Advantages in use of the MVR method in the XRD bath acidity analysis

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Introduction

Hydro is a global supplier of aluminium and aluminium products. Based in Norway, the company employs 19,000 people in 40 countries and has activities on all continents.

Hydro operates one of the industry's leading research centres in Årdal

Typical Bath Composition

Aluminium is produced in the electrolytic reduction of alumina (Al_2O_3)

The electrolyte, consisting of:

- Cryolite (Na_3AlF_6) – approx. 80 wt%

Pure cryolite melts at about 1010 ^oC, so additives are used to lower the melting point:

- Aluminium Fluoride (AlF_3) – 8-13 wt%
- Calcium Fluoride (CaF_2) – 4-7 wt%

Bath temperature can be 955-965 ^oC during normal cell operation.

Sampling – 960°C Bath

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Sampling Tongs

Sampling – Cooling Sample

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Sampling – 21 gram Sample

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Crystallized phases that can be formed during cooling electrolyte bath sample

- Cryolite (Na_3AlF_6)
- Chiolite ($Na_5Al_3F_{14}$)
- 2 Calcium Cryolites ($NaCaAlF_6$, $Na_2Ca_3Al_2F_{14}$)
- Fluorite (CaF_2)
- Sodium Fluoride (NaF)
- Alumina (Al_2O_3)
- Aluminium Fluoride (AlF_3) - is in chiolite and the two Ca-cryolites

Why bath analysis is important ?

Bath acidity analyses are performed to control fluoride content.

The electrolyte acidity (amount of AlF_3 in excess of cryolite) can be expressed:

$$Excess\ AlF_3, the\ mass\%\ AlF_3\ in\ excess\ of\ the\ Na_3AlF_6\ composition$$

$$BR = \frac{weight\ NaF}{weight\ AlF_3} \qquad CR = \frac{mole\ NaF}{mole\ AlF_3}$$

Basic melt: Excess AlF_3<0 CR>3.0

Acidic melt: Excess AlF_3>0 CR<3.0

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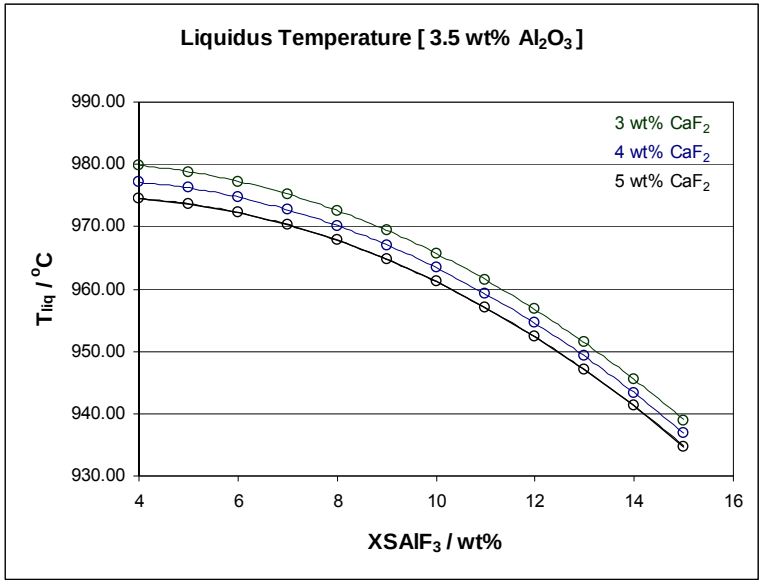
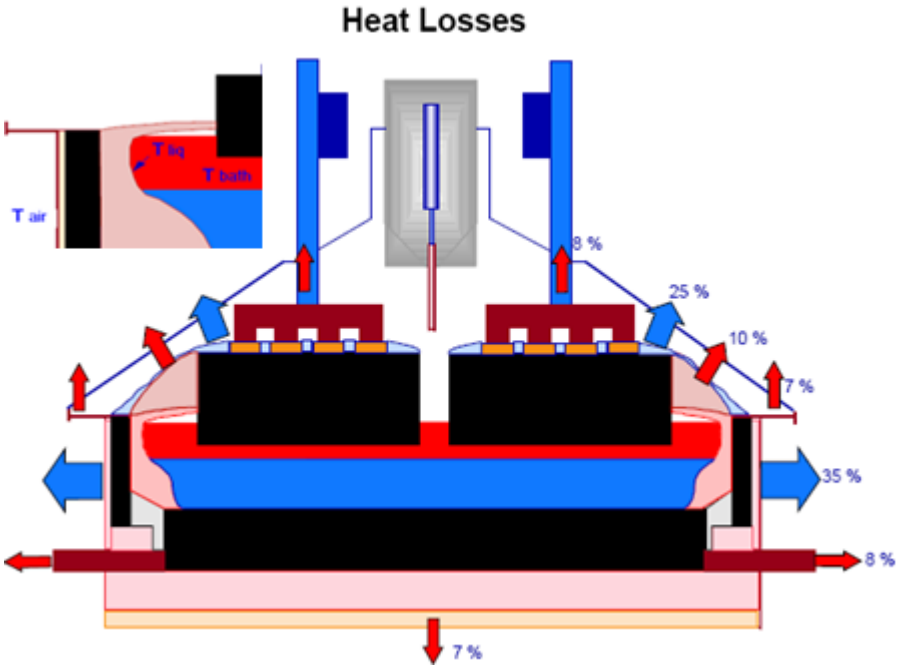
Why bath analysis is important ?

How can the $XSAlF_3$ value contribute to monitor the process ?

- Change T_{liq} → Increase operating temperature → Unstable side ledge thickness



Solheim, A., Rolseth, S., Skybakmoean, E., Støen, L., Sterten Å., Støre, T., Metall. Matter. Trans. B, 27B,739 (1196)



Kavnde, H., Slåttavik, A., Heat Balance in Aluminium Electrolysis BathTemperature and Superheat, Hydro Aluminium Primary Metal

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CURRENT BATH ACIDITY ANALYSIS

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Potflux method (routine analysis)

Hydro certificate up to 17 wt%, measured on:

Chiolite and Fluorite by XRD and total Ca as CaF_2 by XRF (CaF2XRF)

$XSAlF_3$ = Chiolite + CaFactor * (CaF2XRF-Fluorite)

Assumptions:

- Acidity is bound in chiolite and Ca-cryolites
- Calcium and chiolite calibration is linear
- CaFactor is constant 0.53
- Fluorite measured if chiolite < 3.0 wt%

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Low-Acidic (start-up cell)

Range of measurement: Bath acidity <5.0 wt%

Chiolite, Calcium (CaF2XRF), Fluorite, 2 Ca-Cryolites, Sodium Fluoride

Assumptions:

- Acidity is associated with chiolite, Ca-Cryolites, NaF or calcium
- For all phases calibration is linear
- The difference between calcium (XRF) and calcium bound in detectable phases is bound as $NaCaAlF_6$, and the associated bath acidity is determinated with a CaFactor of 0.717

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MULTIVARIATE REGRESSION

BATH ACIDITY ANALYSIS

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Multivariate Regression Principle

The MVR equations in XRD application represent relations between more than one variable e.g. calcium and chiolite, and value of interest which is bath acidity (Excess AlF_3 wt%)

Example for Routine range:

Excess AlF_3 = 0.002224*Ca+0.01280*Chio-1.334

(Some more details on MVR will be given)

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Multivariate Regression Principle

Most bath samples would have three or two important phases only.

Therefore it is possible to divide measurements into acidic ranges:

routine, low acidic, basic.

The programming algorithm can distinguish between different acidic ranges and only required phases for the range are measured.

This saves time.

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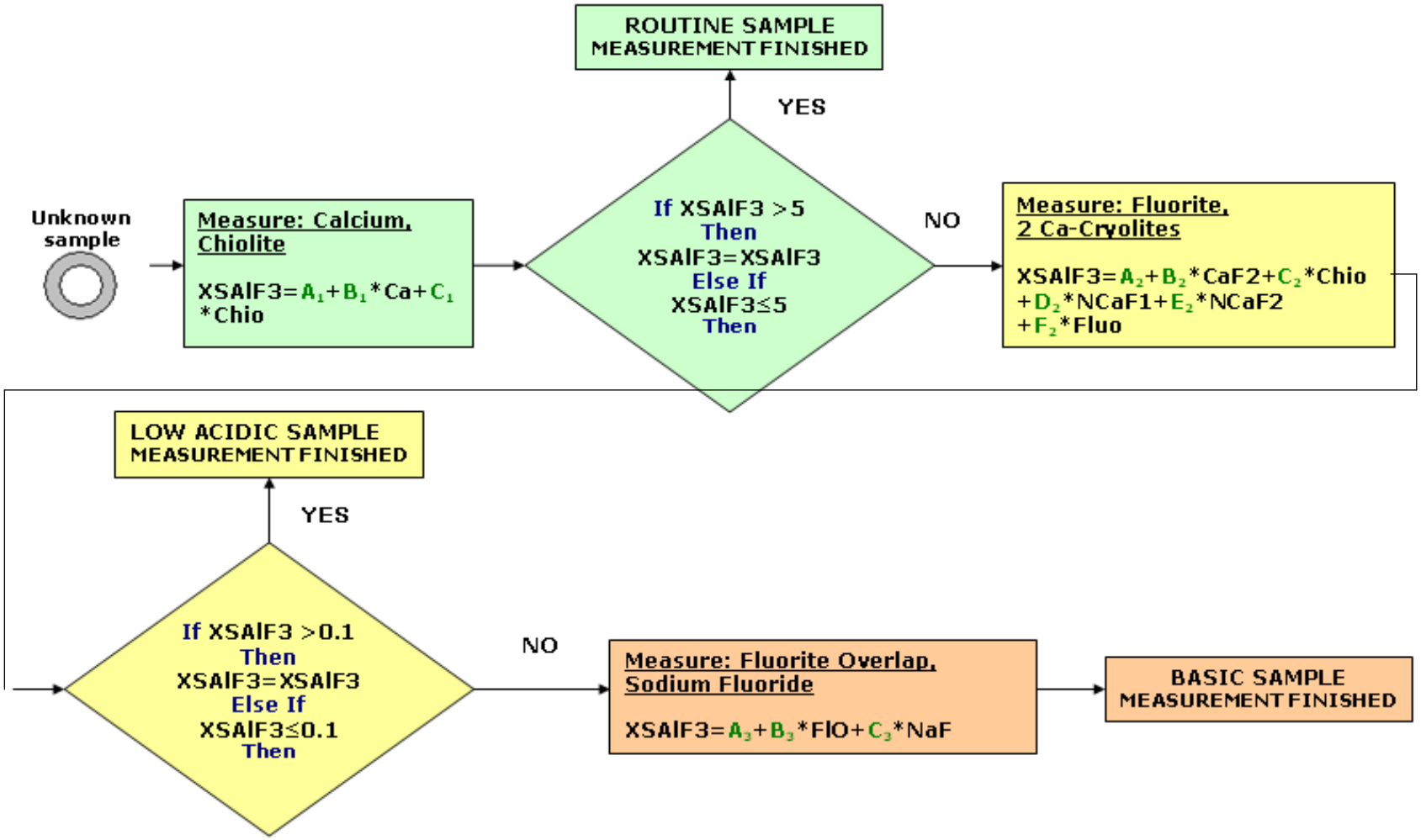
Idea behind Programming Algorithm



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MVR Method Advantages

Reduced time spent on measurements

- Only significant phases for the acid range are measured.
- Analysis can be performed over the full range of Acid and Basic bath without changing programs.

Improved standard error for calibration

- Segmented approach to calibration
- The method uses more sample information to compensate for varying bath sampling cooling rates by including two Calcium Cryolites phases.

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MVR Method Advantages

Accuracy Improvement – Round Robin measurements 2008

The RR analysis material set for routine bath – ten cells with three splits from each

XSAlF3 Instrument average compared to Grand Average and Acceptance Limits –routine bath analysis

	Average	Grand Aver	_accep	U_accep	NOM_LCL	NOM_UCL
Ardal-MVR CubiX HAL_BA	**11.45**	11.26	**11.01**	**11.51**	11.17	11.35
Ardal-MVR CubiX HAL_BA	**11.43**	11.26	**11.01**	**11.51**	11.17	11.35
Kurri-MVR XRD HAL_BA	**11.45**	11.26	**11.01**	**11.51**	11.17	11.35
Kurri-MVR XRD HAL_BA	**11.48**	11.26	**11.01**	**11.51**	11.17	11.35
Karmoy Line1 HAL_BA01	**11.07**	11.26	**11.01**	**11.51**	11.17	11.35
Karmoy Line2 HAL_BA01	**11.13**	11.26	**11.01**	**11.51**	11.17	11.35
Kurri CubiX HAL_BA-MVR	**11.42**	11.26	**11.01**	**11.51**	11.17	11.35
Kurri 9900XP HAL_BA26	**11.49**	11.26	**11.01**	**11.51**	11.17	11.35
Sunndal CubiX1 HAL_BA	**11.20**	11.26	**11.01**	**11.51**	11.17	11.35
Sunndal CubiX2 HAL_BA	**11.15**	11.26	**11.01**	**11.51**	11.17	11.35
Ardal CubiX HAL_BA26	**11.21**	11.26	**11.01**	**11.51**	11.17	11.35
Ardal CubPRO HAL_BA26	**11.26**	11.26	**11.01**	**11.51**	11.17	11.35
Slovalco PW18 HAL_BA2	**11.42**	11.26	**11.01**	**11.51**	11.17	11.35
	#N/A	11.26	**11.01**	**11.51**	11.17	11.35

Accuracy level is indicated by the close agreement of averages

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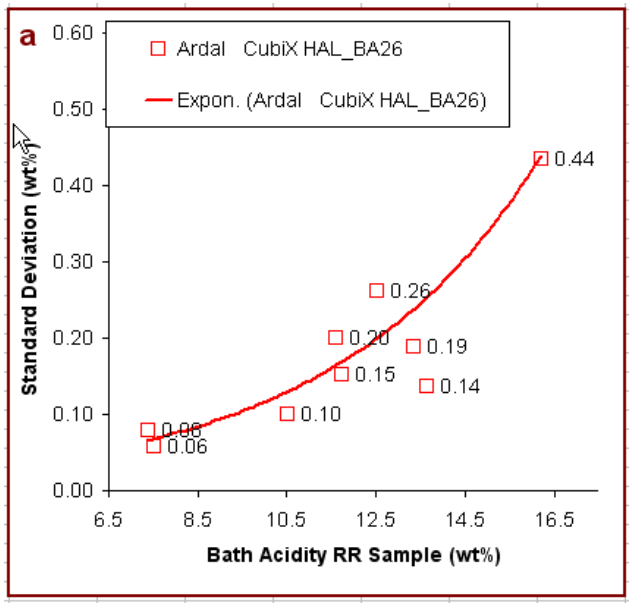
More Precision Improvement –PeakXRD vs. AreaXRD command

MVR application uses AreaXRD command instead of PeakXRD command used in Potflux and Low Acidic methods.

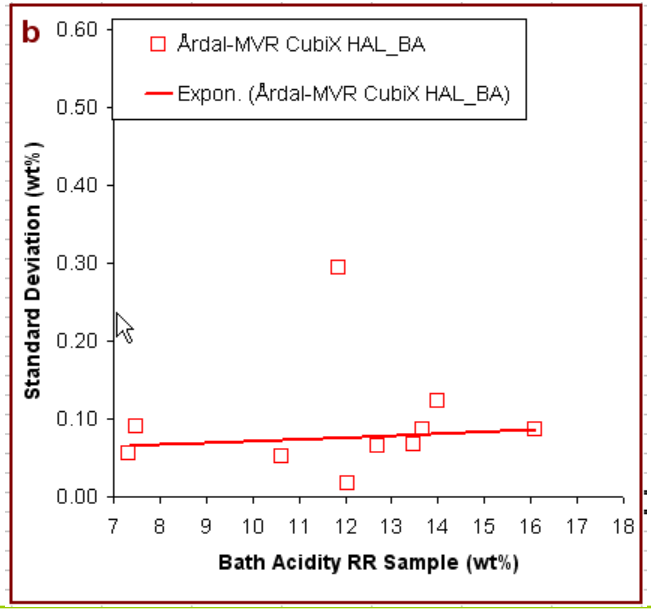
The use of AreaXRD command provides better precision and lower calibration standard error than the PeakXRD command

Standard deviation vs. bath acidity per instrument, 2007 Round Robin

Potflux (PeakXRD)



MVR (AreaXRD)



Establishing HAL_MVR in other laboratories

MVR is similar to current Hydro procedures

It uses the same standard sets and monitors as the current Low Acidic and Potflux applications.

However

For laboratories that are using X'Pert Industry software (PANalytical) some small change might be needed in programming due to different software versions (e.g. MAXXRD↔XRDMAX).

Laboratories not using XPI may experience problems with translating MVR algorithm into their instrument ? This has not been done yet.

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Summary

Multivariate Regression method in XRD bath analysis:

- Combines use of two applications (Potflux and Low Acidic) into one
- Improves measurement precision over the whole analytic range
- Saves analysis time thanks to measuring only necessary phases for the defined acidic range
- Is economic and simple to implement in laboratories that are already using X'Pert Industry

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