Application Note 41403

Total analysis of aluminum bath with the Thermo Scientific ARL 9900 'Pot Flux Analyzer CaMg'

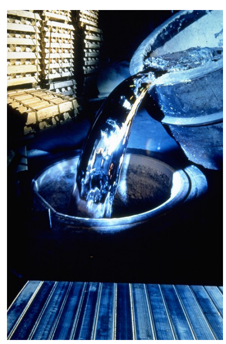
Raphael Yerly, Thermo Fisher Scientific, Ecublens, Switzerland

Key Words
Aluminum bath, ARL 9900, XRD, XRF

Goal

Samples from aluminum bath have been measured by XRD for many years. We describe an improved method that integrates elemental results for total Mg and total Alumina while still offering high sample throughput.

Introduction



Aluminum is the second most produced metal in the world, after iron. To make aluminum, bauxite is mixed with sodium hydroxide; this forms aluminum hydroxide and separates other elements in a red mud. Aluminum hydroxide is then heated and transforms into alumina (Al_2O_3).

Alumina goes through an electrolysis process in order to obtain aluminum metal. Carbon anodes are dipped in an alumina bath and a high current is applied. This burns the anodes and forms CO_2 thus removing oxygen. Conductivity of the melt improves with the addition of fluorides, but the proportion of aluminum fluoride to sodium fluoride is critical and must be monitored in order to avoid "anode effects".

A typical aluminum bath is composed of chiolite ($Na_5Al_3F_{14}$), cryolite (Na_3AlF_6) and a number of minor components. The bath ratio determination (NaF/AlF_3) requires a combination of elemental and phase analysis. Historically, simple XRD instruments fitted with an additional calcium detector were used to measure chiolite and total calcium. α-alumina (corundum) was measured by XRD as an approximation of free-alumina (total Al_2O_3).

Recent developments show that a better control of the bath can be achieved by measuring more compounds. On the elemental side, there is a need for total calcium (reported as CaF_2), total magnesium (reported as MgF_2) as well as total oxygen (reported as Al_2O_3). On the phase side, chiolite is required together with fluorite (CaF_2) and α-alumina. Such a complete analysis, including oxygen, is only possible in a combined XRF-XRD instrument working under vacuum.

Instrument

The Thermo Scientific ARL 9900 Series consists of a spectrometer that can be fitted with several XRF monochromators for elemental analysis. In addition, an XRF goniometer can be installed for analysis of any of 83 elements on the periodic table. It is also fitted with a compact integrated XRD system which is capable of measuring chiolite, cryolite, fluorite and corundum. Hence, this instrument performs XRF and XRD analysis under vacuum on a single hardware and software environment.

The configuration of the test instrument and the analytical conditions are shown in Table 1. The ADP crystal is recommended when analyzing Mg in presence of high levels of Al. The AX06+ crystal is a specially designed multi-layer crystal to detect oxygen in presence of high levels of Na. Ease of operation is obtained through the state of the art OXSAS software running under MS Windows environment.

Goniometer	Crystal	Detector	Collimator
Ca *Kα1,2*	LiF200	FPC	0.6
Mg *Kα1,2*	ADP	FPC	0.6
O *Kα1,2*	AX06+	FPC	0.6

Phase	hkl	Detector
Chiolite	202	XRD
Fluorite	111	XRD
α-Alumina	104	XRD

Table 1: Analytical parameters

Thermo
SCIENTIFIC

Calibration and results

A series of aluminum bath standards were used for calibration. Excitation conditions were 40 kV/80 mA and counting time was optimized for each element. Typical ranges are shown in Table 2. Excess aluminum fluoride ($XsAlF_3$) is calculated from XRD measurements of chiolite and fluorite. The critical bath ratio parameter is calculated from the amount of $XsAlF_3$, CaF_2, MgF_2 and Al_2O_3.

Compound	Channel	Time [s]	LoD [%]	Range [%]	
CaF_2	Ca *Kα1,2*	4	0.0076	4.5	9.5
MgF_2	Mg *Kα1,2*	8	0.019	0.22	0.62
Al_2O_3	O *Kα1,2*	8	0.11	2.7	7.8
Phase					
$XsAlF_3$	Chiolite+Fluorite	48+8	-	1.3	12.7
α-Alumina	Corundum	12	0.023	0.3	5.8
Bath Ratio	Calculation	-	-	1.03	1.45

Table 2: Analytical conditions and dynamic ranges

The ARL 9900 instrument can be factory calibrated for a bath ratio program using commercially available standards. It can also be calibrated on-site using well analyzed samples from the user.

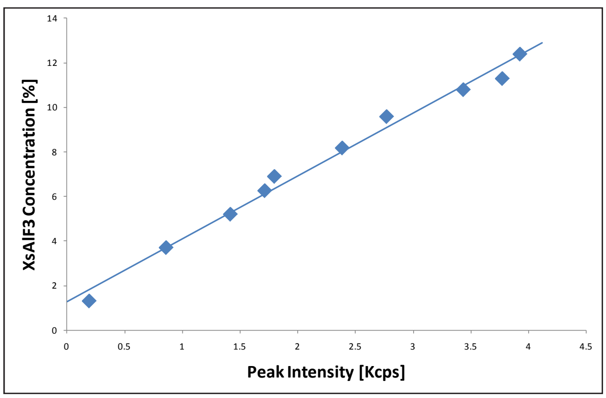


Figure 1: Calibration curve for excess AlF_3

Precision test

A typical bath ratio sample was analyzed ten times in order to show the precision of the ARL 9900. Excellent preicsion is obtained despite very short counting time on the XRF channels. The total counting time for bath ratio determination does not exceed 90 seconds.

Type	XRF			XRD		
Run	CaF_2	MgF_2	Al_2O_3	$XsAlF_3$	α-Alumina	Bath Ratio
Time	*4*	*8*	*8*	*48+8*	*12*	-
1	6.31	0.33	6.11	12.61	1.18	1.055
2	6.32	0.32	5.94	12.64	1.16	1.054
3	6.32	0.33	5.91	12.63	1.21	1.055
4	6.32	0.34	5.87	12.62	1.18	1.055
5	6.30	0.34	6.07	12.65	1.17	1.054
6	6.32	0.33	5.97	12.61	1.16	1.055
7	6.33	0.32	5.88	12.60	1.15	1.056
8	6.33	0.33	6.05	12.59	1.16	1.055
9	6.33	0.35	6.03	12.63	1.18	1.054
10	6.31	0.33	6.03	12.65	1.19	1.054
Average	**6.32**	**0.33**	**5.99**	**12.62**	**1.18**	**1.055**
St.Dev.	**0.009**	**0.010**	**0.08**	**0.021**	**0.019**	**0.0007**
Unit	*%*	*%*	*%*	*%*	*%*	-

Table 3: Repeatability results on a single pellet

Conclusion

These results show that aluminum bath samples can be quantified with high sensitivity, reliability and excellent stability. The integration of XRF and XRD capabilities in a single instrument provides complete analyses, allowing better control of the melt.

In addition, thanks to the XRF goniometer and optional fixed element channels, the ARL 9900 spectrometer can be calibrated for other typical applications required in the aluminum industry like cast iron, pitch, alumina and carbon anode material.

To see our full X-ray product portfolio, please visit **www.thermoscientific.com/xray**

Africa-Other +27 11 570 1840
Australia +61 2 8844 9500
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China +86 10 8419 3588
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland /Norway/Sweden +46 8 556 468 00
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9434
Italy +39 02 950 591
Japan +81 45 453 9100
Latin America +1 608 276 5659
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
South Africa +27 11 570 1840
Spain +34 914 845 965
Switzerland +41 21 694 71 11
UK +44 1442 233555
USA +1 800 532 4752

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

AN41403_E 03/12C