

Combined Quantitative Analysis of Salt Fluxes Composition by X-ray Diffraction and X-ray Fluorescence in Process Control

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Abstract

Salt flux treatment of molten aluminium is common practice in aluminium production and recycling used to decrease oxidation and metal losses and to clean the metal. The most common class of fluxes contain a mixture of sodium chloride and potassium chloride, and minor amounts of fluoride compounds. Fluxes are specified to certain chemical compositions to produce defined process parameters, such as melting point, surface activity and refining efficiency. Thus, salt flux composition directly affects both the efficiency of the treatment operation and the final product quality.

As metal quality standards grow more demanding, it is necessary to measure the composition of delivered flux and verify that the blend matches the desired specifications. X-ray diffraction (XRD) and X-ray fluorescence (XRF) are the most suitable methods to do this in laboratory. However, in most cases the analysis is made using semiquantitative pre-calibrated programs, which does not assure the accuracy required by the industrial production. This is because neither certified reference materials nor suitable measurement techniques had been available. This paper describes a comprehensive XRD-XRF system for measuring the entire phase and elemental flux composition from major compounds to minor impurities. First, we developed and certified 14 reference materials as National or Branch Measurement Standards. Then certified measurement techniques were developed to measure main flux compounds including NaCl, KCl, AlF₃, Na₂SiF₆, K₂SiF₆ and Na₃AlF₆. Finally, we complemented the certified measurement techniques with reference-free options and formulated the methodology of how to apply them in combination to fully characterize the flux composition. In addition, the paper gives examples of industrial fluxes analyses.

Keywords: Salt flux, X-ray diffraction, X-ray fluorescence, Reference materials, Quantitative analysis

1. Introduction

The treatment of molten aluminium with salt fluxes is a common practice in aluminium production. Fluxes are mixtures of salts used to remove impurities such as alkali and alkaline earth metals and oxides, to modify the metal, or to protect it from oxidation. The most popular class of fluxes are multifunctional fluxes, which allow several operations, such as cleaning the melt from non-metallic inclusions and protecting against oxidation, to be performed in one step. The chemical composition of the flux can be tailored to adjust properties such as density,

viscosity, reactivity, and wettability. The main compounds commonly found in solid fluxes are chlorides and fluorides, oxidizing compounds, and solvents of alumina.

Chlorides typically consist of NaCl and KCl. The molar ratio of NaCl and KCl in the mixtures varies as NaCl = 0,5–0,7 and KCl = 0,3–0,5. Although their reactivity with molten aluminium is negligible compared to fluorides, chlorides are used for their fluidizing effects at temperatures of 650–750 °C and act as fillers and carriers for the other compounds [1].

Fluorides play an essential role in fluxing by acting as surfactants to adjust the wettability between the salt and the molten aluminium. This ensures efficient extraction of impurities. The most commonly used additives are simple fluorides such as AlF₃, CaF₂, NaF, KF, MgF₂, and double fluorides such as Na₃AlF₆, K₃AlF₆, Na₂SiF₆ and K₂SiF₆. The amount of fluorides in the salt flux should be minimized for environmental and health reasons. However, it varies widely depending on several factors, including the desired metal quality, the concentration of inclusions in the melt, and environmental regulations [1].

Both the qualitative and quantitative composition of salt fluxes determine fluxing efficiency and affect the process economy. Moreover, the global green trend implies reducing the amount of the flux being used in casting. In this case, the highest fluxing efficiency is achieved by using of complex fluxes with a carefully adjusted composition. However, there are at least two factors that can deviate an adjusted composition. First, fluxes are generally produced from minerals, as well as by-products and wastes of aluminium production, rather than from pure salts. These raw materials are sources of impurities, the presence of which reduces the concentration of desirable components. This in turn reduces fluxing efficiency and final product quality. Second, KCl is about three times as expensive as NaCl, so flux suppliers have a strong motivation to keep the blend as close to the lower KCl limit as possible [2].

To maintain foundry technology, it is essential to verify that the blend matches the desired specifications. Concentrations of major compounds, mineral impurities, and elements degrading the metal quality should be measured quantitatively. However, there are two possible scenarios for flux acceptance in foundry practice. The first is that technologists rely only on the quality certificates provided by the suppliers. The second is that a flux is analysed in the smelter laboratory using semiquantitative pre-calibrated XRD and XRF programs that do not provide the accuracy required for the industrial production. This is because neither certified reference materials (RMs) nor suitable measurement techniques had been available.

X-ray diffraction (XRD) and X-ray fluorescence (XRF) are the most appropriate laboratory methods for quantitative analysis of flux composition. X-ray methods are non-destructive, universal, rapid and require simple sample preparation. Their combination allows complete characterization of phase and elemental composition. Due to these characteristics, both X-ray methods are widely used at aluminium smelters to measure electrolyte composition [3–4], raw material composition and by-product composition.

This paper presents the development of reference materials and a comprehensive XRD-XRF system for measuring the entire phase and elemental composition of NaCl–KCl–Na₂SiF₆–K₂SiF₆–AlF₃ fluxes, from major compounds to minor impurities. In addition, examples of industrial flux analyses are given.

2. Methods and Instruments

2.1 X-ray Fluorescence Spectrometry

XRF spectrometry was used to determine the elemental composition of industrial fluxes and reference samples. In this study, we used Shimadzu XRF – 1800 4 kW instrument (Shimadzu Corp.) and Zetium 2.4 kW instrument (Malvern Panalytical B.V.) were used to analyse pressed pellets.

The reference-free fundamental parameter (FP) method [5] was applied for the semi-quantitative analysis of industrial fluxes. XRF instrument calibration was also used to assess the quality of the prepared RMs and to develop the measurement procedure.

2.2 X-ray Diffraction

X-ray diffraction was employed to determine the phase compositions of industrial fluxes and the reference materials. The powder diffraction patterns were obtained from samples using Shimadzu XRD – 7000 3 kW (Shimadzu Corp.) and Bruker D8 ADVANCE 3 kW (Bruker Corp.) diffractometers.

The reference-free semiquantitative phase analysis (QPA) was performed in the RETRIEVE copyright software [6], which integrates the cluster phase identification method [7] and the multireflex Reference Intensity Ratio (RIR) method [8]. The software retrieves reference diffraction powder patterns of inorganic phases, along with their Reference Intensity Ratios [8], from the PDF2 database [9]. The challenge lies in the fact that at least ten reference patterns from the PDF2 are potentially related to a true phase. Therefore, QPA requires a careful selection of the most appropriate reference pattern.

Like XRF analysis, diffractometer calibration was used for assessing of the RMs' quality and developing the measurement procedures.

2.3 State Standards of Mass Fractions and Molar Concentrations

The RMs were characterized using the following facilities:

- State primary standard GET 176 based on controlled-potential coulometry method [10];
- State secondary standard GVET 196–1–2012 based on spectral methods [11].

3. Reference Materials

3.1 Reference Materials Composition

As mentioned above, salt fluxes are made from mineral raw materials. Not only the raw materials contain impurities, but also the major salt components are often distributed among several mineral phases. Therefore, when designing composition of the RMs, one should not confine itself to flux specifications. The RMs must also imitate the qualitative and quantitative composition of real industrial fluxes to ensure that they are correctly analysed.

To provide this match, we studied 19 industrial flux samples using the reference-free XRD and XRF techniques outlined in Section 2. According to XRD results, the chlorides found in the samples are mainly NaCl, KCl, and their solid solutions. In contrast, there is a variety of fluorides present. Electrolyte mineral phases, such as cryolite Na_3AlF_6 , chiolite $\text{Na}_5\text{AlF}_{14}$, KAlF_4 and K_3AlF_6 are detected along with mallardite Na_2SiF_6 and hieratite Na_2SiF_6 . The total

concentration of phase impurities, such as carnallite $\text{KMgCl}_3 \times 6\text{H}_2\text{O}$, anhydrite CaSO_4 and $\text{CaMg}_2\text{Al}_6\text{O}_{12}$, varies as 2–10 wt.%. Anhydrite present in most samples at concentrations up to 3.5 wt.%. The results of XRF analysis correlate well with the XRD results. Elemental impurities detected by XRF spectrometry in most samples include calcium, magnesium, and sulfur (up to 1.5 wt.%), iron, bromine, strontium, and rubidium (up to 0.1 wt.%).

The qualitative composition of the RMs was tailored to match specifications and general recommendations in terms of main components, and to imitate real industrial salt fluxes in terms of impurities. The chosen qualitative composition of the RMs meets these requirements (Table 1). Cryolite, chiolite and anhydrite are present in most of the industrial fluxes at concentrations above 0.5 wt. %, so they were included in the mixtures. Iron oxide Fe_2O_3 was also included because iron degrades the quality of primary aluminum.

Table 1. The planned composition of salt flux reference materials.

Components									
NaCl	KCl	Na_2SiF_6	K_2SiF_6	AlF_3	Na_3AlF_6	$\text{Na}_5\text{Al}_3\text{F}_{14}$	CaSO_4	MgF_2	Fe_2O_3

When planning the composition of the RMs, we considered that KCl and Na_2SiF_6 must not be mixed in the same material to ensure the stability of the blend. The results of the XRD analysis of the trial reference materials (Figure 1) confirmed that the chemical reaction described in Equation (1) [12] takes place in the mixtures under standard conditions in air:

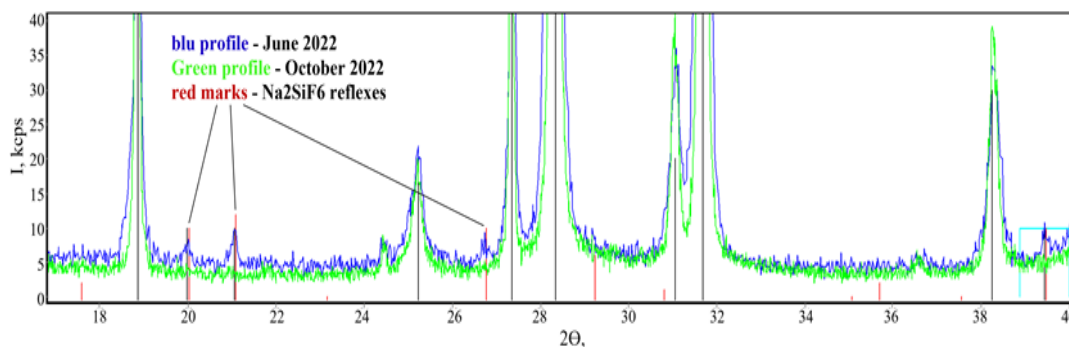
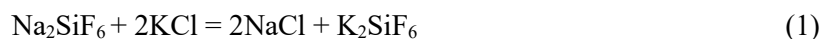


Figure 1. A compare-view of XRPD patterns of the trial reference material FPR-5. 2 wt.% of Na_2SiF_6 fully transforms in K_2SiF_6 in three months in air.

Since the RMs are intended to serve as calibration standards for XRF and XRD instruments, their quantitative composition is designed to overarch the phase concentrations given in the specifications and those indicated in industrial samples. To meet the specifications, mass fractions of all the components listed in Table 1, except the Fe_2O_3 , and all the related elements, have been certified in the RMs. Mass fractions of iron were not certified but are provided in the certificates for the calibration of reference-free XRF programs.

3.2 Reference Materials Preparation

As fluxes are mixtures of original salts, we prepared 14 reference materials by mixing the compounds listed in Table 1. For the preparation of the RMs, we used pure chemical reagents. The exceptions were cryolite and chiolite, which we synthesized because they are not available in pure form.

The RMs were prepared as follows:

- Calcination of the reagents at 450 °C for 1 hour;
- Portioning of the reagents. The masses of the weighed portions were calculated based on the planned concentrations to prepare 400 g of each RM;
- Mixing of the weighed portions in a Y-shaped mixer for 1 hour;
- Milling of the mixtures in a Pulverisette 6 (FRITSCH) planetary mill equipped with ZrO grinding bowls and balls. Milling time and speed were chosen using XRD to obtain a particle size < 100 µm without altering the diffraction characteristics of the compounds.

3.3 Reference Materials Characterisation

The uniformity of the certified elements and compounds in the RMs was tested according to standard [13]. However, there had been neither XRF, nor XRD measurement procedures applicable for flux composition analysis to measure elemental and phase concentrations. To address the issue, we developed an alternative approach based on the use of XRF intensities instead of elemental concentrations. Thus, the standard deviation of uniformity for elements is calculated as:

$$S_{uk} = \frac{S_{k,I} \times A_k}{\bar{I}_k} \quad (2)$$

where:

- S_{uk} The standard deviation of uniformity of an element k , wt. %
 $S_{k,I}$ The standard deviation of uniformity of $I_{K\alpha}$ intensity for the element k , calculated according to [12], counts/s
 A_k Certified concentration, wt. %
 I_k Average intensity of $K\alpha$ characteristic XRF line of element k , counts/s

The standard deviation of uniformity for a chemical compound m is calculated as:

$$S_{um} = \max(S_{uk}) \quad (3)$$

where:

- S_{uk} Standard deviation of uniformity of an element k composing phase m , wt. %

The stability of the RMs was experimentally tested using XRD data. Our team has collected dozens of X-ray powder patterns from industrial flux samples over the past few years that have the same qualitative phase composition as the RMs. A comparison of the powder patterns from the same industrial samples collected five years apart revealed no change in qualitative or quantitative phase composition. Therefore, we conclude that the RMs are stable over a five-year period, and the standard deviation of stability is negligible compared to the other certified error's compounds.

The certified values A_i are calculated according to Recommendations MI 1992–98 [14] applicable to RMs prepared by mixing:

$$A_i = \frac{\sum_{n=1}^N A_{in} \times q_n}{Q} \quad (4)$$

where:

- A_i Certified mass fraction, wt. %,
 N Number of initial chemical reagents,
 A_{in} Mass fraction of a certified compound i in an original chemical reagent n , wt. %,

- q_i Mass of an initial chemical reagent i , g,
 Q Total mass of a reference material, g.

Mass fractions A_{in} of all the certified elements and compounds in chemical reagents NaCl, KCl, Na₂SiF₆, and K₂SiF₆ were measured using the State primary standard GET 176 [10] and State secondary standard GVET 196–1–2012 [11].

The mass fraction of AlF₃ in the original chemical reagent was measured according to the National standard GOST 19181–78. Technical aluminium fluoride. Specification. [15]. The mass fractions of the certified elements in this chemical reagent were measured using reference-free XRF analysis.

The mass fractions A_{in} of the other certified compounds, namely Na₃AlF₆, Na₅Al₃F₁₄, CaSO₄, and MgF₂, in their original chemical reagents were measured using reference-free XRD as described. The mass fractions of the certified elements in these reagents were measured using reference-free XRF.

The certified errors D_i are calculated according to Equation (5) in compliance with [14]:

$$D_i = \sqrt{D_{Mi}^2 + D_{Ti}^2 + 4 \times S_{ui}^2} \quad (5)$$

where:

- D_i Certified error, wt. %;
 D_{Mi} Error of mass fractions measurement, wt.%;
 D_{Ti} Error of preparation technology, wt.%;
 S_{ui} The standard deviation of uniformity for a certified compound i , wt.%.

The certification of the reference materials was conducted based on the traceability of their certified values. One group of seven RMs was prepared from such chemical reagents, as NaCl, KCl, Na₂SiF₆, K₂SiF₆, and AlF₃. The other group was prepared by mixing these reagents with Na₃AlF₆, Na₅Al₃F₁₄, CaSO₄, MgF₂, and Fe₂O₃. The certified values of the RMs in the first group are traceable to State measurement standards. In contrast, the certified values of the RMs in the second group are only partially traceable due to the use of reference-free XRD and XRF methods for analysis of Na₃AlF₆, Na₅Al₃F₁₄, CaSO₄, and MgF₂.

Due to the difference in the traceability levels, the two groups of RMs were certified as separate sets at different levels. The first group was certified as State measurement standards GSO FPR-SFU [16], while the second group was certified at the branch level in the aluminium industry as OSO FPR-SFU (Table 2).

Table 2. The variation of metrological characteristics of the reference materials (for a confidence probability of P = 0.95), wt.%.

Components									
	NaCl	KCl	Na ₂ SiF ₆	K ₂ SiF ₆	AlF ₃	Na ₃ AlF ₆	Na ₅ Al ₃ F ₁₄	CaSO ₄	MgF ₂
Min.	27.3 ± 0.5	39.9 ± 0.8	4.10 ± 0.11	0.503 ± 0.029	0.60 ± 0.11	3.79 ± 0.04	0.995 ± 0.026	1.14 ± 0.11	0.62 ± 0.11
Max.	58 ± 1	64 ± 1	9.10 ± 0.22	23.9 ± 0.6	8.51 ± 0.15	9.96 ± 0.07	9.00 ± 0.04	3.99 ± 0.11	3.02 ± 0.11
Elements									
	Na	K	Cl	F	Si	Al	Ca	S	Mg
Min.	10.73 ± 0.14	5.62 ± 0.05	31.0 ± 0.8	0.743 ± 0.030	0.076 ± 0.011	0.166 ± 0.009	0.27 ± 0.06	0.24 ± 0.06	0.21 ± 0.06
Max.	27.24 ± 0.27	34 ± 1	53 ± 1	27.4 ± 0.5	4.37 ± 0.06	5.21 ± 0.04	1.47 ± 0.06	1.3 ± 0.06	1.27 ± 0.07

4. Measurement Techniques Development

After RMs certification, the next step was to develop measurement procedures for phase and elemental quantitative analysis of the fluxes. An XRD measurement procedure was created to quantify major components, including NaCl, KCl, AlF₃, Na₂SiF₆, K₂SiF₆ and Na₃AlF₆. To measure concentrations of all the certified elements, an XRF measurement procedure was developed

The accuracy (trueness and precision) of the measurement procedures and their results was evaluated according to the International Standard ISO 5725–2:2019 [17] and recommendations RMG 61–2010 Accuracy, trueness and precision of the measurement procedures for quantitative chemical analysis. Methods of evaluation. [18]. The precision of both measurement procedures was experimentally evaluated using 13 industrial flux samples. To evaluate the trueness, in both cases we used 6 evaluation samples, which were prepared similarly to the RMs of the same original chemical reagents. As a result, the two measurement procedures were certified in compliance with the National standard GOST P 8.563–2009 Procedures of measurements.

5. Combined XRD-XRF methodology

In the final stage of our study, we developed a comprehensive methodology of combined XRD-XRF analysis to measure the complete phase and elemental composition of the flux, from the major compounds to the minor impurities. To do this, we first supplemented the certified measurement techniques with the reference-free options provided in Section 2, and then formulated the methodology of how to apply them all in combination (Figure 2).

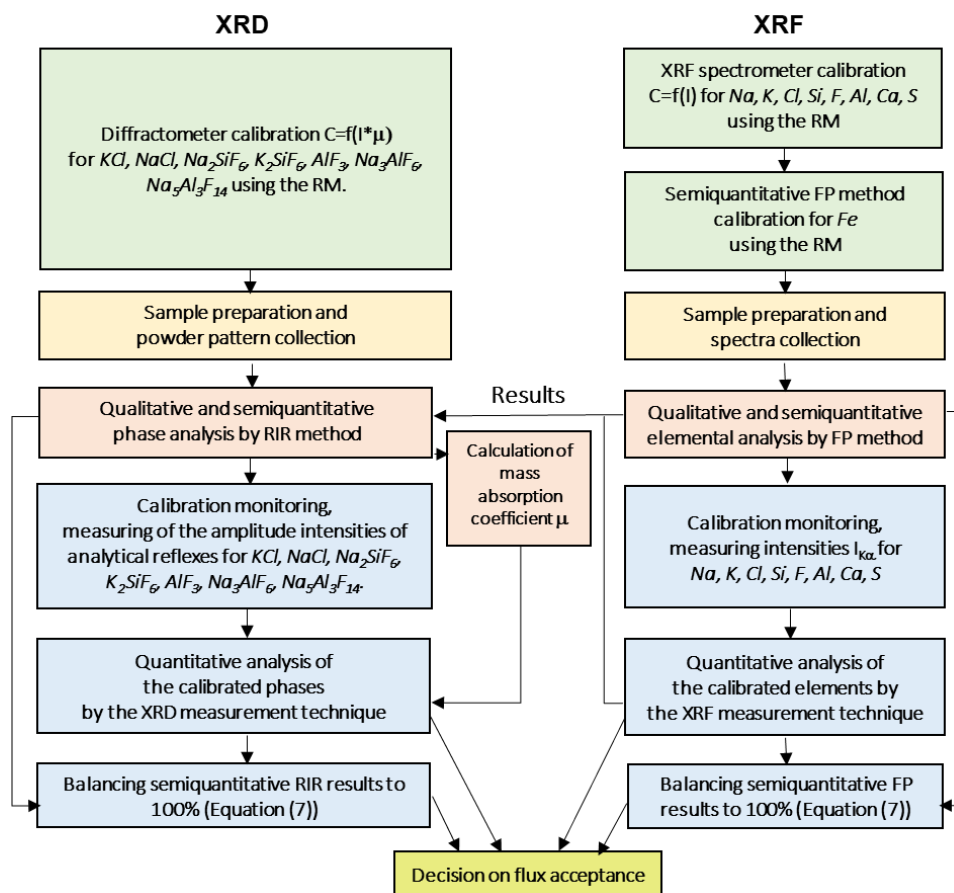


Figure 2. The block diagram of the combined XRD-XRF analysis.

The key feature of the quantitative XRD phase analysis is the use of the mass absorption coefficients μ in diffractometer calibration (Figure 2). This increases the accuracy of QPA by compensating the X-ray absorption characteristics that vary with quantitative composition. The mass absorption coefficients of both the RMs and routine samples are determined using Equation (6):

$$\mu_i^* = \sum_j \mu_j^* \cdot C_{ij} \quad (6)$$

where:

- μ_i^* Mass absorption coefficient of a sample i , cm^2/g ,
- μ_j^* Mass absorption coefficient of a phase j , cm^2/g ,
- C_{ij} Concentration of the phase j in sample i , wt. %.

The final stage of both XRD and XRF analysis is the balancing of the semi-quantitative results to 100 %. The concentrations of impurities measured by the RIR method of the FP method are balanced as:

$$C_{imp,j} = \frac{C_{impSQ,j} \times (100 - \sum_k C_{quant,k})}{100} \quad (7)$$

where:

- $C_{imp,j}$ Balanced concentration of an impurity j , wt. %;
- $C_{impSQ,j}$ Concentration of the impurity j , calculated using RIR or FP method, wt. %;
- $C_{quant,k}$ Concentration of a phase or an element k , measured using calibration, wt. %.

6. Examples of Industrial Flux Analyses

The developed combined methodology was implemented in a casthouse laboratory and is used to analyse fluxes delivered to the casthouse. Here, two examples of such analysis are presented.

Table (3) compares the elemental composition measured by the measurement techniques with those measured semi quantitatively by the FP method, without (FP) and with balancing according to (7) (FP balanced). The difference between semiquantitative and quantitative results reaches 6.2 wt% for Na in Sample #1, which illustrates that pre-calibrated analytical programs provide unreliable results for major elements and should be avoided in flux quality assessment.

However, in the case of Sample #1, the accumulation of the error introduced by the measurement technique leads to an overestimation of the semiquantitative results for bromine dew to the balancing. Therefore, the methodology of concentration balancing needs to be refined. This can be achieved by setting a concentration limit below which the relevant elements will not be involved in the balancing to prevent their overestimation. The effectiveness of this approach and the specific limit value will be evaluated in further study.

The low accuracy of semiquantitative results for major elements is apparently caused by the way the FP method is implemented in the software. The analytical procedure involves three steps. First, the measured fluorescent intensities of elements are recalculated to theoretical intensities using spectrometer transmission factors determined with a RM. The concentrations of elements are then calculated using an algorithm that solves the set of nonlinear equations describing the dependence of the theoretical intensity on the concentration and layer thickness of each element. The algorithm utilizes fundamental parameters such as absorption coefficients, emission wavelengths, and absorption edges. Finally, the sum of the calculated concentrations is normalized to 100 % [5].

Table 3. The elemental composition of the samples measured using different techniques, wt.%.

Element	Sample #1			Sample #2		
	FP without balancing	Measurement technique (P = 0.95)	FP balanced (Equation 7)	FP without balancing	Measurement technique (P = 0.95)	FP balanced (Equation 7)
Cl	47.2	51.0 ± 1.1	51.0	36.4	44.1 ± 1.1	44.1
K	23.5	27.8 ± 0.9	27.8	16.9	20.7 ± 0.9	20.7
Na	22.6	16.4 ± 0.9	16.4	24.7	20.0 ± 0.9	20.0
F	5.31	1.80 ± 0.51	1.80	12.6	5.9 ± 1.0	5.9
O	-	-	-	4.83	-	5.7
Al	0.03	0.01 ± 0.07	0.01	3.80	2.87 ± 0.07	2.87
Ca	0.32	0.23 ± 0.12	0.23	0.27	0.27 ± 0.12	0.27
S	0.18	0.14 (OL)*	0.14	0.19	0.14 (OL)*	0.15
Si	0.75	0.58 ± 0.04	0.58	0.17	0.12 ± 0.04	0.12
Br	0.04	-	1.99	0.04	-	0.06
Mg	0.04	0.02 (OL)*	0.03	0.10	0.03(OL)*	0.04
Fe	-	-	-	0.02	-	0.02

*out of the measurement limits

Each step presents a potential source of error. Spectrometer transmission factors change over time. Despite their accuracy, the theoretical models that describe the dependence of intensity on the concentration as well as the tube spectrum of the X-ray tube used are designed with assumptions and simplifications. The normalization step introduces an absolute error for each element that is proportional to its concentration determined in the second step.

While the error introduced at the first step can be eliminated by monitoring and timely measuring the spectrometer transmission factors, a user does not have access to the programmed theoretical models to correct the relevant error. Given the above, quantitative analysis of flux composition by calibrations is preferable because the use of appropriate RMs ensures an accurate experimental description of how the measured fluorescence intensity depend on element concentration.

The QPA results obtained by different techniques are given in Table 4. They indicate that Sample #1 is made of relatively pure salts. In contrast, the presence of phases such as $KAlF_4$ and K_3AlF_6 in Sample #2 indicates that it is prepared of by-products from aluminium production. This proves that the casthouse is indeed supplied with fluxes of widely variable compositions.

Table 4. Quantitative results of phase analysis of the industrial fluxes, wt.%.

Sample	Technique	$\mu, \text{cm}^2/\text{g}$	NaCl	KCl	K_2SiF_6	Na_2SiF_6	$KAlF_4$	AlF_3	$CaSO_4$	K_3AlF_6
#1	RIR	0.975	53.6	40.9	2.6	2.6	-	1.0	0.6	-
	MT+ Balanced		53 ± 3	41 ± 4	1.61	2.0 ± 0.7	-	1.4 ± 0.7	0.77	-
#2	RIR	0.876	47.2	28.9	0.5	-	15.2	2	0.9	5.3
	MT+ Balanced		44 ± 3	28 ± 4	0.1	-	15.9	2.2 ± 0.7	0.9	9.3

One issue in analyzing fluxes of the composition presented is the simultaneous presence of anhydrite $CaSO_4$ and Oskarssonite AlF_3 . These phases have overlapping major reflexes (see Figure 3), leading to an overestimation of the concentration of AlF_3 when measured using the measurement technique.

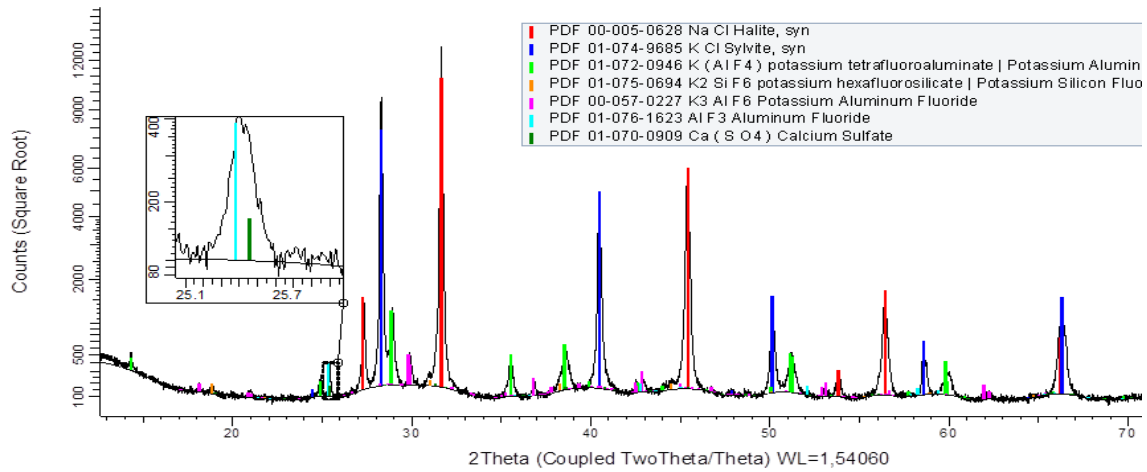


Figure 1. XRPD pattern of flux sample #2.

The interference of CaSO_4 is compensated by calculating the concentration of AlF_3 according to the Equation (8):

$$C_{\text{AlF}_3} = A_{\text{AlF}_3} + B_{\text{AlF}_3} \times \left(I_{\text{sum}} - \frac{C_{\text{Ca}(\text{SO}_4)} - A_{\text{Ca}(\text{SO}_4)}}{B_{\text{Ca}(\text{SO}_4)}} \right) \quad (8)$$

where:

- $A_{\text{AlF}_3}, B_{\text{AlF}_3}$ Regression coefficients for AlF_3 calibration, calculated using the RMs,
- I_{sum} Measured intensity of the overlapped reflex, counts,
- $C_{\text{Ca}(\text{SO}_4)}$ Concentration of CaSO_4 calculated from XRF data, wt%,
- $A_{\text{Ca}(\text{SO}_4)}, B_{\text{Ca}(\text{SO}_4)}$ Regression coefficients for CaSO_4 calibration, calculated using the RMs.

The decision to accept the fluxes into production is based on whether the total concentrations of elements and refining compounds meet the specifications. The total concentrations of the refining compounds that are calculated from the QPA results (see Table 5), along with elemental concentrations provided in Table 4, confirm that the two delivered fluxes are acceptable for the production.

Table 5. Total concentrations of refining compounds, wt.%.

Sample	NaCl	KCl	KF	NaF	AlF_3	SiF_4
#1	57.80	38.90	0.90	1.30	-	1.10
#2	45.00	28.95	13.20	-	12.80	0.05

7. Conclusions

An original approach involving the use of reference-free XRD and XRF techniques was developed to characterize and certify reference materials. Two sets of reference materials of the salt flux composition were certified at national and branch levels using this approach.

A measurement procedure for quantitative XRD analysis of NaCl , KCl , AlF_3 , Na_2SiF_6 , K_2SiF_6 and Na_3AlF_6 in salt flux was developed and certified. Also, the measurement procedure utilizing XRF spectrometry was certified for the measurement of Na, K, Cl, Al, Si, F, Ca, S, and Mg.

On the top of all the developments, a methodology of the combined XRD-XRF analysis was formulated. It combines the two certified measurement techniques with reference-free XRD and XRF techniques to provide a comprehensive characterization of the salt flux composition. The

methodology has been implemented in a casthouse laboratory and is used to make decisions on whether a flux should be accepted into the production.

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