

## MEASUREMENT AND CONTROL OF THE CALCINING LEVEL

IN

## ANODE BAKING FURNACES

T. Foosnæs<sup>1)</sup>, N. Kulset<sup>2)</sup>, H. Linga<sup>1)</sup>, G. R. Næumann<sup>1)</sup> and A. Werge-Olsen<sup>1)</sup><sup>1)</sup> Hydro Aluminium a.s, Technology Center Årdal, N-5870 Øvre Årdal<sup>2)</sup> Hydro Aluminium a.s, Årdal Karbon, N-5875 Årdalstangen**Abstract**

In the production of prebaked anodes the calcining process takes place in the baking furnace. A commercial baking furnace usually produces from 50,000 to 100,000 mt/year. Regular thermocouples are most commonly used for control of the flue gas temperature. However, the use of thermocouples for calcining level monitoring of individual anodes inside a section is a laborious and costly method. The calcining level of the anodes depends on both temperature and time. We present a monitoring method based on the structural development ( $L_c$ ) with temperature and time of a reference green coke sample. A link is thus established between the total time/temperature history in the various anode positions of a furnace section and the  $L_c$  of a reference sample following each anode. Examples of application for baking furnace tuning together with correlations between raw material and baked anode properties are presented.

**1. INTRODUCTION****1.1. General**

The reactivity of anode carbon, and hence the anode consumption in the reduction process, depends on numerous parameters from raw material properties to production process characteristics, and especially on the calcining level and its homogeneity in the baking furnace.

In horizontal flue (open) baking furnaces, the instant temperature distribution in a section is easily measured by moving thermocouples to different positions in short intervals. In vertical flue (closed) furnaces the thermocouples must be placed in position before the heating cycle starts. These thermocouples only last one heating cycle, and make continuous spatial temperature monitoring an expensive method.

The maximum temperature itself may be of limited interest when it comes to the final chemical properties of the baked material. In a baking furnace, indirect heating causes temperature gradients between individual anodes in different positions. The resulting carbon structure by baking is a result of both the soaking temperature and time the carbon blocks are kept at this temperature. Hence, to quantify the calcining level in various anode positions in a furnace, the combined effect of temperature and time must be reflected by the method.

**1.2. Requirements to methods for calcining level determination**

For evaluation of the specific reactivity of a calcined anode material, one can perform reactivity analysis on samples taken from the anode blocks or from especially selected standard samples baked in the same pit/cycle. The disadvantage of these methods will be that the samples will reflect absorption of contaminants from the anode butts, and the measured values will be influenced by the local heating rate. Hence, the interpretation of such data in terms of the calcining level may give dubious results.

Other methods would be to measure properties related to the structural development of the carbon material during baking; for instance the real density or the hydrogen content. However, these methods would be too laborious.

The average calcining level in a section can also be correlated to the area under the temperature/time curve during baking, but this will not give information on the spatial distribution of the baking level.

A method for determination of the calcining level in baking furnaces should hence have the following features:

- The measured parameter(s) should be independent of the heating rate.
- The method should correlate the effect of time and temperature on the reactivity of the petrol coke and the binder in the anode. Also, the method should reflect the average calcining level in the section.
- The method should be easily applicable for routine analysis.
- The method should be simple, inexpensive and fast; it must not disturb the process or the working routines of the baking furnace.
- The method must be applicable for evaluation and control of alternative working routines or operational strategies in baking furnaces.
- The method should have the highest possible degree of confidence by single tests.
- The method should provide data on the calcining level of individual anodes, traceable to section number and pit position during baking.

**2. THE EQUIVALENT TEMPERATURE METHOD****2.1. General**

The purpose of the baking process is to transform the binder phase into solid carbon with the desired chemical and structural properties in a way that ensures

- No or minimum baked rejects
- The highest possible binder coke yield

- Minimum tensions in the anodes during baking
- Maximum binder coke - petrol coke strength
- Low specific electrical resistivity
- Uniform and low reactivity for all carbon phases

In order to satisfy the requirements above, both the furnace design and the operational characteristics are important. In addition, analytical tools which are sensitive to baking furnace specifics are needed.

### 2.2. The equivalent temperature

The Hydro Aluminium method<sup>1)</sup> uses the average crystallite height ( $L_c$ ) of a "standard" reference green coke as indicator for the calcining level in the baking furnace. A calibration curve for the development of  $L_c$  vs. temperature was obtained by heat treating samples of the green coke by rapidly increasing the temperature to the desired level, where the soaking time was  $120 \pm 0.5$  min. The samples were quenched and subjected to X-ray diffraction analysis for determination of the average crystallite height. The resulting curve is shown in Fig. 1, and the equivalent temperature is defined as follows:

*Any heat treatment can be described by an equivalent heat treatment temperature ( $E$ ), which is numerically equal to a temperature ( $C$ ) kept constant for 2 hours.*

The notion equivalent temperature is chosen because in traditional calcining processes the temperature is measured directly and related to the calcining level, even if there are variations in soaking time and/or maximum temperature. The equivalent temperature is described by the structural impact on the reference coke by baking, and hence gives the true calcining level, in contrast to direct temperature measurements. Fig. 2 shows the equivalent temperature development vs. soaking time at  $1100^\circ\text{C}$ .

### 2.3. Application of the method in the baking furnace

Reference green petrol coke samples (10 g, maximum grain size 5 mm, preheated to  $550^\circ\text{C}$ ) are packed in reusable graphite cylinders (OD 40 mm, ID 20 mm, l 90 mm) and sealed with a graphite plug. A 3 mm $\phi$  hole is drilled through the plug, and acts as a pressure equalizer.

The loaded cylinders are placed in the stub holes (using refractory wool for stabilizing) of the green anodes before pit charging. After the baking cycle, the cylinders are removed, and the average crystallite height of the reference coke is determined by XRD. Using the calibration curve, the equivalent temperature in the actual furnace position is calculated. The standard deviation for 3 or more repeated analyses at  $1100^\circ\text{E}$  equivalent temperature is  $\pm 8^\circ\text{E}$ .

## 3. PRACTICAL ASPECTS USING THE EQUIVALENT TEMPERATURE METHOD

The baked anodes have to be analyzed (usually about 2 % of the production) with respect to various chemical and physical parameters in order to ensure that the product fulfills the properties which have been agreed upon in a sales contract.

The analytical results also provide vital process feedback on a continuous basis. The calcining level during baking is in theory reflected in the  $L_c$  of the anode material, which is the weighed average of  $L_c$  in the constituent phases: petrol coke (c), butts (b) and the coked pitch (p), where the latter provides information on the baking furnace calcining level;

$$L_{c(\text{Anode})} = X_c L_{cc} + X_b L_{cb} + X_p L_{cp} \quad (1)$$

Since less than 10 % of a prebaked anode is pitch coke, the contribution to  $L_{c(\text{Anode})}$  from this phase is easily obscured by process variations both in the baking furnace and in the paste plant. Hence,  $L_{c(\text{Anode})}$  does not necessarily indicate the equivalent temperature in the actual furnace position. However,  $L_{c(\text{Anode})}$  can be used to estimate the degree of

post calcining of the coke aggregate during baking. Post calcining of the aggregate coke occurs when the combined temperature-time action of the baking cycle exceeds that of the previous petrol coke calcining process.

The selection of anodes to be analyzed can be done in several ways; one possibility is to pick at random every 50th anode coming from the baking furnace. Another strategy would be to choose every 50th anode produced in the green mill. We have chosen the last alternative for two main reasons:

- Every 50th green anode is given a proper marking (the production day and a serial number). A reference green coke sample is placed in one of the stub holes of the anodes. By using a special system for registration of the marked anodes during baking furnace charging, every analyzed anode can be traced back to the exact time of production in the paste plant and its position in the baking furnace.
- Mounting the green coke sample in the stub hole is done in the paste plant as part of the routine check on production. Therefore, this is not a laborious routine.

All analyzed anode data are stored in a database together with analytical results for the raw materials. Over time the combination of such data provides valuable information on raw material performance in terms of anode quality.

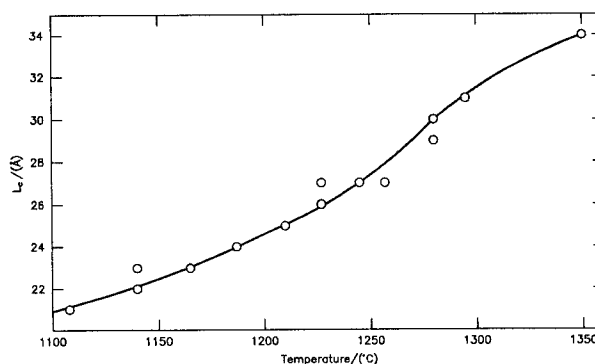


Fig. 1.  $L_c$  development of the standard green coke as function of temperature. The soaking time at top temperature is 2 hours.

Since the test anodes in this way are linked to the exact time of production, each of these anodes can be identified with all relevant production data such as dry aggregate recipe, pitch content, temperatures at preheating, mixing and forming, and also at which vibrocompactor the anode is made. Hence, the quality of raw materials, anodes and carbon production characteristics can be related to anode performance during reduction.

## 4. RESULTS AND DISCUSSION

### 4.1. The calcining level during anode baking

For a smooth potroom operation we want the variation in anode properties to be as small as possible. Ideally, all anodes should be calcined to the same equivalent temperature. However, industrial baking furnaces show a certain temperature distribution, due to design, operational practice and general furnace condition<sup>2)</sup>. The equivalent temperature method offers a simple technique where the effect of these features are easily monitored.

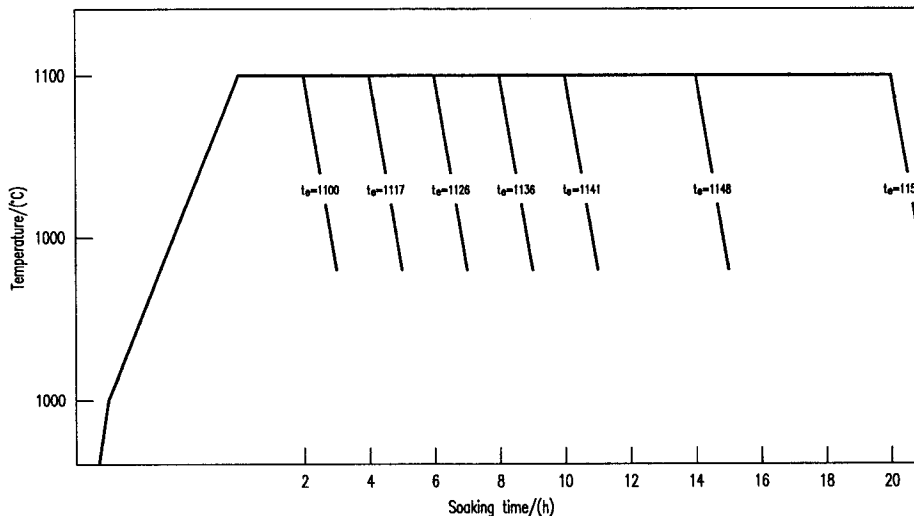


Fig. 2. Equivalent temperature vs. soaking time at 1100 °C.

It is known from the literature<sup>3,4</sup> that a too low calcining level gives rise to high reactivities and poor dusting properties. On the other hand a too high baking level increases the energy consumption and leads to anodes with in general deteriorating properties. The goal is therefore to establish the optimum baking level.

Examples of the equivalent temperature distribution for two different baking furnaces are shown in Fig. 3. The operational challenge is to tune each burner individually to achieve an equivalent temperature distribution which is as "narrow" as possible. Knowing the position of each anode in a section the data in Fig. 3 can alternatively be presented in a 3-d plot, and will then give information on the spatial equivalent temperature distribution, *i.e.*, the hot and cold regions of a section can be traced. This allows the burner settings to be adjusted to provide optimum conditions both with respect to the level and homogeneity of the baking.

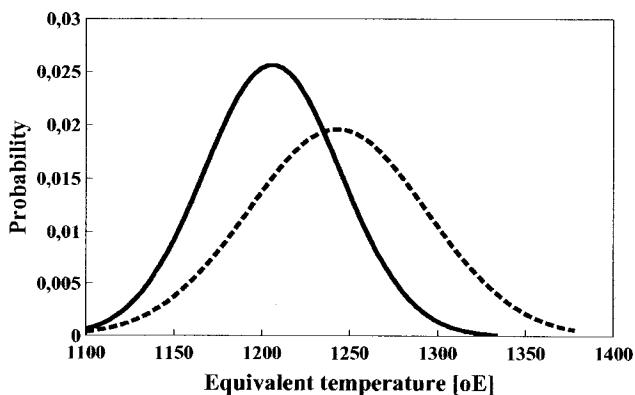


Fig. 3. Examples of equivalent temperature distributions for two different baking furnaces.

#### 4.2. Anode properties as function of the baking level

Five anode quality parameters ( $\text{CO}_2$ - and air reactivity,  $\text{CO}_2$ -dusting, specific electrical resistivity and air permeability) are directly influenced by the baking level. These properties to a large extent govern the anode consumption in the potroom. Taking into account the natural variation in the baking level, it is important to apply a baking level where the variation in these quality parameters is at a minimum.

Figs. 4 (coke A) and 5 (coke B) show the  $\text{CO}_2$ -reactivity for anodes based on two different regular petrol cokes. We see that the  $\text{CO}_2$ -reactivity is essentially constant over a broad equivalent temperature range. The slight increase in reactivity with equivalent temperature, although in this case hardly significant, may indicate beginning post calcining of the coke aggregate at the highest equivalent temperatures.

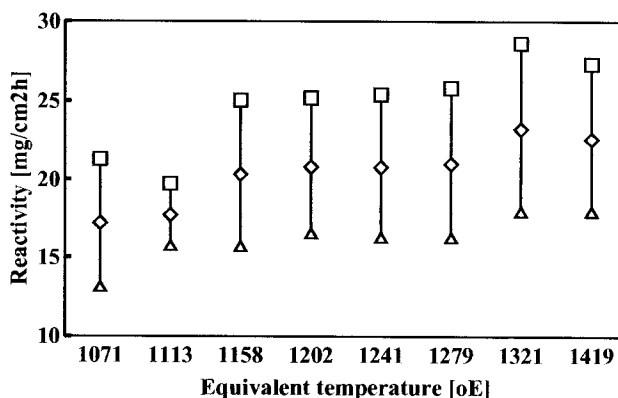


Fig. 4.  $\text{CO}_2$ -reactivity vs. equivalent temperature for coke A.

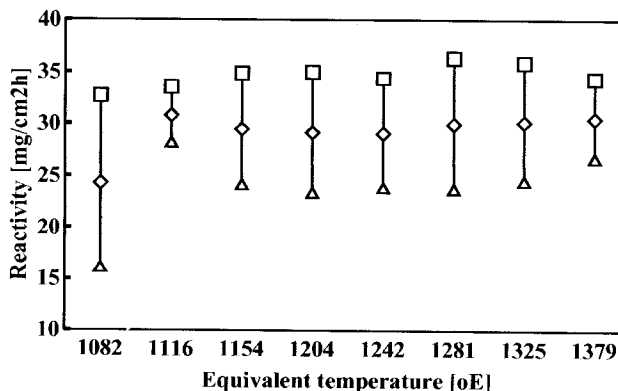


Fig. 5.  $\text{CO}_2$ -reactivity vs. equivalent temperature for coke B.

In Fig. 6 the CO<sub>2</sub>-dusting is shown as function of the equivalent temperature for coke B. The CO<sub>2</sub>-dusting is defined as per cent loose dust generated during the CO<sub>2</sub>-reactivity test (Hydro Aluminium method) related to the total weight loss. The dust generation is seen to accelerate at low equivalent temperatures.

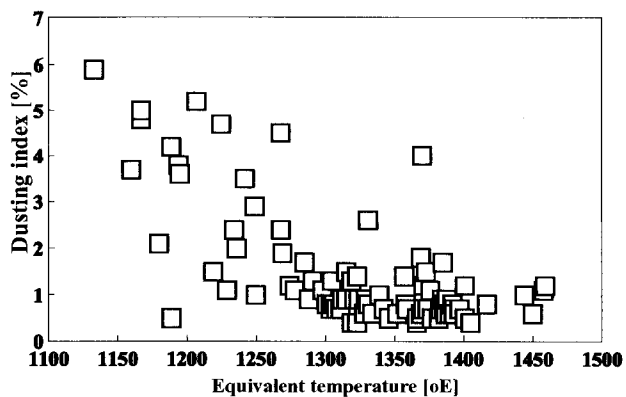


Fig. 6. CO<sub>2</sub>-dusting as function of equivalent temperature for coke B.

Figs. 7 (coke A) and 8 (coke B) show the variation of the specific electrical resistivity. Post calcining of the aggregate coke can give rise to shrinkage cracks around coke grains which lead to an increased level and standard deviation for the resistivity. In this case this effect is not observed.

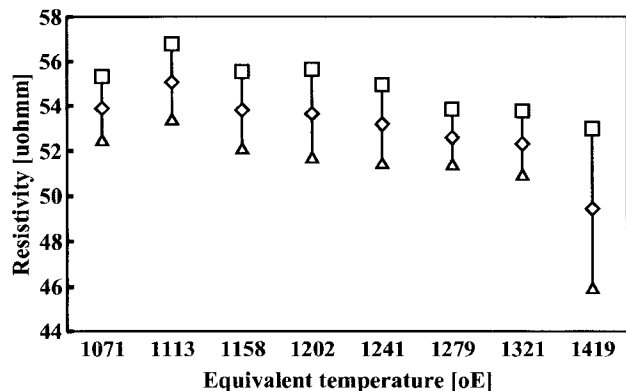


Fig. 7. Specific electrical resistivity vs. equivalent temperature for coke A.

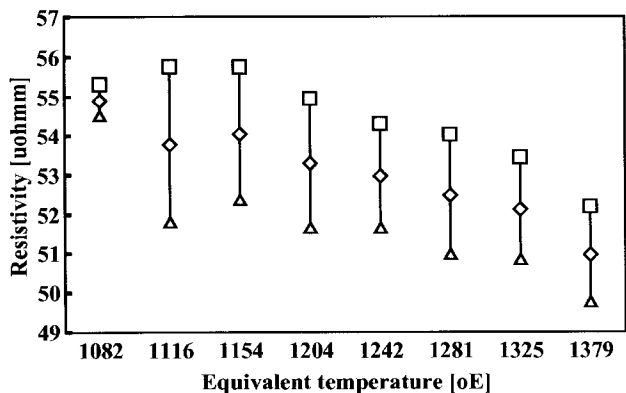


Fig. 8. Specific electrical resistivity vs. equivalent temperature for coke B.

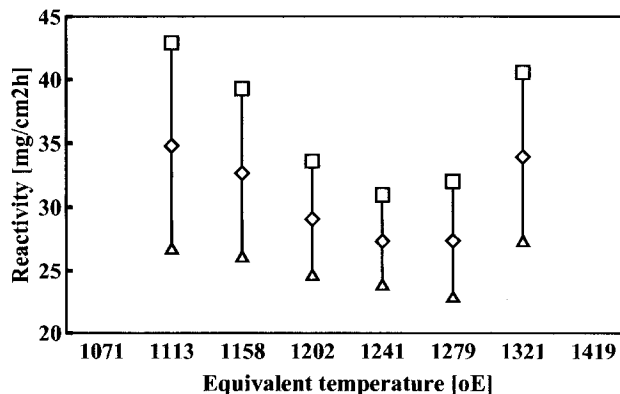


Fig. 9. Air reactivity for anodes (coke B) with/without butts addition vs. equivalent temperature.

In Fig. 9 the air reactivity for coke B anodes (with and without butts addition) is shown as function of the equivalent temperature. A broad minimum between 1150 and 1300 °E is noted. The interesting feature is the strongly accelerating air reactivity at high equivalent temperatures, starting at 1300 °E. The increasing air reactivity starts when the baking level exceeds the calcining level of the petrol coke, and is independent of butts addition. This can be explained by the formation of micro-cracks and increased accessible surface to air.

The optimum baking level depends on the properties of the raw materials. The optimum baking level for the actual coke (B) is found to be between 1200 (to avoid dusting) and 1300 °E (to avoid excessive air reactivity). Therefore, the baking furnace in this case should be optimized (Fig. 3) to achieve this calcining level.

5. REFERENCES

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