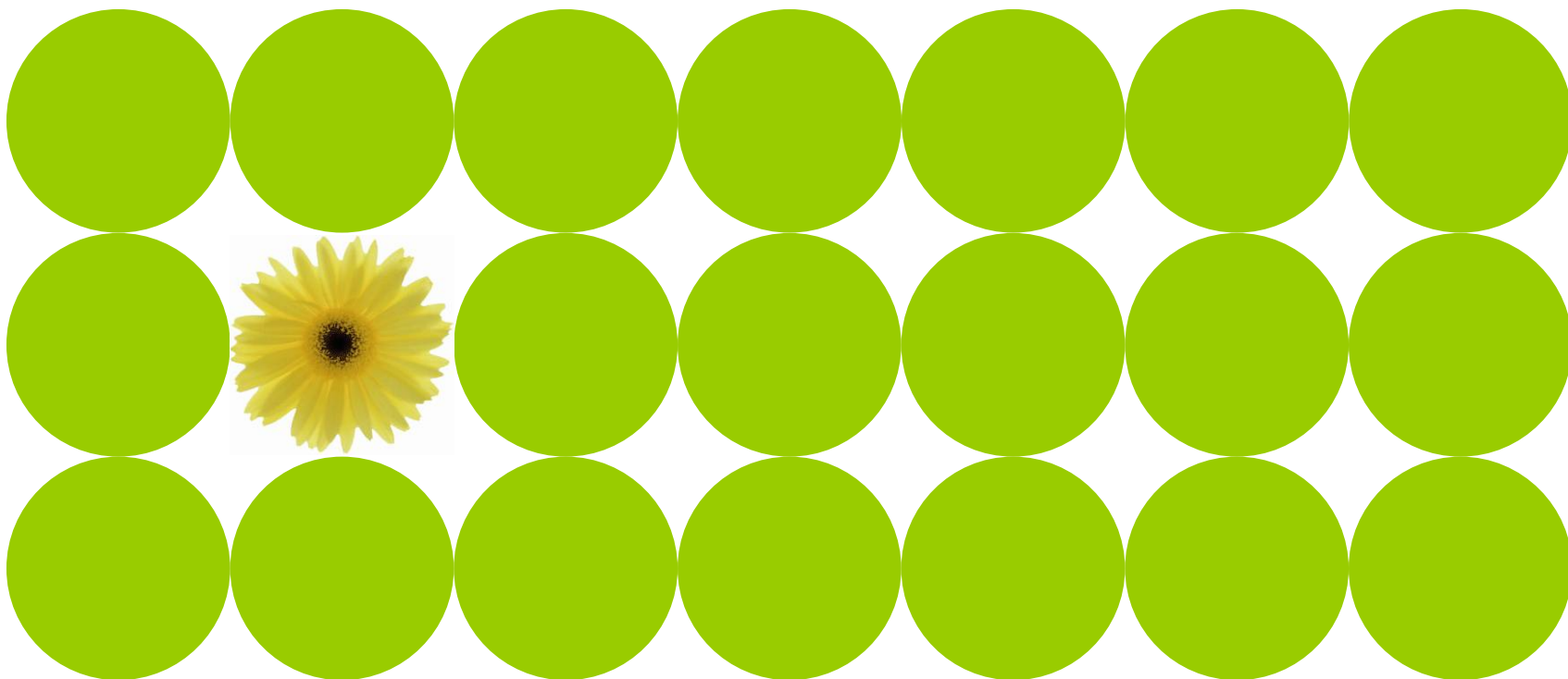


Advantages in use of the MVR method in the XRD bath acidity analysis



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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 °C, 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 °C during normal cell operation.

Sampling – 960°C Bath



Sampling Tongs



Sampling – Cooling Sample



Sampling – 21 gram Sample



Crystallized phases that can be formed during cooling electrolyte bath sample

- Cryolite (Na_3AlF_6)
- Chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$)
- 2 Calcium Cryolites (NaCaAlF_6 , $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$)
- 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

$$BR = \frac{\text{weight NaF}}{\text{weight } AlF_3}$$

$$CR = \frac{\text{mole NaF}}{\text{mole } AlF_3}$$

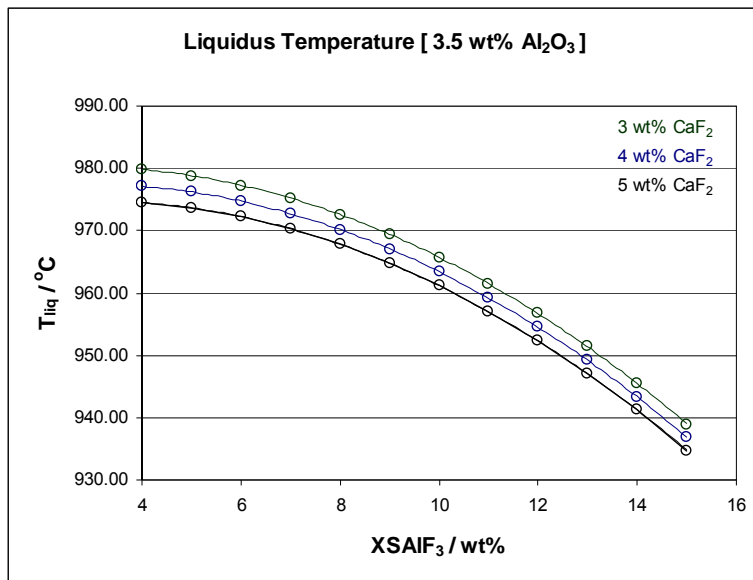
Basic melt: Excess $AlF_3 < 0$ $CR > 3.0$

Acidic melt: Excess $AlF_3 > 0$ $CR < 3.0$

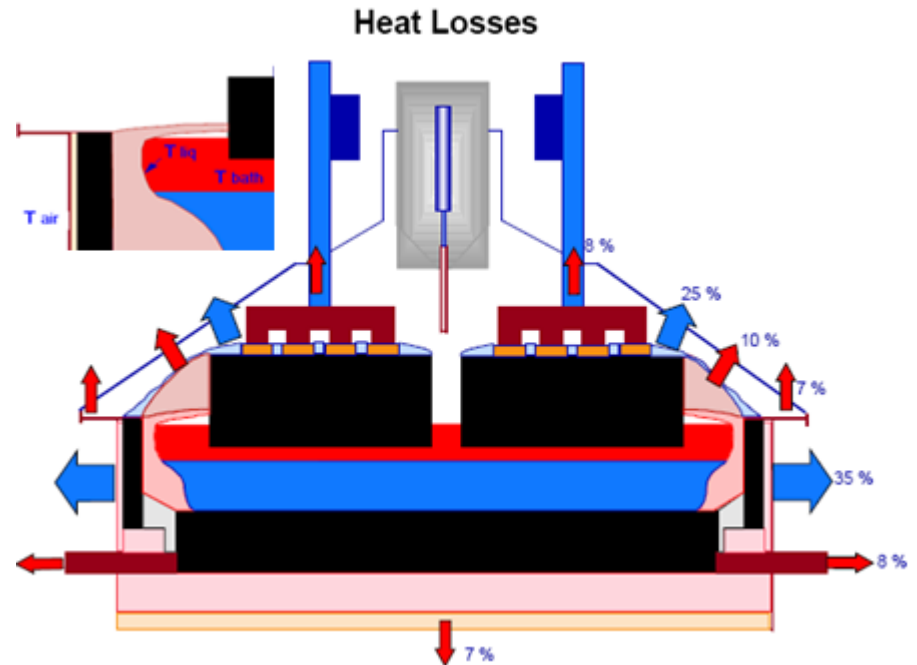
Why bath analysis is important ?

How can the X_{AlF_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
Bath Temperature and Superheat, Hydro Aluminium Primary Metal

CURRENT BATH ACIDITY ANALYSIS

Potflux method (routine analysis)

Hydro certificate up to 17 wt%, measured on:

Chiolite and Fluorite by XRD and total Ca as CaF₂ by XRF (CaF₂XRF)

$$\mathbf{XSAIF_3 = Chiolite + CaFactor * (CaF_2XRF - Fluorite)}$$

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%

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 NaCaAlF₆, and the associated bath acidity is determined with a CaFactor of 0.717

MULTIVARIATE REGRESSION

BATH ACIDITY ANALYSIS

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:

$$\text{Excess AlF}_3 = 0.002224 * \text{Ca} + 0.01280 * \text{Chio} - 1.334$$

(Some more details on MVR will be given)

Multivariate Regression Principle

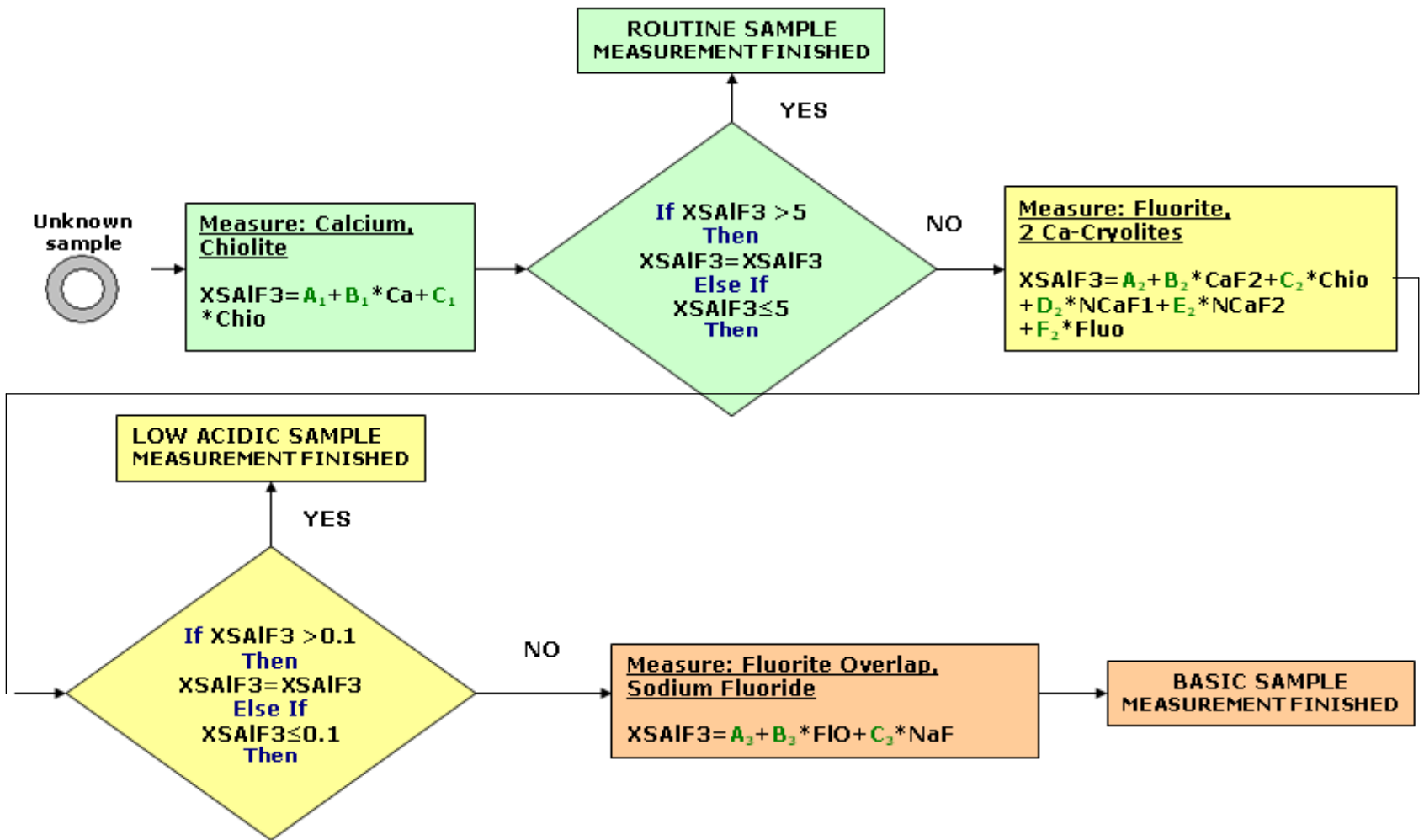
Most bath samples would have three or two important phases only.

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.

Idea behind Programming Algorithm



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.

MVR Method Advantages

Accuracy Improvement – Round Robin measurements 2008

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

XSAIF3 Instrument average compared to Grand Average and Acceptance Limits –routine bath analysis

	Average	and Average	Acceptance	Acceptance	NOM_LCNOM_UCL	NOM_UCL
ArdalMVR CubiX HAL_BA	11.45	11.26	11.01	11.51	11.17	11.35
ArdalMVR 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 CubiX 1 HAL_BA01	11.20	11.26	11.01	11.51	11.17	11.35
Sunndal CubiX 2 HAL_BA01	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_BA21	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

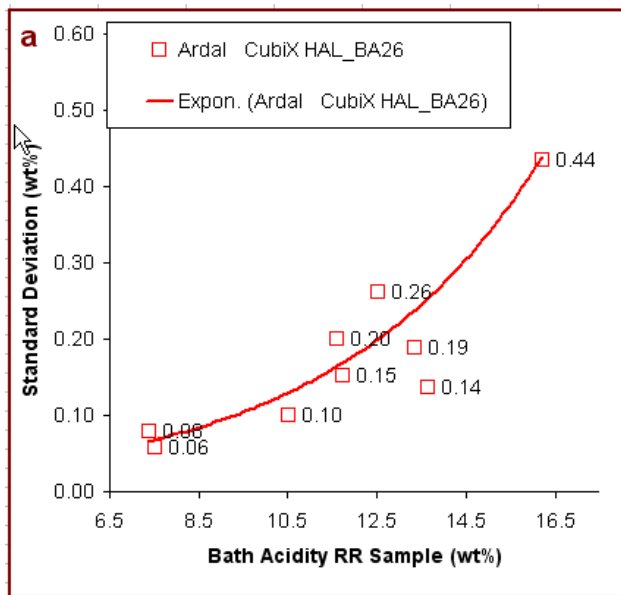
More Precision Improvement –PeakXRD vs. AreaXRD command

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

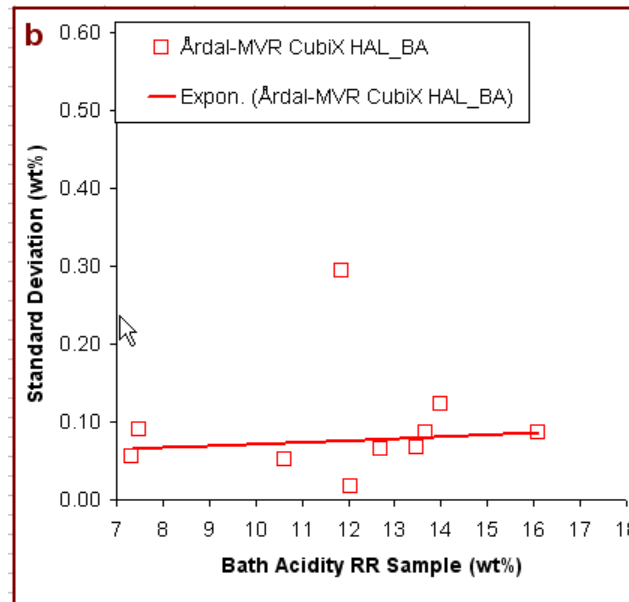
The use of AreaXRD command provides better precision and lower calibration standard error than the PeakXRD command

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.

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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