Light Metals 2012 *Edited by: Carlos E. Suarez*
TMS (The Minerals, Metals & Materials Society), 2012

ALUMINUM FLOURIDE PURITY TEST BY DIFFERENT TECHNIQUES

Hussain Al Halwachi
Alba Laboratory, Aluminium Bahrain (Alba), P.O. Box570 Manama Kingdom of Bahrain

Keywords: Aluminium Fluoride, NMR, SEM, Qualitative XRF

Abstract:

The purity test is one of the key parameter for aluminum fluoride material used in aluminum smelting process. Aluminum fluoride is added to the reduction cell to react with alumina impurities such as CaO and Na_2O and to generate more alumina (Al_2O_3) and cryolite to the reduction cell. Good quality of AlF_3, usually having purity between 89 to 93%, has to be measured accurately, through a quick and safe method. This study provides several solutions for measuring the AlF_3 purity by instrumental methods such as NMR, XRF dilution, SEM and XRF standard as an alternative for the wet chemical methods. This approach is applicable also for Al_2O_3/ AlF_3 mixed samples.

Introduction

Aluminum fluoride (AlF_3) is one of the most important raw materials used in the aluminium smelting process. In Hall-Heroult aluminium electrolysis process, alumina is dissolved in the molten cryolite bath along with AlF_3 to produce aluminium through the electrolysis process. AlF_3 is playing an important role in controlling the thermal balance of the reduction cell, due to the inverse relation between the cell temperature and the concentration of AlF_3 in electrolytic bath. A good quality of AlF_3 is required in the electrolysis process to insure smooth operation in the reduction cell.

AlF_3 is examined physically and chemically to compare its properties with the operational specification: Table1 shows the list of tests carried out at Alba Laboratory for AlF_3 and the operational specifications. The commercial value of any raw material will depend on its purity; AlF_3 is usually contaminated with alumina (about 6 to 8 %) in addition to other traces compounds such as CaO, Fe_2O_3, P_2O_5, SO_3 and SiO_2. The desirable purity of AlF_3 is between 89 to 92%. Aluminum fluoride with a low purity results in more of other contaminated components to the reduction cell which will affect directly the cell thermal balance and the metal purity.

Table1: list of AlF_3 tests and Alba operational specifications

AlF_3 test	Unit	ALBA Spec.
Flow ability	sec	60 Max.
Purity	%	89.9 Min.
Free Alumina (Al_2O_3)	%	8.1 Max.
Calcium Fluoride (CaF_2)	%	0.14 Max.
Silicon Oxide (SiO_2)	%	0.20 Max.
Iron Oxide (Fe_2O_3)	%	0.03 Max.
Sulphite (SO_3)	%	0.05 Max.
Phosphorus Pentoxide (P_2O_5)	%	0.030 Max.
LOI @ 450°C	%	0.50 Max.
LOI @110-600°C	%	0.75 Max.
Vibrated Bulk Density	g/cm^3	
Apparent Density	g/cm^3	1.300 Min.
Compressibility	%	
+ 212 mm (+65 mesh)	%	
+ 150 mm (+100 mesh)	%	10.0 Max.
+ 106 mm (+150 mesh)	%	
+ 75 mm (+200 mesh)	%	
+ 45 mm (+325 mesh)	%	
+ 38 mm (+400 mesh)	%	
- 38 mm (-400 mesh)	%	
- 45 mm (-325 mesh)	%	9.0 Max.
Angle of Repose	deg	35.0 Max.

Experimental method and procedure

The determination of AlF_3 purity is carried out in Alba Laboratory by the Pechiney/Alcan Wet Chemical Volumetric method, which is a long wet chemical method involving a lot of chemical

preparation and titration. The wet chemical procedure takes long time and requires a lot of safety precautions especially during the dilution in sulphuric acid (conc.). Alba Laboratory was following this procedure until September 2004, were an accident happened in ALUCAM Lab during the handling of sulphuric acid, the analyst added sulphuric acid to water which led to an explosion. At that time Alba Lab were asked to stop this procedure until further investigation. Since that accident, Alba Laboratory started looking for other alternative methods.

Purity test by XRF method (quantitative analysis)

The alternative method for the Wet Chemical Procedure is the use of X-Ray Fluoresce spectrometry, which is faster, and involves no extra chemicals. This method is widely used by a lot of laboratories in the world, and the calibration is straight-forward. The method depends on the correlation between a standard concentration and the X-ray intensities.

Option1: XRF calibration.

The AlF_3 tablet is prepared by grinding the sample into a powder form, and mixed it with stearic acid, boric acid or wax as a binder, and then the total fluorine is measured in XRF spectrometer. The calibration of fluorine is carried out by using certified standards; in our case we calibrated the XRF using Pechiney certified standards. The calibration is highly accurate as reflected by the RMS value of the calibration.

Table 2: the concentration of Fluorine in Pechiney standards

Pechiney STD	Fluorine (%)
CAB	57.2
CAO	57.7
CAA	60.4
CAC	61.8
CAN	62.4
ALF02	63

Option2: Dilution of AlF_3 samples with primary Alumina:

In the absence of fluorine high range standards, it is possible to measure the fluorine content by diluting AlF_3 samples with a known amount of primary alumina. Then a measure of the fluorine content in fluorinated alumina is performed as a calibration (low fluorine range between 1.4 to 2.4 %). Primary alumina contains no fluorine, so it is a suitable dilution agent although we can change it with any other material having the same properties. Primary alumina is a good choice due to the high level of homogeneity obtained with AlF_3 and the availability of the material in any aluminum laboratory. In this option, a specific amount of AlF_3 and alumina is mixed, ground and pressed. The fluorine is back calculated as per the difference in weight between AlF_3 and alumina in the sample.

The main problem in this method is the preparation steps: due to the high number of electrolyte bath samples in aluminium laboratories contamination with other fluoride materials is highly probable so the possibility of human errors is high, especially in the preparation step, as the grinding step is carried out in the same machines used for other materials.

Purity by NMR

Measuring fluorine in fluorinated alumina is done at Alba Laboratory by Nuclear Magnetic Resonance (NMR): the machine is designed to measure low fluorine level (1.4 to 2.4%). The advantage of this method is its independance to the preparation step, there is no need to grind the sample, it can be analysed as received. On the other hand, the total analyses time is only two minutes. The available NMR machine in Alba Laboratory is specified for measuring fluorine in fluorinated alumina which is usually between 1.4 to 2.5%.

Several internal standards of AlF_3 purity were developed by the Wet Chemical Method. These standards were used to calibrate the NMR machine for fluorine at high range (59 to 63 % of fluorine). Since the machine was designed to measure low fluorine range (between 1.4 to 2.4% of fluorine), we faced some difficulties in the beginning, as the capacity of the Analog–to–Digital converter (ADC) was not adjusted to cope with such high concentrations, there was an overflow problem and the instrument parameters (i.e. gain, frequency and pulse times) were adjusted with the consultant of the manufacture

to enable us measuring such a high fluorine concentration.

Purity by Qualitative Analysis

Qualitative analysis is widely used nowadays to explore the phase and element peaks available in any unknown material: the sample is scanned by the spectrometer and then the individual peaks are studied carefully to identify the element of each peak and the element concentration, in our AlF_3 case. It is possible to scan the sample and obtain the fluorine content and the other traces elements. Note that the aluminum peak will be the sum of aluminum available in alumina and in AlF_3, so fluorine peak is the most suitable peak to determine the purity of AlF_3. The fluorine peak is found in the analysis pattern of PX1 crystal which is synthetic crystal manufactured by Panalytical-Holland. The available set–up standard for fluorine is (SAMPLE B) which is developed by Panalytical.
In such type of calibration, the accuracy will be certainly low. To avoid such constrains, the whole quantitative calibration was modified by adding internal standards of fluorine with high content.

Table 3: Content of SAMPLE B in qualitative calibration

Compound	Conc. (%)
$Li_2B_4O_{10}$	65.5
SO_3	3.43
F	7.2
BaO	6.57
Y_2O_3	0.50
MgO	4.0
Na	3.93
Cl	6.07
Li	2.70

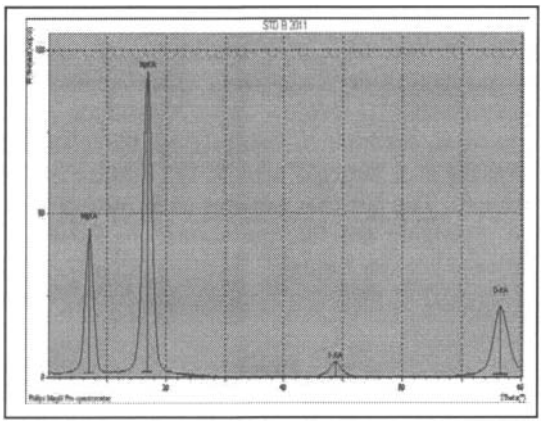

Figure 1: Scan of fluorine peak by the XRF quantitative method.

Purity by SEM:

Purity by SEM

Scanning Electron Microscopes are available in most of modern aluminum laboratories to study the microstructure of the aluminum alloys, alloying additives, refractory materials, inclusions/defect analysis and a number of other applications. The instrument has the capability to view a range of materials at magnifications up to 100,000X and beyond (Figure 2).

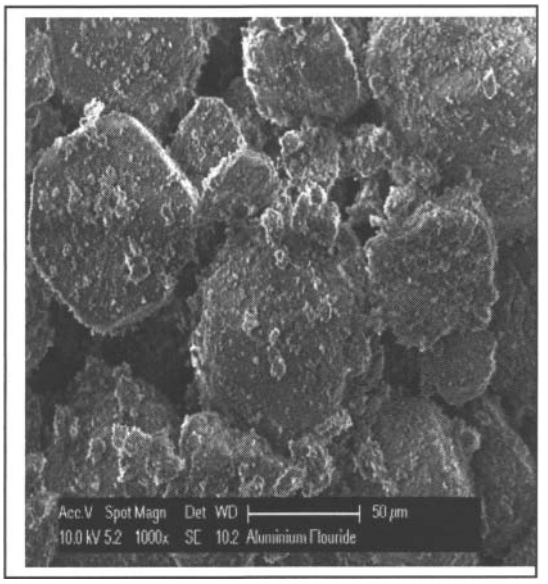

Figure 2: AlF_3 particle by SEM microscopy.

The instrument is also attached to an energy-dispersive X-ray analyzer which makes the instrument able to produce a spectrum/quantitative analysis of the elements present in a targeted area in the surface of the sample. The AlF_3 sample was examined in SEM to determine the fluorine content in loose and pressed powder forms.

Theory

Due to the availability of alumina in any AlF_3 material, it is not possible to calculate the total content of AlF_3 depending on the aluminum concentration: the only option is to measure the total fluorine content and then back calculate the AlF_3 concentration. This principle is used in most of AlF_3 purity methods including the Wet Chemical Procedure. The calculation is simply depending on the ratio between Fluorine and Aluminium in AlF_3:

AlF_3 = 26.98 g/mole + 3(19.0 g/mole) = 83.98 g/mole.
In this case, the ratio between AlF_3 and F is:
AlF_3 = (83.98/27) = 1.47338.

AlF_3 Dilution Factor

As mentioned in Option 2 of the quantitative method, the AlF_3 is diluted by primary alumina and then measured on fluorinated alumina calibration. Knowing that the range of fluorine in fluorinated alumina is between 1.4 to 2.4 %, the fluorine of the diluted AlF_3 should fall in this range. The XRF tablet contains 12 g of the unknown sample and 3 grams of the binder, in case of 40% dilution of AlF_3, which is equal to 2.5% of the total sample weight:
97.5% alumina + 2.5% AlF_3
11.7 g of alumina + 0.3 g of AlF_3

Total fluorine = diluted fluorine content obtained from XRF x 40%.

Results

The calibration of fluorine is carried out accurately in XRF machine using Pechiney/ Alcan standards; the RMS value is 0.48319, which is a good level of accuracy.

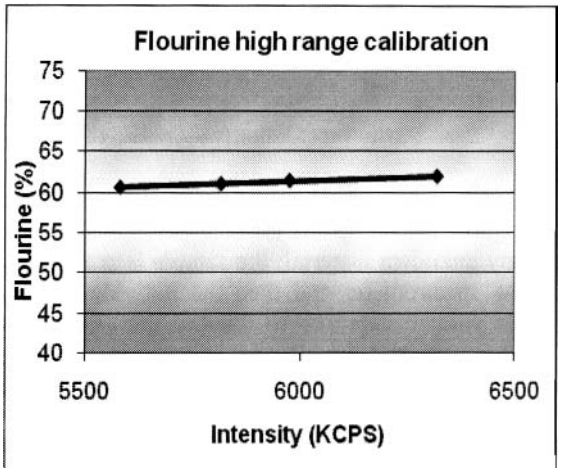

Figure 3: XRF calibration of high florune content

Several samples were diluted and tested against fluorinated alumina calibration. The results were compared with NMR, and fluorine high range calibration in XRF. Table 4 shows the comparison of the results using different methods:

Table 4: Results of Fluorine content by different methods

Standard	Total fluorine	Wet Chem.	Diluted sample	XRF
Internal STD 1	60.8	89	89.5	89.2
Internal STD 2	63.2	92.8	93.1	93
Internal STD 3	61.4	90	90.4	90.3
Internal STD 4	60.6	88.7	89.3	89
Internal STD 5	61.2	90	90.2	90.3

NMR Calibration

The calibration obtained by the NMR instrument, after adjusting the gain of the electronic amplifier, showed a good accuracy line with R^2 = 0.998 and SD = 0.025 (Figure 4).

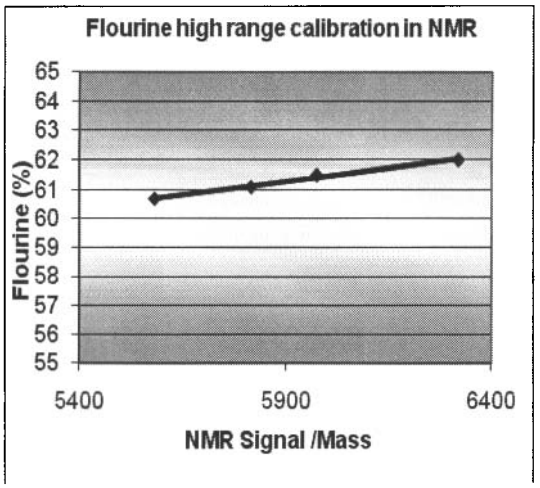

Figure 4: NMR calibration for high range of Fluorine

Results of the Qualitative Method

To avoid the one single point calibration, we added two internal standards to the standardless qualitative calibration. The calibration obtained was so accurate and the added standards were inline with SMPLE B standard which is having only 7.3% fluorine. To make sure also that other element of our internal standards are used in the calibration such as silicon, titanium, and sulphur, the values of other elements available in the two standards were added to other calibrations lines.

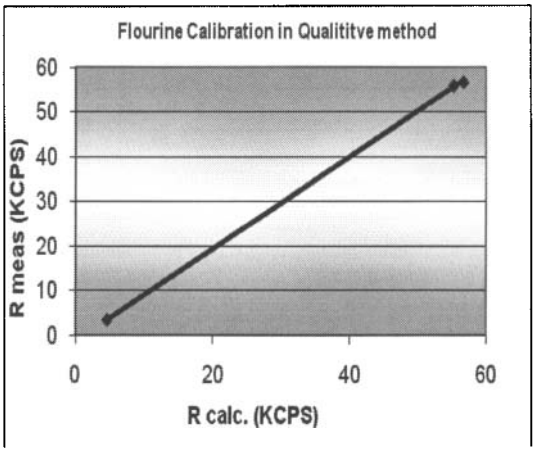

Figure 5: Fluorine calibration in the qualitative method.

SEM Results

Several trials were carried out to obtain accurate fluorine content by SEM. A clear fluorine peak was obtained in each trial along with aluminum peaks, but the results were showing a lower fluorine content in SEM with low vacuum system. The samples were tested later by a high vacuum system and yielded closer results, but still lower than the certified value.

Table 5: results of fluorine in SEM

Sample ID	Wet Chem.	SEM
Sample1	60.7	54.68
Sample2	62.1	58.4
Sample3	61.5	57.47
Sample4	61.7	57.97

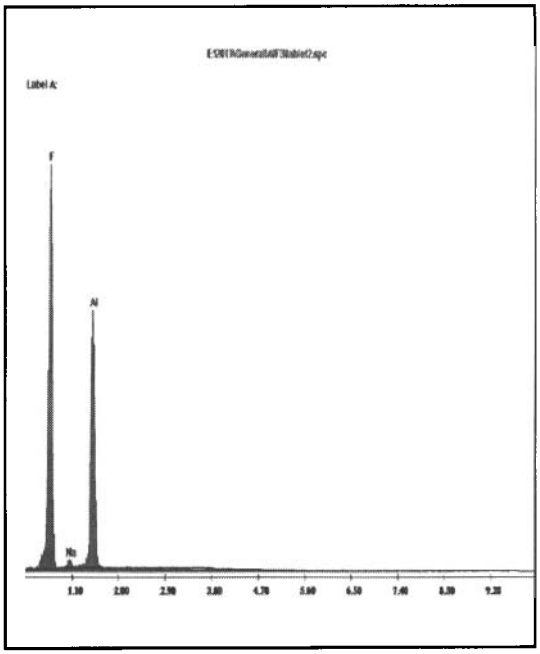

Figure 6: scan pattern of AlF_3 in SEM

Discussion

Five analytical techniques were used to obtain the fluorine content in aluminium fluoride powder materials as an alternative to the Wet Chemical Procedure. The X-ray fluorescence method is typically used to measure the fluorine content with a high accuracy; the only problem is the contamination with other fluorine sources during the preparation step. The method also can

be used to differentiate between alumina and AlF_3. Diluted XRF tablets can be used to measure the high fluorine content in fluorinated alumina calibration.

To avoid the contamination during the preparation step, NMR is a good choice to measure the fluorine content without the usual AlF_3 preparation step, as there is no need to grind the sample in NMR procedure. NMR is a good choice as it provides a prompt analysis for cell reduction teams in case they have a doubt about the material fed to the cell, whether it is alumina or AlF_3. The calibration of NMR is accurate with $R^2 = 0.998$ and SD = 0.025.

The modified qualitative XRF method for AlF_3 measurement, provided extra information about the available trace elements in the material in addition to the require purity percentage such as zirconium, gallium and arsenic which is not usually certified by AlF_3 suppliers.

Although the SEM results were less accurate than other techniques used, the obtained fluorine peak and the close results of fluorine content can be used to differentiate between alumina and AlF_3 materials promptly.

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