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Gudrun Saevarsdottir
Reykjavik University
Reykjavik, Iceland

IMPROVING XRD ANALYSIS FOR COMPLEX BATH CHEMISTRIES – INVESTIGATIONS AND CHALLENGES FACED

Nursiani Indah Tjahyono[1], Tania Groutso[1], David S. Wong[1], Pascal Lavoie[1], Mark P. Taylor[1,2]
[1]Light Metals Research Centre (LMRC), [2]Department of Chemical and Materials Engineering,
The University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract

An accurate bath composition analysis is essential for regulating an electrolysis cell's mass and thermal balance. XRD is widely utilised in smelters to analyse % excess AlF_3 ($xsAlF_3$) and Cryolite Ratio (CR) of bath samples. However, the conventional method of analysis can provide misleading results for the more complex bath chemistries usually found in, but not limited to, Chinese smelters. This complexity is due to the presence of Li, K and Mg constituents coming into the bath from alumina impurities. They react with AlF_3 and cryolite, producing additional AlF_3-containing phases other than chiolite and Ca-cryolite, which are not accounted for in the conventional $xsAlF_3$ or CR analysis.

Improvement of the $xsAlF_3$ analysis for complex bath chemistries was investigated and presented in this paper. The aim was to provide an XRD methodology to measure the LiF, KF and MgF_2 levels in the bath through an intensity calibration method, so that they can be integrated into the $xsAlF_3$ and CR analyses. The challenges faced will also be discussed in this paper.

Introduction

Bath composition is one of the most important control parameters in the aluminium production process, with the main control action being the adjustment of AlF_3 additions. It can be expressed as Cryolite Ratio (CR), % excess AlF_3 ($xsAlF_3$) or liquidus temperature, and all three are interrelated. XRD is the most commonly used technique in smelters for analysing bath samples. It usually involves the scanning of peak intensities for chiolite, CaF_2 and Al_2O_3 phases by XRD and total calcium measurement by XRF. The intensities are then translated into a weight % (wt%) through calibration. Equations typically used to calculate $xsAlF_3$ and CR through the XRD method are shown in Equations (1) and (2) [1, 2]. These equations are designed for conventional bath, utilise only the wt% of chiolite, Ca-cryolite and Al_2O_3, to calculate $xsAlF_3$ and CR.

$$xsAlF_3 = ChFactor * Chiolite + CaFactor * (CaF_2 - Fluorite) \quad (1)$$

$$CR = 2 * \frac{(100 - CaF_2 - Al_2O_3) - xsAlF_3}{{}^2\!/_3\,(100 - CaF_2 - Al_2O_3) + xsAlF_3} \quad (2)$$

whereby *Chiolite*, *Fluorite* and *Al_2O_3* are wt% of chiolite, CaF_2 and Al_2O_3 as measured by XRD; *CaF_2* is wt% of total calcium measured by XRF and expressed as CaF_2; *ChFactor* and *CaFactor* are the stoichiometric factors of Chiolite and Ca-cryolite for conversion into $xsAlF_3$, respectively. The *(CaF_2-Fluorite)* term represents the wt% of Ca-cryolite compound, which usually occurs in the form of $NaCaAlF_6$ and/or $Na_2Ca_3Al_2F_{14}$. Although Al_2O_3 content is usually measured by

XRD, often a fixed Al_2O_3 content (e.g. 5 wt%) is assumed for the purposes of CR analysis.

In recent years, there has been increased interest in the analysis of complex bath chemistries usually found in, but not limited to, China, due to the presence of Li, K and Mg modifiers in the bath. These modifiers are sometimes introduced voluntarily (in the form of LiF, KF, MgF_2, Li_2CO_3 etc.) to adjust the properties of the electrolyte (e.g. reduce liquidus temperature [3]), but most often come into the bath as impurities in alumina. Table I shows examples of Li and K impurity levels in different Chinese aluminas. As these impurities are not present as controlled additions to the process, their levels can significantly vary over time, forcing the smelter to adjust its operating cell parameters (e.g. operating temperatures, target $xsAlF_3$) [4]. Figure 1 shows the extent of LiF% variations in the bath that can occur with time in a smelter due solely to alumina impurities.

Table I. Impurity of aluminas produced in Henan province [5].

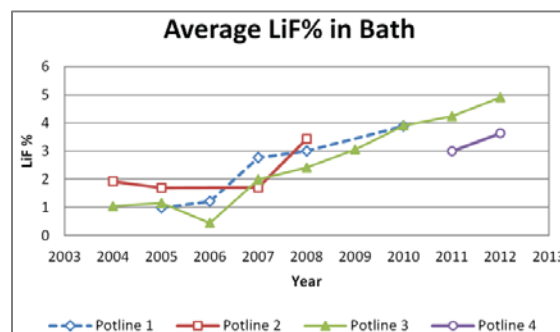|	*Li*	*K*	*Ca*	$\alpha - Al_2O_3$
Zhongzhou	0.014	0.052	0.02	2.5
Wanji	0.084	0.019	0.02	1.4
Kaiman	0.039	0.0001	0.037	2.4
Easthope	0.053	0.022	0.035	3.8
Xiangjiang Wanji	0.073	0.015	0.020	12
Yixiang	0.040	0.018	0.021	0.9

Figure 1. Variations of average LiF% in the bath with time due to alumina impurities at one smelter.

In heavily modified bath samples, Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7 phases can also be present [6-8] from the reaction of Li, K and Mg constituents with AlF_3 and cryolite, respectively. For an accurate measurement of $xsAlF_3$ and CR of the sample, these phases also need to be accounted for in the analysis, however, as shown by Equations (1) and (2), they are often excluded from conventional bath analyses.

Improvements to analytical methods for complex bath chemistries have been attempted by many researchers. Gao et al. [7] tried to formulate a calibration which takes into account the error of the conventional XRD method for known modified bath compositions, however, such a correlation was not found. Qiu et al. [8] concluded that the fluoride-selective electrode method provides an accurate, lower cost and less time consuming method in analysing CR of complex bath. However, this analysis method requires each sample to be heated to 600-650°C for 30 minutes, a time frame that is impractical for smelters analysing a few hundred bath samples. Wet chemistry analysis of Li, K and Mg is often conducted in smelters operating with these modifiers. The main drawback is also the length of time it takes for each analysis, preventing this analysis to be carried out for all bath samples.

XRD is still the most convenient method in analysing bath composition. XRD equipped with fast detectors and software for Rietveld analyses has been pointed out to be the future direction for bath analysis [1]. However, the large majority of XRD instruments currently employed by smelters are *not* properly equipped to easily support Rietveld analysis.

The following paper therefore details attempts to provide an XRD methodology through intensity calibration method to analyse complex bath chemistries in a smelter that did not have XRDs equipped with fast detectors and Rietveld programme. The aim was to produce an accurate measurement of the LiF, KF and MgF_2 levels in bath samples through XRD, so they can be integrated into the conventional $xsAlF_3$ and CR determination.

Calibration for LiF, KF and MgF$_2$

A method was developed to relate the intensity of a marker phase to its alkali-fluoride concentration counterpart. In this case, the Li in the form of LiF is represented by Na_2LiAlF_6, K in the form of KF is represented by K_2NaAlF_6 and Mg in the form of MgF_2 is represented by Na_2MgAlF_7. The recommended scan angles for these phases are shown in Table II. These scan angles need to be refined on each diffractometer to get a more accurate 2θ range.

Table II. Recommended scan angles for Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7.

Constituents	Marker Phase	2θ XRD Scan Angle
LiF	Na_2LiAlF_6	$47.9 - 48.6°$
KF	K_2NaAlF_6	$31.1 - 31.5°$
MgF_2	Na_2MgAlF_7	$30.1 - 30.4°$

Once the LiF, KF and MgF_2 contents in the bath are measurable by XRD, the typical equations to calculate $xsAlF_3$ and CR through XRD can be modified to include them, as shown in Equations (3) and (4).

$$xsAlF_3 = ChFactor * Chiolite + CaFactor * (CaF_2 - Fluorite) + \\ 1.0791 * LiF + 0.4818 * KF + 0.4493 * MgF_2 \quad (3)$$

$$CR = 2 * \frac{(100 - CaF_2 - Al_2O_3 - LiF - KF - MgF_2) - xsAlF_3}{^2/_3(100 - CaF_2 - Al_2O_3 - LiF - KF - MgF_2) + xsAlF_3} \quad (4)$$

whereby, the *ChFactor, Chiolite, CaFactor, (CaF₂-Fluorite)* are the same terms as in Equations (1) and (2). The *LiF, KF* and *MgF₂* terms refer to the LiF, KF and MgF_2 wt% concentrations as calculated by the calibration model (see later sections for details).

The factors for LiF, KF and MgF_2 are calculated based on 100% reaction of each of these alkali-fluorides with AlF_3 and cryolite to produce Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7, respectively.

To ensure a wide range of concentration for each alkali-fluoride calibration and to cover any potential for high concentrations not currently observed in pots, it was initially decided that calibration samples were to be made synthetically. Apart from ensuring a wide range of concentration for LiF, KF and MgF_2 calibration, it also provided basis for comparison for the $xsAlF_3$ calculation. Using industrial samples from the pot confines the calibration to the range of concentrations currently encountered at the smelter and re-calibration would be needed should concentrations fall outside of this range.

Different compositions of bath samples were produced by mixing and melting of laboratory grade cryolite, AlF_3, CaF_2, Al_2O_3, LiF, KF and MgF_2. The powdered mixtures were heated in furnace to about 30°C above the calculated liquidus temperature (based on the work by Solheim et al. [9]). Molten samples were poured onto a steel mould and quickly cooled. The samples were then ground and split between LMRC and a smelter where this calibration work was to be applied. Full XRD scans (2θ of 10-80°) for phase identification were conducted by LMRC and intensity measurements for each phase were performed by the smelter. The phases of interest were initially limited to Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7, but then extended to also include cryolite, chiolite and fluorite. The concentrations of LiF, KF and MgF_2 were also confirmed by wet chemistry analysis.

Formation of Calibration Models based on In-House Calibration Samples

Initial calibration curves were based on linear relationship models of each marker phase to its alkali-fluoride counterpart, i.e. linking the intensity of Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7 phases to the measured LiF, KF and MgF_2 concentrations, respectively. However, it was soon realised that there were other factors influencing the intensity of the phases above other than solely their alkali-fluoride concentration counterparts. This was apparent by the lack of a strong linear correlation between the two components, as shown in Figure 2. As such, more complex relationship models were needed.
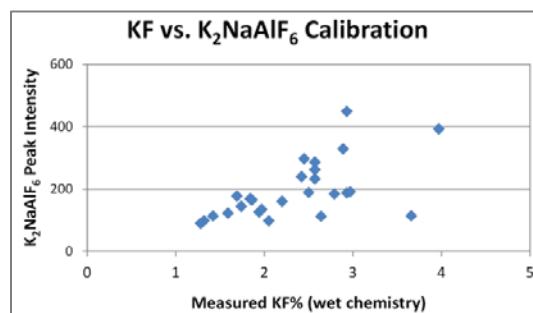

Figure 2. Analysed KF% vs. intensity of K_2NaAlF_6 phase showing the lack of correlation between these two components.

Based on the intensities of cryolite, chiolite, fluorite, Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7, multivariate calibration models for LiF, KF and MgF_2 were formulated based on the Least Squares

Regression method. This method minimises the sum of squared residuals (errors) between model output (e.g. *LiF%* in Equation (5)) and measured values (*Cryolite, Chiolite, etc., the phases' intensities*) by varying the coefficients of the model's input (*A, B, C, etc.*). The simplest form the model can take is the simple linear model shown in Equation (5). In many cases, these phases also interact together and these interactions need to be accounted for. Other terms are then added to the equation as either squares (e.g. *Cryolite²*) or interactions (e.g. *Cryolite*Chiolite*). Equation (6) is an example of the squares and 2-way interaction model.

$$LiF\% = A + B * Cryolite + C * Chiolite + D * Na_2LiAlF_6 + E * K_2NaAlF_6 + F * Na_2MgAlF_7 + G * Fluorite \quad (5)$$

$$LiF\% = A + B * Cryolite + C * Chiolite + D * Na_2LiAlF_6 + E * K_2NaAlF_6 + F * Na_2MgAlF_7 + G * Fluorite + H * Cryolite^2 + I * Chiolite^2 + \cdots + N * Cryolite * Chiolite + P * Cryolite * Na_2LiAlF_6 + \cdots \quad (6)$$

The comparison between the fitting of the simple linear model and the squares, 2-way interactions for KF% calibration is shown in Figure 3. The model based on the regression with squares and 2-way interactions resulted in a higher capability to infer the alkali-fluoride content to within 0.03%, i.e. the inferred concentration from the model and the measured concentration differs by only ±0.03%. The 15 terms used in the model to infer the KF% concentration from the intensity are shown in Table III. Clearly, the simple linear model is easier to formulate but its precision may be limited. Similarly, while the more complex model with squares and 2-way interaction is more precise, the data can be over-fitted and hence its applicability may also be limited. Regardless of which model to use, this result shows that it is possible to infer the content of alkali-fluorides in a bath sample through an XRD method. Hence, a more accurate analysis of $xsAlF_3$ and CR through XRD method is possible.
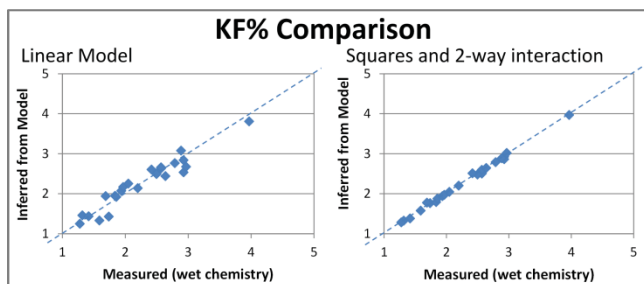

Figure 3. KF% comparison between wet chemistry analysis and inferred from the model based on in-house calibration samples, [Left] linear model and [Right] squares and 2-way interaction.

Model Validation with Industrial Samples

A set of industrial samples was used to validate the applicability of the models formed using the in-house calibration samples. This was conducted by measuring the intensity of different phases and then inputting these intensities into the model. The LiF, KF and MgF_2 contents of these samples were also analysed independently for comparison.

Unfortunately, neither calibration models (linear nor with squares, 2-way interaction) based on the in-house calibration samples were compatible with the industrial bath samples. The inferred alkali-

fluoride contents matched poorly with independent wet chemistry analysis results, as shown in Figure 4.

Table III. Terms and coefficients used to infer the KF% concentration from the in-house calibration samples.

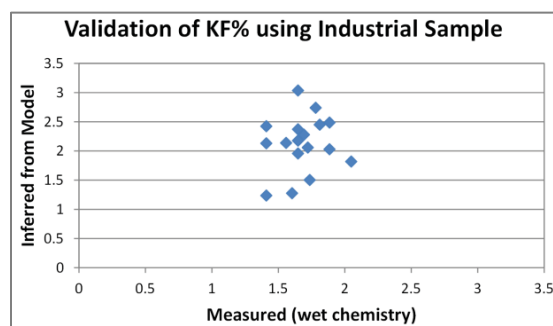| Coefficient	Term	Coefficient	Term
0.0042	Chiolite	$-3.04*10^{-6}$	Chiolite*Cryolite
-0.0026	Cryolite	$9.05*10^{-6}$	Chiolite*CaF_2
$6.05*10^{-4}$	Na_2LiAlF_6	$-3.71*10^{-4}$	Cryolite*K_2NaAlF_6
0.013	K_2NaAlF_6	$-1.61*10^{-6}$	Cryolite*Fluorite
0.0023	Fluorite	$-4.53*10^{-6}$	Na_2LiAlF_6*K_2NaAlF_6
$-1.56*10^{-6}$	$Chiolite^2$	$-1.34*10^{-6}$	Na_2LiAlF_6*CaF_2
$1.02*10^{-6}$	$Cryolite^2$	$-2.91*10^{-6}$	K_2NaAlF_6*Fluorite
$6.12*10^{-7}$	$Fluorite^2$		

Figure 4. Model validation with industrial samples, showing lack of agreement between the measured and inferred KF%.

As mentioned earlier, the in-house calibration samples were made by melting of the synthetic samples without electrolysis. The Li, K and Mg components in the bath were also added in the form of pure LiF, KF and MgF_2 rather than impurities from alumina. Furthermore, the sampling techniques employed were different, resulting in possible variation in cooling rate and cleanliness of bath (i.e. presence of carbon dust [10]). These factors may contribute to the observed difference between the in-house calibration model and the industrial samples. Hence, it was concluded that any practical calibration model needs to be formed based on industrial bath samples for it to be compatible.

Formation of Calibration Models based on Industrial Samples

Calibration models based on industrial samples were formulated in the same manner as for the in-house calibration samples, i.e. obtaining bath samples, scanning of intensity, independent analysis of LiF, KF and MgF_2 contents and fitting them into a multivariate model using the Least Squares Regression method. Two sets of samples were obtained on two different occasions, in the space of a few months. The model was formulated using one set of samples (Set 1) and validated with the other set (Set 2). The fluoride-alkali concentration range of Sets 1 and 2 is shown in Table IV.

Table IV. Alkali-fluoride concentration range of Set 1 and Set 2.

	%LiF		%MgF₂		%KF	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
Min	2.90	3.42	0.55	0.58	1.41	1.28
Max	5.18	5.15	1.15	1.09	2.05	2.21

Mixed results were observed during validation. The model was able to infer accurate LiF, KF and MgF_2 contents in one portion of the samples, while other samples lay outside predicted accuracy limits despite being within the concentration range of Set 1 used to formulate the model. In some samples, intensities of some of the phases were observed to lie outside the range measured in Set 1, even though the concentration of the alkali-fluorides was similar. There are few possible causes of this. The two sets of samples might have been sampled and/or analysed differently. This may include different cooling rates of samples, manual methods of sample preparation that have low repeatability and reproducibility (major influence to the precision of the model, see next section), and drifting of the XRD machine (X-ray source decaying over time) that has not been taken into account in the model formulation. Another possibility is that the chemistry of the bath has moved sufficiently between the two sets that the composition of phases forming is slightly different. This, however, should have been accounted for by the interaction in the model, as long as the samples are within the boundaries of the model. Using Set 2 as the calibration samples to formulate the model and Set 1 to validate yielded similar results.

Due to the time constraints and limitations identified throughout this work, especially the manual pressing that produce a wide range of intensity measurements (see later section), it was not possible to carry on the work to develop a more stable model based on these two sets of samples. Ideally, an automatic grinding and pressing system should be used for sample preparation to ensure the intensity measurement as the input data for the model is reliable and consistent, however, it was not possible for the smelter to obtain one. Therefore, it was decided that monthly average wet chemistry analyses of LiF, KF and MgF_2 would be used for each pot section to improve the $xsAlF_3$ and CR analysis. Equation (3) and (4) can still be used to calculate the updated $xsAlF_3$ and CR.

Further Challenges Identified in XRD Bath Analysis

Several challenges were identified along the way, some of which still require further study. These challenges are elaborated below.

Overlapping of Phases at 2θ Region of Interest

The recommended 2θ scan angles for Na_2LiAlF_6 and Na_2MgAlF_7 peaks overlap with a minor peak of cryolite and a major peak of $Na_2Ca_3Al_2F_{14}$, respectively, as shown in Figure 5 (continuous line represents conventional bath samples without any or very low level of modifiers; dotted line represents complex bath samples with high level of modifiers). Despite these overlaps, these scan angles were recommended as stand-alone peaks for both Na_2LiAlF_6 and Na_2MgAlF_7 phases could not be found. The overlapping of Na_2MgAlF_7 and $Na_2Ca_3Al_2F_{14}$ peaks can lead to inaccurate analysis when using peak intensity-based XRD methods in samples where $Na_2Ca_3Al_2F_{14}$ is present as a result of bath samples' cooling rate.

Furthermore, the 2θ position for the highest Na_2LiAlF_6 peak can shift anywhere within the recommended 2θ area, as shown in Figure 6. This again will lead to inaccuracies in the XRD analysis if the intensity measurement is conducted at the incorrect part of the peak (e.g. at the shoulder instead of at the maximum point of the peak). For an accurate representation of the peak, this wide area needs to be scanned to find the top of the peak before the

intensity measurement should be conducted. However, this will require more analysis time per sample.
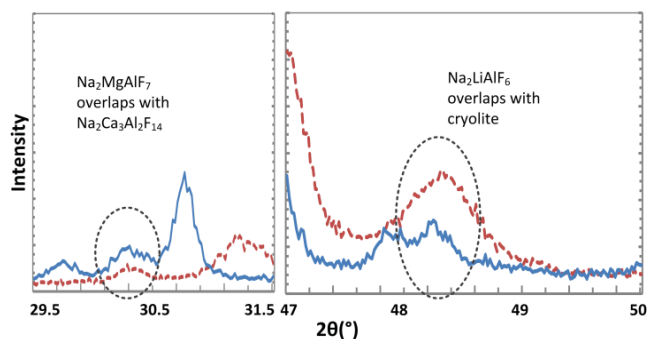

Figure 5. Overlapping of phases in the 2θ region recommended for Na_2MgAlF_7 and Na_2LiAlF_6 intensity determination. Dotted line: high modifiers bath. Continuous line: conventional bath.
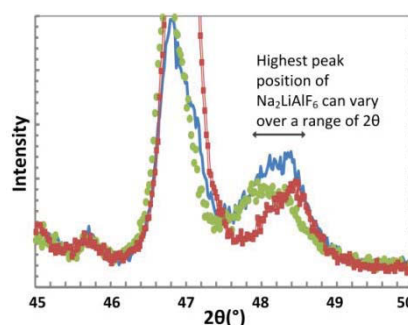

Figure 6. The position of Na_2LiAlF_6 phase of three different samples, showing that the highest peak position can vary over the range of recommended 2θ scan angles.

Total Calcium as Measured by XRF

The total calcium (expressed as CaF_2) as measured by XRF was observed to be higher compared to that analysed by wet chemistry analysis, as shown in Figure 7. This discrepancy was thought to be attributed to the presence of potassium in the bath. Mitall et al. [11] mentioned the difficulty in determining calcium and potassium content in plant samples containing both elements due to the magnified matrix effects (enhancement and absorption). This phenomenon may also be the cause in this instance, i.e. the higher potassium content in the sample enhances the x-ray of calcium present in the sample, resulting in overestimation of measured total calcium, especially if the original calibration samples for calcium do not contain any potassium. Hence, the higher the potassium content in the bath, the higher the total calcium that will be measured by XRF. This is illustrated in Figure 7 by the higher XRF measurement of CaF_2 of Set 2 compared to Set 1, although the average CaF_2 content in both sets, as measured by wet chemistry, is similar.

This situation will lead to another inaccuracy in the $xsAlF_3$ and CR analysis. As shown in Equations (1) and (3), the Ca-cryolite contribution to $xsAlF_3$ is measured from the *CaFactor*(CaF_2-Fluorite)* term. Hence, the higher the *(CaF_2-Fluorite)* component, the higher the estimated $xsAlF_3$ will be, resulting in the pot being perceived as operating with higher acidity than it actually is. A new calibration for total calcium will need to be formed to take the potassium content into consideration.
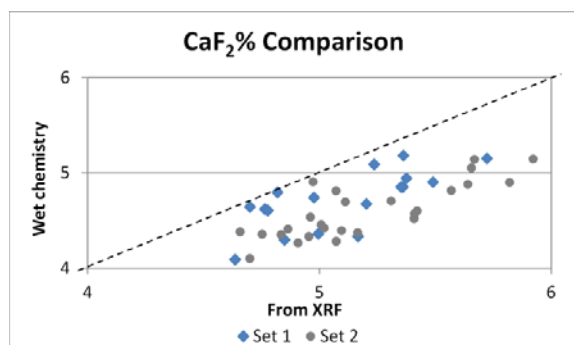
Figure 7. CaF$_2$% comparison between wet chemistry analysis and XRF. The average KF content of Set 1 and Set 2 are 1.68% and 1.83%, respectively.

Repeatability and Reproducibility

As the xsAlF$_3$ and CR analysis is based solely on intensity scans of different diffraction peaks, sample preparation for the analysis is highly important. This sample preparation includes bath sampling, grinding and pressing of the powdered sample for XRD. A simple reproducibility study was conducted in a smelter that was not equipped with an automatic press for sample preparation. The study involved the pressing of two different samples manually by three different operators. XRD intensities obtained were then used as input data for one of the models above to infer the content of LiF, KF and MgF$_2$, which in turn used to measure the xsAlF$_3$ and CR. Table V shows the results.

Table V. A simple reproducibility study on the manual pressing of powdered samples based on two samples and three operators. *Actual* refers to the wet chemistry analysis results and *Inferred* refers to XRD analysis by peak intensities method.

Sample	Opera-tor	Inferred/Actual (%)			xsAlF$_3$	CR
		LiF	KF	MgF$_2$		
A	1	3.87	2.40	0.35	6.67	2.46
	2	3.89	2.30	0.60	6.99	2.44
	3	4.48	2.25	0.82	7.88	2.37
	Actual	4.47	2.04	0.75	-	-
B	1	3.45	1.65	0.85	9.75	2.26
	2	3.25	1.47	0.82	9.46	2.28
	3	3.35	1.44	0.90	9.66	2.26
	Actual	3.27	1.41	0.85	-	-

The standard deviation of CR based on the three measurements was 0.047 and 0.011 for sample A and B, respectively. The standard deviation of sample A is in the range that may well exceed the allowable standard deviation or specification limits used for control of CR. This can result in false triggers for process control actions, e.g. a bath sample is actually at target CR, but is analysed to be at least one standard deviation away from target due solely to the variation from sample pressing and resulting in an incorrect adjustment of AlF$_3$ additions to the cell.

Although this simple study did not fully assess the reproducibility and repeatability of the entire bath chemistry analysis system at the smelter, it did illustrate the need of a more consistent system with regards to sample preparation. Manually prepared powder samples using cavity slides have been cited as having poor accuracy [1]. The best quality analytical surfaces and most reproducible material densities sample are instead produced by pressing powdered samples into briquettes. Hence, an automatic grinding and pressing system will greatly aid in achieving a better control over the uniformity of the pressed samples compared to a manual system. However, obtaining an automatic pressing system can require significant capital investment, which may not be possible. In this case, a more complete repeatability and reproducibility study of the entire sampling and sample preparation system needs to be conducted and the tolerance around control limits for process control needs to be adjusted to reflect the capability of the analysis system.

Limitations of xsAlF$_3$ Calculation

Although Equation (3) takes into account the extra contribution of LiF, KF and MgF$_2$ to xsAlF$_3$, it assumes full reaction of these modifiers with AlF$_3$ and cryolite to produce Na$_2$LiAlF$_6$, K$_2$NaAlF$_6$ and Na$_2$MgAlF$_7$, respectively. This assumption may not be true for samples with very low levels of xsAlF$_3$; such samples might be termed as having 'insufficient xsAlF$_3$' for a complete reaction with these alkali-fluorides. For such samples, a minimum xsAlF$_3$ will instead be calculated based on these alkali-fluoride, chiolite and Ca-cryolite concentrations, resulting in an overestimation of 'actual' xsAlF$_3$ presents in the bath, as illustrated in Figure 8.
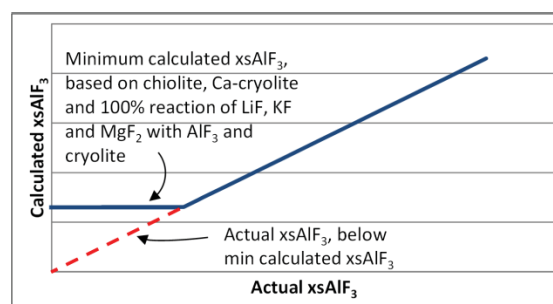

Figure 8. Illustration of the difference between calculated xsAlF$_3$ and actual xsAlF$_3$ in the 'insufficient xsAlF$_3$' sample.

For control purposes, an accurate CR measurement is required so that a correct AlF$_3$ addition can be prescribed for the pot. An overestimation of xsAlF$_3$ as mentioned above will lead to higher CR measurement than actual. This is likely to mean that less AlF$_3$ will be prescribed, which can result in a slower response for the CR of a pot to return to target range.

Currently, it is not possible to assess the degree of reaction between these alkali-fluoride, AlF$_3$ and cryolite in the 'insufficient xsAlF$_3$' scenario. Any "excess" Li, K and Mg could solidify as other phases or "hide" in the interstitial site of other phases, which are not detectable by XRD, especially in the peak intensity-based XRD technique.

Discussions

The process to develop a model to relate the alkali-fluoride concentration to the different phase intensities is relatively straight forward, as shown in this paper, but the model is only as accurate as the data set used to formulate it. The many challenges identified above, especially the low reproducibility of the manual pressing of the powdered samples, highly contribute to the limited accuracy and applicability of the developed model.

Apart from overcoming the challenges mentioned above, periodic assessment and calibration procedure of the model needs to be developed and included in the running of the laboratory. This is to ensure that the model is still valid for the range of bath samples present in the smelter and identify when re-calibration is required should the concentration falls outside of the calibration range. The drifts from the machine itself will also need to be incorporated into the model. Since the completion of this work, the smelter has had an increase in the concentration of these modifiers.

A standardless method of fast detection XRD with Rietveld analysis capability has many advantages compared to the peak intensity calibration method. It is seen as applicable for all types of bath and capable of producing the same result, regardless of the operator's skill. The method is also independent of equipment, machine drifts and samples properties [1], which will solve some of the challenges mentioned above. However, for this method to be applicable for complex bath chemistries, it needs to be able to identify and account for all the phases present in the bath, including the possibility of "excess" Li, K and Mg that may be hiding in the interstitial site of other phases in the 'insufficient $xsAlF_3$' sample, as mentioned above. To the knowledge of the authors, the literature available on Rietveld analysis for complex bath chemistry is still very limited.

The method proposed in this paper, although it has yet to reach the state where it can be applied in the smelter, has the potential to revolutionise the way complex bath chemistries are analysed as part of the day-to-day running of a smelter. Further understanding into this complex bath system is evident from this study and given more time, it is possible to develop a more stable calibration model. The success of this development will enable the following:

- Ability to identify and track changes in modifiers content as part of the routine bath sample analysis (i.e. no other analysis is needed to measure the content of Li, K and Mg).
- Provide an analysed CR that reflects changes in the modifiers content over time, giving the possibility of changing AlF_3 target to maintain operating temperature.
- Provide better correlation between temperature and $xsAlF_3$ or CR to allow for multivariate control of pot heat balance.

Conclusions

The approach for relating intensities of marker phases (chiolite, cryolite, fluorite, Na_2LiAlF_6, K_2NaAlF_6 and Na_2MgAlF_7) as measured by XRD to the LiF, KF and MgF_2 concentration present in the bath through the Least Squares Regression method is presented in the paper. This method, especially the squares and 2-way interaction model, was highly capable to define the relationship between intensities and modifier concentrations for any single set of samples. However, this relationship was not necessarily valid in inferring the modifier concentrations of other sets of samples. Factors associated with different sets of samples include possible variation in sampling preparation, low reproducibility of the pressing of samples and changes in bath chemistry between different sampling periods that alter the composition of phases formed. Before the analytical method can be developed further, consistent sample preparation is essential to ensure that the marker phase intensities obtained for samples are accurate, repeatable and reproducible.

As the concentration of these alkali-fluorides can vary over time, the re-calibration process needs to be made as simple as possible so that the smelter can perform this process quickly every time these concentrations fall outside of the calibration window. Simple linear models are certainly easier to formulate but their precision may be limited. The more complex models with squares and 2-way interactions may offer higher precision, but can be over-fitted, hence its applicability may be also be limited. Although the work has yet to reach the state where LiF, KF and MgF_2 levels are measurable through XRD, it has undoubtedly provided further understanding into this complex bath system.

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