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Electrochemical bath chemistry control with the Thermo Scientific™ ARL™ X'TRA Companion X-ray Diffractometer

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Introduction

Aluminum, the second most extensively produced metal globally, plays a vital role across a broad spectrum of industries including aerospace, automotive, packaging, and battery manufacturing. Its distinctive blend of low density, high strength, excellent corrosion resistance, and superior electrical conductivity makes it an essential material driving advancements in modern engineering and production technologies.

The extraction of aluminum metal is carried out through electrolytic reduction of alumina, utilizing carbon anodes immersed in a molten electrolyte bath. This bath primarily contains alumina dissolved in cryolite and is subjected to a strong electric current, reducing aluminum oxide to metallic aluminum. The overall efficiency of this process—as well as the quality of the final metal is heavily influenced by the precise chemical makeup of the bath. As such, accurate monitoring and control of bath chemistry are critical and rely on detailed compositional analysis and optimization of key smelting parameters.

The electrolytic bath typically comprises cryolite, chiolite, calcium cryolites, fluorite, and various minor constituents formed during the process. Historically, analysis of these phases have been performed using calcium-specific XRF channels and isolated XRD diffraction peaks. However, recent observations highlight the frequent formation of calcium cryolite in significant concentrations during smelting. This phase has proven to be a critical indicator in achieving tighter control over bath chemistry.

In response to this, updated analytical methodologies now include precise quantification of calcium cryolite along with traditional bath components. These measurements are integrated into advanced data models that provide enhanced real-time bath parameter estimations, offering improved operational control and production consistency.

By understanding the mineralogical intricacies of aluminum bath matrix through XRD, industry professionals can enhance process efficiency, reduce production loss, and optimize resource utilization, ultimately leading to more sustainable and cost-effective aluminum production.

Instrument and software

The Thermo Scientific ARL X'TRA Companion X-Ray Diffractometer (cf Figure 1) is a simple, easy-to-use benchtop instrument for routine phase analysis as well as more advanced applications. The ARL X'TRA Companion XRD uses a θ/θ goniometer (160 mm radius) in Bragg-Brentano geometry coupled with a 600 W X-ray source (Cu or Co). The radial and axial collimation of the beam is controlled by divergence and Soller slits, while air scattering is reduced by a variable beam knife. An integrated water chiller is available as an option. Thanks to the innovative solid-state pixel detector (55 x 55 µm pitch), the ARL X'TRA Companion XRD provides very fast data collection and comes with single-click Rietveld quantification capabilities and automated result transmission to a LIMS (Laboratory Information Management System), seamlessly integrated into Thermo Scientific™ SolstiX™ Pronto Instrument Control Software.

Figure 1. ARL X'TRA Companion X-ray diffraction system.

Experimental

Traditional Alcan standards are often found to be the most suitable choice owing to their portrayal of real-time bath chemistry scenarios and covering the complete analytical range. Here, a series of Alcan standards (BA 01 – BA 10) were measured in reflection mode using Cu Kα (1.541874 Å) radiation for 2 minutes (cf Figures 2 and 3). Quantitative analysis (Rietveld method) was performed by Profex software (BGMN) which can be designed as single-click method for enhanced user experience. Bath parameters were calculated.

Results and discussion

Electrolytic bath consists of multiple crystalline phases that hold strongly correlated relationships when it comes to deriving bath parameters. Traditionally, bath parameters are determined with the help of XRD and XRF (X-ray fluorescence), where floor model equipment is needed. Here, we have demonstrated the utility of the ARL X'TRA Companion XRD in the determination of critical parameters e.g. bath ratio (cf Table 1), Excess AlF3 (cf Table 1), total Calcium content (cf Table 3).

Bath ratio

Alcan STD	Cert.	Dev	New
BA-01	1.06	0.1	1.06
BA-05	1.02	0.1	1.01
BA-10	1.30	0.1	1.28

Table 1. Certified **bath ratio** comparison with **bath ratio** determined from Rietveld analyses.

ExAlF3

Alcan STD	Cert.	Dev	New
BA-01	12.40	0.2	12.6
BA-05	11.30	0.3	11.3
BA-10	5.20	0.2	5.5

Table 2. Certified **Excess AlF3** comparison with **Excess AlF3** determined from Rietveld analyses.

Ca (Calculated from XRD)

Alcan STD	Cert.	Dev	New
BA-01	6.2	0.1	6.3
BA-05	4.5	0.1	4.6
BA-10	6.7	0.1	6.6

Table 3. Certified **Calcium content** comparison with **Calcium content** determined from Rietveld analyses.

We have also recorded data of BA-07 standard 20 times and analyzed which shows excellent precision of the method (cf Table 4).

Precision results

Sample ID	Bath Ratio		ExAlF3	
	Certified	Observed	Certified	Observed
BA07	1.23 (0.1)	1.22	6.9 (0.2)	7.1
		1.22		7.1
		1.22		7.1
		1.22		7.1
		1.22		7.0
		1.22		7.2
		1.22		7.1
		1.22		7.0
		1.23		6.9
		1.22		7.1
		1.22		7.2
		1.22		7.2
		1.22		7.1
		1.23		6.9
		1.22		7.2
		1.22		7.0
		1.22		7.0
		1.22		7.2
		1.22		7.1
		1.22		7.1
ESD		0.003		0.078
3σ		0.01		0.23

Table 4. Bath ratio and ExAlF3 repeatability of sample BA07 calculated from 20 runs compared with the certified value and its ESD.

Conclusion

Overall, the single-click analytical method uses 2-minute scan XRD data recorded by the ARL X'TRA Companion XRD to derive the bath parameters by applying an advanced correlation function between phases. The optimized tube power and the advanced detector with energy filtering capability of the ARL X'TRA Companion XRD ensure excellent data quality even when measured in 2 minutes. The SolstiX Pronto Software reduces operator burden by making one-click analysis accessible to everyone and increases your efficiency while still maintaining high-quality results.

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