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# THE EQUIVALENT TEMPERATURE METHOD FOR MEASURING THE BAKING LEVEL OF ANODES

Lorentz Petter Lossius, Inge Holden, Hogne Linga
Hydro Aluminium a.s Technology & Operational Support, P.O.Box. 303, NO-6882 Øvre Årdal, Norway

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## Abstract

The equivalent temperature is a measure of baking level using a temperature scale (°E) based on heat treatment temperatures.

The method has been established as an ISO method, ISO 17499: "Carbonaceous materials used in the production of aluminium — Determination of the baking level expressed by the equivalent temperature". The background for the ISO method is described, including the 2003 round robin for determining the precision which resulted in a repeatability of 9 °E and reproducibility (between laboratories) of 14 °E in the range 1050 to 1400 °E.

The main use is for monitoring anode quality in routine production and for performance testing. Examples will be given from Hydro Aluminium baking furnaces where the method has been in use since 1982 [1,2].

## Introduction

The equivalent temperature is determined by placing a test portion of a reference coke in a graphite holder with a small hole in the lid to secure gas outlet. The holder is sent with the anode through the baking furnace. Following baking the holder is recovered and the now-calcined reference coke is analysed with regard to $L_c$ using ISO [3] or ASTM [4] methods.

A pre-determined calibration curve linking equivalent temperature with the $L_c$ crystallite height is used to determine the equivalent temperature from the measured $L_c$-value.

Figure 1. Storage of used and new 100 mm high holders.

## The ISO Standard Method

In 1998 ISO Technical Committee TC226 "Materials for the production of primary aluminium" decided to establish the principle of the equivalent temperature as a standard method [5].

The precision statement is a critical part of a standard method. The ISO meeting in Rigi, Switzerland, June 2002 initiated the round robin (RR), which was run by Hydro Aluminium in 2002-3. The results were presented to ISO at the meeting in Tromsø, Norway, September 2003.

The standard proposal went through Committee Draft and Draft International Standard votes and was accepted for publication at the ISO[1] meeting in Jeju, Korea, April 2005 as method ISO 17499: "Carbonaceous materials used in the production of aluminium — Determination of the baking level expressed by the equivalent temperature".

## Definition and Calibration

Equivalence

The term equivalent temperature ($T_{eq}$) comes from "level of calcination equivalent with a two hour heat treatment at the temperature". A small (20-gram) portion of a reference coke is calcined in a fast heating and cooling furnace by soaking for 2-hours. The heat treatment temperature is the equivalent temperature. After calcining, the crystallite height measurement ($L_c$) is made, and the ($L_c$, $T_{eq}$) pairs are used to determine a calibration curve, see Figure 2 and Eq. 1 [6].

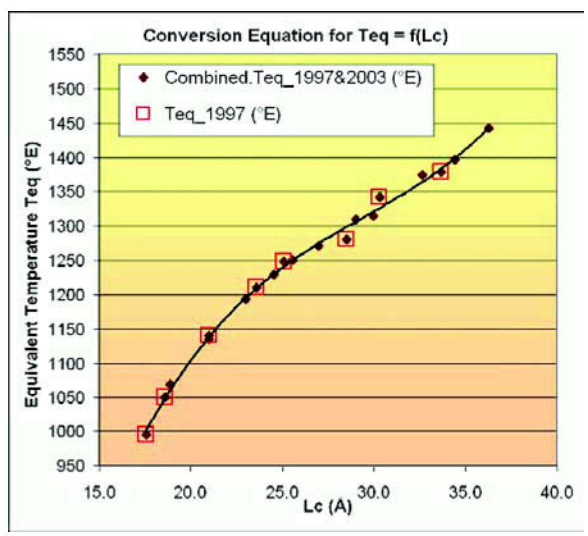


Figure 2. Calibration curve based on ($L_c$, $T_{eq}$) pairs for the reference coke. Two series of 2-hour heat treatments (1997, 2003) have been combined to give the calibration curve.

$$T_{eq} = 0.0812 * L_c^3 - 7.1537 * L_c^2 + 225.16 * L_c - 1187.5 \qquad Eq.1$$

[1] Until 2004 Technical Committee TC226 was TC47, Sub-Committee 7 for "Aluminium oxide, cryolite, aluminium fluoride, sodium fluoride, carbonaceous products for the aluminium industry"

A third order expression fitted the data best. Colin P. Hughes reported a similar behaviour in the 1996 TMS presentation [7].

Figure 3. Tray with samples for x-ray diffraction analysis for $L_c$.

## ISO Round Robin

RR Procedure

The participants are listed in Table 1.

**Table 1**. Participants in the ISO RR for the precision statement.

| Metal Plant | Contact Person |
|---|---|
| Albras Aluminio | Max Heilgendorff |
| Angelsey Aluminium Metal Ltd. | Donna W. Evans |
| Comalco Research and Tech. Support | Dr Alan Tomsett |
| Dubai Aluminium Co Ltd | S. C. Tripathi |
| Elkem Aluminium ANS Research | Turid Vidvei |
| Hydro Aluminium Kurri Kurri Pty Ltd. | Darrell Harman |
| Hydro Aluminium Neuss | Marco Nierfeld |
| Hydro Aluminium Sunndal | Frank Aune |
| Hydro Aluminium Årdal | Kirsti Gulbrandsen |
| R&D Carbon | Stefan Meichtry |
| Slovalco | Jozef Lovcican |

The RR samples consisted of two green petrol cokes, ISO249 (Statoil Mongstad) and ISO250 (Conoco), each heat-treated to eleven baking levels in a large laboratory furnace. Six of the eleven were used as RR standards for the calibration curve; see Table 2, and five as RR unknowns. The equivalent temperature was determined at Hydro Aluminium LSS Årdal using separate $T_{eq} = f(L_c)$ calibrations for each coke.

**Table 2**. Example of RR standards from the ISO249 sample set.

| Sample | Teq Value (°E) |
|---|---|
| M1050 | 1069 |
| M1150 | 1190 |
| M1200 | 1245 |
| M1250 | 1311 |
| M1300 | 1398 |
| M1350 | 1502 |

The $L_c$ analysis was performed according to the standard laboratory practice of each participant. The following requirement was made regarding precision: If one parallel of three was more than ±0.5 Å different from the average it was considered an outlier and a new portion should be milled and analysed. If again one parallel was more than ±0.5 Å different from the average it was considered an outlier and discarded. Then the average of the remaining two was used. All participants used specially distributed, tailored Excel-spreadsheets for calibration and return of results. This simplified the final data-treatment considerably.

Precision Calculation

The precision was determined using ASTM E691 "Interlaboratory Study of Precision Program". With ten participants, ten materials and three parallels for each unknown the round robin more than met the minimum requirements prescribed by ASTM E691 [8].

Result

The precision was

- *Repeatability: r = 9 °E*
- *Reproducibility (between-labs): R = 14 °E*

in the range 1050 °E to 1400 °E. The precision figures were independent of the measured equivalent temperature values as can be inferred from Figure 4 [9].

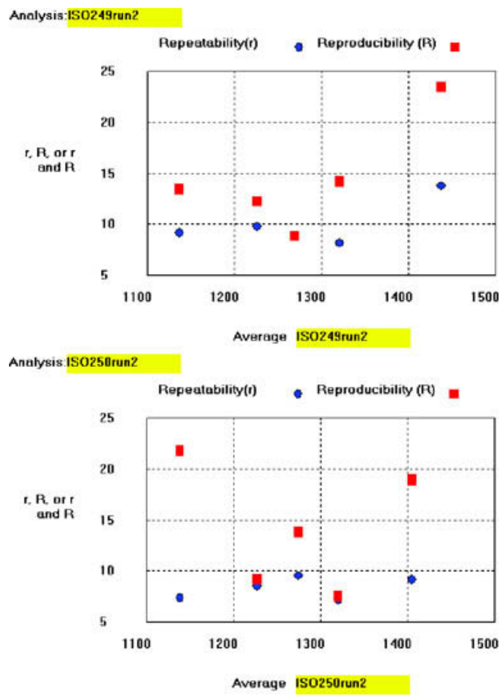


Figure 4. Precision for each of the RR "unknowns" (from E691).

Usage

Repeatability: Given a number of anodes (or test portions) all with equivalent temperature 1200 °E, if measured by the same operator at the same laboratory, the repeatability expresses that 95 out of 100 measurements will be within the range [1191, 1209] °E.

Reproducibility: Given a number of anodes (or test portions) all with equivalent temperature 1200 °E, if measured by different laboratories, the reproducibility expresses that 95 out of 100 measurements will be within the range [1186, 1214] °E.

Discussion

The span of equivalent temperatures tested in the RR was 1050 to 1400 °E. This encompasses the span of normal variation observed for anodes in baking furnaces. The Repeatability (within-lab) was 9°E, and relative to the span of 350°E this is as low as 2.6 %rel, at the 95 % confidence level. This is a very promising result both as regards monitoring anode quality and seeing differences when mapping the baking level in anode furnace sections.

### Using the Equivalent Temperature

The Green Reference Coke

A calibration is unique for a chosen green petrol coke. A substantial amount of green reference coke should be stored. For use in Hydro Aluminium baking furnaces, 12 tons of green 1982 Mongstad coke has lasted 20 years and still 2-3 tons are left.

The reference coke should be a single source petrol coke. Before determining the calibration curve the coke should be dried at 540 °C, crushed to ±4 mm particle size and thoroughly mixed.

Reference Coke Standard Sets

The sets of reference coke are available with Certificate of Analysis; please contact the authors for information. The sets are useful for

- Making it easier to recalibrate
- Starting using analysis of equivalent temperature if a fast heating and cooling furnace is not available
- Starting a new reference coke

**Table 3**. Reference material for a calibration consisting of eleven samples spanning a wide range of equivalent temperatures.

| Standard | Equivalent Temperature, $T_{eq}$ (°E) |
|---|---|
| C1050 | 1061 |
| C1100 | 1138 |
| C1150 | 1195 |
| C1180 | 1230 |
| C1200 | 1250 |
| C1220 | 1275 |
| C1250 | 1306 |
| C1260 | 1321 |
| C1300 | 1364 |
| C1325 | 1399 |
| C1350 | 1443 |

Starting Using the Equivalent Temperature

A reference coke standard set can be used to establish a new reference coke. The following procedure avoids the complex heat treatments with a fast heating and cooling furnace to get the ($T_{eq}$, $L_c$) data pairs. The procedure requires green coke of both the old and new reference cokes.

To get a good calibration twelve pairs of graphite sample holders with old and new green reference coke should be used. The holders are sent pairwise through a baking cycle positioned in a section so as to reflect the entire span of equivalent temperatures expected. Ideally, some pairs should be calcined under controlled conditions to have one low result with $T_{eq}$ of approximately 1050 °E and two high results with $T_{eq}$ in the range 1300-1400 °E, to stabilize the curve fit.

Analysing the pairs of test portions with the calibration based on the reference materials yields ($L_c$, $T_{eq}$) points for the new reference coke via the $T_{eq}$ values determined fro the old reference coke. The calibration equation for the new coke can then be determined.

### Example: Quality Control

As part of routine anode quality follow-up, the equivalent temperature is determined for 1.6 % of the produced anodes. A quality specification is in use, e.g. baking level minimum 1200 °E.

In routine analysis the equivalent temperature calibration is programmed into the x-ray diffractometer application and the result is calculated and uploaded to the product quality database automatically.

### Example: Mapping a Section

After approximately 7 months of operation of the new Årdal Carbon Furnace #3 a comprehensive performance test was carried out. Furnace #3 is a 2-fire, 30-section vertical flue furnace with annual production 105 000 tons of anodes [10]. The sections are 7-pit with totally 168 anodes stacked vertically in three layers.

The baking level distribution was determined for several sections by the equivalent temperature method. Figure 5 and 6 illustrate the baking level in one section vertically by pit and horizontally by anode layer. Pit 1 is the outer pit in the section.

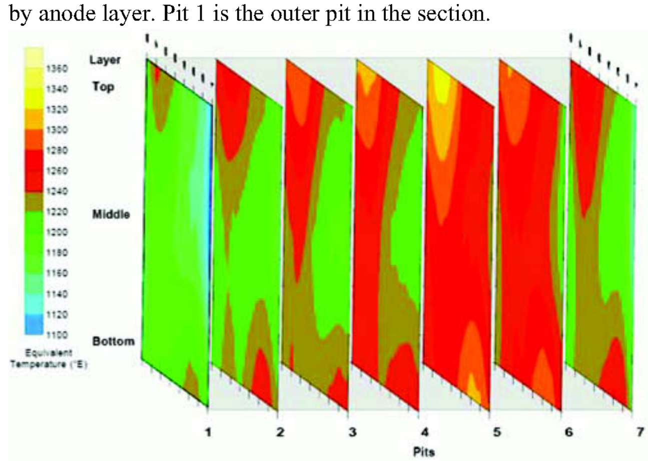


Figure 5. Baking level distribution vertically by pits. The average and standard deviation of the section was $T_{eq}$ = 1236±41 °E.

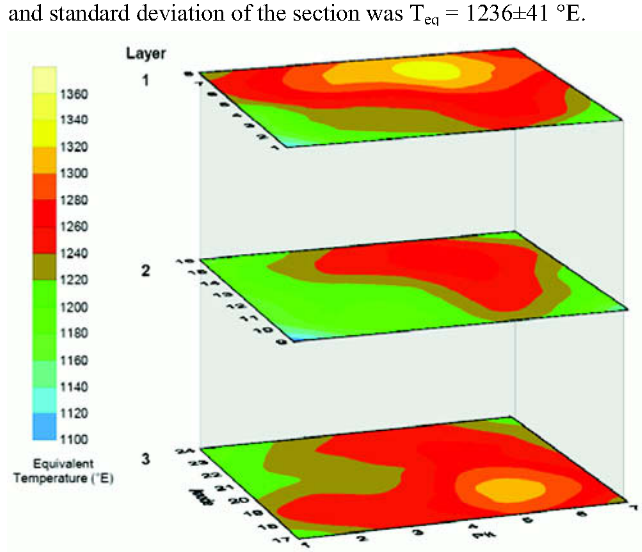


Figure 6. Equivalent temperature distribution by anode layers. Each layer represents 7x8 = 56 anodes.

The plots show that

- The sensitivity of the equivalent temperature method was sufficient for a detailed plot of the balking level distribution
- The baking level along pit five was somewhat higher and the result was useful for tuning the baking through the entire heat treatment including the fire bridge control system

**Example: Position of Sample**

The equivalent temperature sample can be placed in a stub hole or a specially made small depression on the anode. In Årdal Carbon furnaces #3 and #4 anodes are stacked so that the sample is in the centre of the 8-anode pack. A test was run to see if a sample placed toward the pit wall packing coke would show different equivalent temperature level than in the centre of the pit.

In the test an additional reference coke sample was sent with the anode placed in a hole in the anode side. The test comprised 121 anodes. Positioning was random as regards furnace #3 or #4, section, pit or anode layer. Table 4 shows a statistical comparison, and Figure 7 the distribution of values.

**Table 4**. Mean and standard deviation from 121 anodes with equivalent temperature samples in two positions.

| Position | Mean $T_{eq}$ (°E) | StDev $T_{eq}$ (°E) |
|---|---|---|
| Centre of anode stack | 1221.1 | 52.1 |
| Side toward pit wall | 1221.5 | 53.2 |

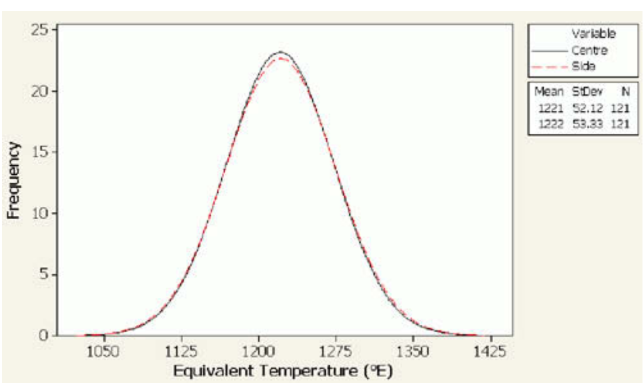


Figure 7. Distribution of two samples in 121 anodes.

A paired t-Test using MiniTab Release 14.13 gave a difference of 0.40 and the confidence interval at 95% confidence level for the two positions being equal was (-4.69; 3.90). This meant

- The equivalent temperature was the same in the anode pack centre and the anode side toward the pit wall packing coke
- The anodes are baked equally all through

Although the anode side toward the pit wall will be heated earlier than the centre, the soaking time and the slower cooling of the centre is sufficient to allow the anode centre to catch up and to equalize the baking all through the anode.

**Example: Laboratory Scale Anodes**

At the Hydro Aluminium testing facility in Årdal laboratory scale pilot anodes are made for petrol coke and anode paste test purposes. Making pilot anodes with properties equal to full scale industrial anodes requires a chain of equal treatments from aggregate handling and recipe through mixing, vibroforming and baking. The control of baking is critical. Full-scale heat treatment has been successfully reproduced in a laboratory furnace using the equivalent temperature method to define the baking level.

Figures 8-11 are included to illustrate this. The results are from a study of the effect of several factors including pitch level on properties of anodes with mixed normal and high sulfur cokes.

In the plots, the pilot anodes (blue points) are compared to industrial scale Årdal Carbon anodes made with petrol coke from three different coke shipments (I, II, III). The production property variation is shown by the average centre point and one standard deviation spread. The pilot anodes were made from coke II.

The baking level of the pilot anodes was 1200 °E, which is the target for the full-scale anodes. Of the properties shown, specific resistivity is most influenced by baking level. The other three are only weakly influenced within the baking level applied.

Observations

- Density – pitch level 14.0 to 14.7 % most similar
- Specific resistivity – pitch level 14.7 %
- Carboxy reactivity – the 15.2 % anodes' deviation due single outlier

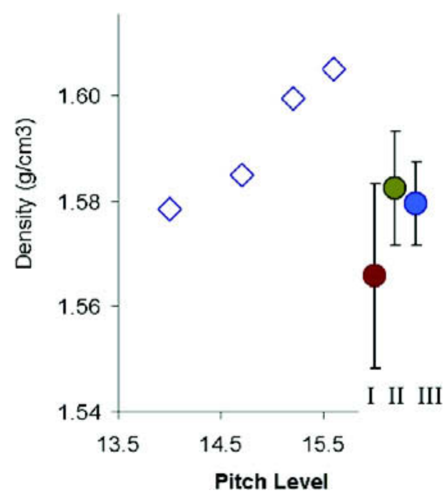


Figure 8. Density (g/cm$^3$) of pilot anode compared to full-scale anodes. Production anode pitch level is not given.

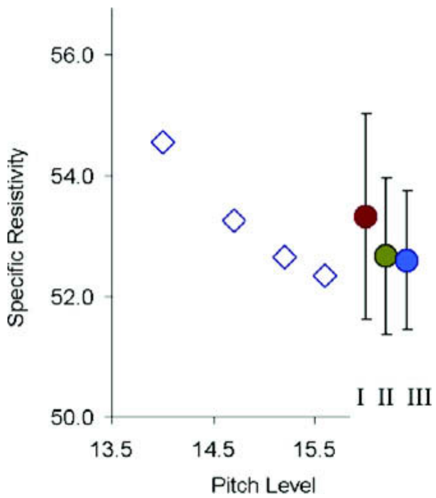


Figure 9. Pilot anode comparison – SR (μΩm).

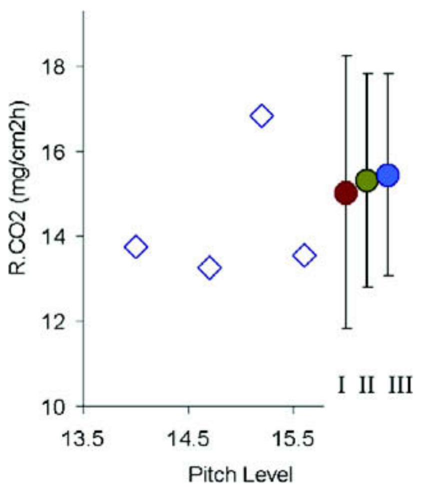


Figure 10. Pilot anode comparison – $CO_2$-reactivity (mg/(cm$^2$h)).

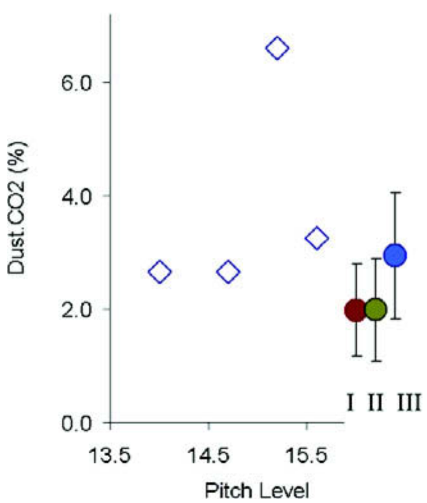


Figure 11. Pilot anode comparison – $CO_2$ dusting (%).

## Conclusions

The equivalent temperature method has been established as an ISO method, ISO 17499:

- The within-lab precision is 9 °E at 95% confidence level, which is small compared to the normal variation range allowing good monitoring of baking level
- The between lab precision is 14 °E, also fairly narrow, which allow comparison of baking furnaces

Examples have been shown of usage in Hydro Aluminium for

- Anode quality control
- Mapping of the baking level in entire sections of a baking furnace
- Test for equal baking all through anodes
- Control of laboratory scale baking to ensure equal baking level with industrial scale anodes

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