. Patent No. 2005/0069018 A1, 2005.
4. Wang, Xiangwen, Bob Hosler, and Gary Tarcy, "Systems and Methods Useful in Controlling Operation of Metal Electrolysis Cells," U.S. Patent No. 2007/0295615 A1, 2007.
5. Mackenzie, R.C., *Differential Thermal Analysis*, Academic Press, London, 1970.
6. Dupuis, M., P. Bouchard, and J.-P. Gagné, "Measuring bath properties using the STARprobe™," 19th International ICSOBA Symposium, 2012.
7. Wang, X., G. Tarcy, E. Batista, and G. Wood, "Active pot control using Alcoa STARprobe™," *Light Metals 2011*, pp. 491-496.
8. Silva, Ari F., et al., "Implementation of STARprobe™ Measurements and Integrated Pot Control at Alumar," ICSOBA Symposium, 2012.