

USE OF UNDER-CALCINED COKE FOR THE PRODUCTION OF LOW REACTIVITY ANODES

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Abstract

The quality of petroleum coke used for the production of anodes for the aluminium industry is declining, with both the density and the purity of the cokes affected. As a result, anodes produced from these cokes will have higher reactivity resulting in higher carbon consumption in the smelter.

Under-calcined coke can be used as a response to this higher anode reactivity. Such coke has a structure more similar to the binder phase (a mix of fine fractions and coal tar pitch), resulting in a more homogenous reactivity of all anode components following baking. The preferential consumption of the anode binder phase by the side reactions with oxygen or carbon dioxide in the cell is thus reduced.

In this paper, the theory behind the performance of under-calcined coke will be reviewed. This will be followed by results from laboratory experiments and industrial tests. Examples of the benefits obtained by plants using under-calcined coke will also be provided.

Introduction

Excess consumption of carbon anodes used for the production of aluminium occurs through attack by O₂ and CO₂ in the pots. An earlier paper presented at TMS in 2001 [1] provided preliminary results on the use of under-calcined coke to reduce the reactivity of carbon anodes. This paper (based on a presentation given to the International Pitch and Calcined Petroleum Coke Conference 2007 [2]) provides an update on the use of under-calcined coke, both in the laboratory and industrially in Rio Tinto Alcan plants.

Definitions

The range of calcination level of cokes, measured by the real density of fines (RDf) and by L_c, commonly used in the aluminium industry can be divided into 3 categories:

- Under-calcined coke: RDf < 2.05 (L_c < 25.3 Å)
- Standard calcined coke: 2.05 < RDf < 2.09 (25.3 < L_c < 32.7 Å)
- Highly calcined coke: RDf > 2.09 (L_c > 32.7 Å).

Note: In this paper, density will be expressed in g/cm³.

Objectives

The calcination level used in the production of calcined petroleum coke affects the structure and, therefore, the reactivity of the coke. The principal objective in working on the calcination level of the coke used for the production of anodes is to improve the anode quality by reducing anode reactivity (both oxy-reactivity and carboxy-reactivity) and the propensity to dust. The reactivities are defined as the sensitivity of an anode to O₂ and CO₂ attack at a given temperature, and dusting is defined as the propensity of the carbon grains to be shed from the anode.

Other characteristics of the anode (including density or more precisely the amount of carbon available for the electrolysis) must also be closely followed to detect any negative impact due to the calcination level of the coke.

An anode is most frequently composed of:

- Calcined petroleum coke and spent anode butts which constitutes its skeleton
- A mixture of fine fractions of coke and butts and coal tar pitch which plays the role of the binder.

The reactivity of these two phases is quite different, the skeleton phase being far less reactive than the binder phase (Figure 1).

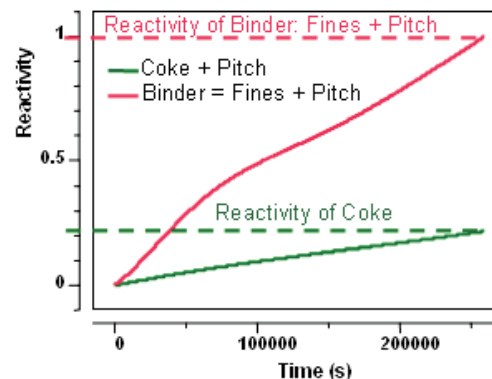


Figure 1: Curves of weight loss as a function of the duration of the exposure of the sample to CO₂.

As a consequence, the binder phase is the most sensitive part of the anode to O₂ and CO₂ attack. Thus, reducing the reactivity of the coke will not reduce the reactivity or dusting tendency of the anode. Reducing the reactivity of the anode requires a reduction of the difference of reactivity between the two phases.

One way of achieving this is by reducing the reactivity of the binder phase (i.e. the coke fines + pitch coke). However, this is becoming increasingly difficult with the deterioration of coke quality. The focus of this work has been on reducing the difference of reactivity between the phases by increasing the reactivity of the coke in the skeleton component.

There are several possibilities to increase the reactivity of the skeleton phase. An increase in the impurity content of the coke is a route that has not been explored as it will affect both the skeleton and binder phases. The preferred method is the supply of a more disordered coke structure through under-calcination of the coke.

Theory

During baking of an anode, the carbon constituents undergo a re-organisation of structure resulting in a global decrease in the anode reactivity. The traditional approach has been to provide sufficient heat treatment during baking to achieve an RDf of the anode just above the RDf of the calcined coke used in the skeleton phase. In this approach, transformation of the pitch in the binder phase occurs but there is minimal transformation of the calcined coke.

With the use of undercalcined coke and traditional baking temperatures, there is a common transformation of both skeleton and binder phases during the baking process. This results in a lower difference of reactivity between the two phases. A more homogenous product with no components preferentially consumed and with a lower dusting tendency is produced.

Typically, the heat treatment seen by the binder phase during baking is far less than the heat treatment of standard calcined coke. When cokes of different calcination levels are compared at a given final anode baking level target, the lower the calcination level of the coke, the longer the transformation undergone jointly by the binder and the skeleton phases during baking. Thus there is a lower difference in reactivity between the phases.

In an extreme case of highly calcined coke, the calcination level of the coke is higher than the target anode baking level. Not only will the phases never be transformed together, but in addition, the skeleton phase itself will not be further transformed during baking. The difference of reactivity between the constituents of such anodes will be maximised resulting in an increased tendency for dusting in the pot.

Laboratory experiments

Anode reactivity has been measured using a thermogravimetric method, with the ability to test materials under both O₂ and CO₂ atmospheres. Thermogravimetry has three advantages over other methods for characterising carbon reactivity:

- The conditions of reaction can be easily controlled, in particular conditions can be set to ensure the samples are tested in the desired regime of reaction.
- Different types of samples can be analysed: both laboratory scale anodes and industrial anode cores and also a mixture of pitch and fine fractions (binder phase). This allows a full evaluation of the sensitive part of the anode.
- Weight loss curves provide more exhaustive information on the reactivity of a given sample than just a final weight loss: the shape of the weight loss curve is an important parameter to evaluate.

The initial study performed was a comparison of the reactivity of laboratory scale anodes produced with the same green coke but calcined at three different temperatures:

- 800°C giving a RDf of 1.80 (L_c of 15.3 Å)
- 900°C giving a RDf of 1.83 (L_c of 15.4 Å)
- 1000°C giving a RDf of 1.95 (L_c of 16.6 Å).

With the exception of the calcination level of the coke, all other conditions were identical including the baking at 1000°C (with all samples baked at the same time).

The results of oxy and carboxy-reactivity and anode density of the samples are shown in Figures 2-6.

Oxyreactivity

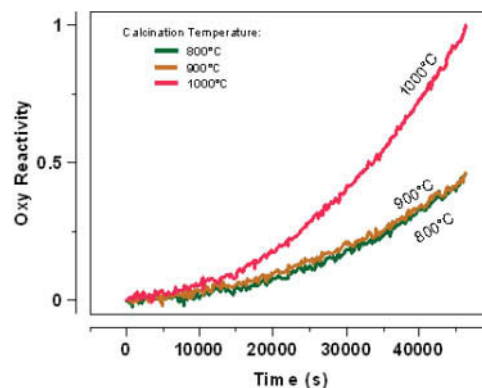


Figure 2: Weight loss curves (O₂) of three laboratory anode samples produced with cokes calcined at different temperature.

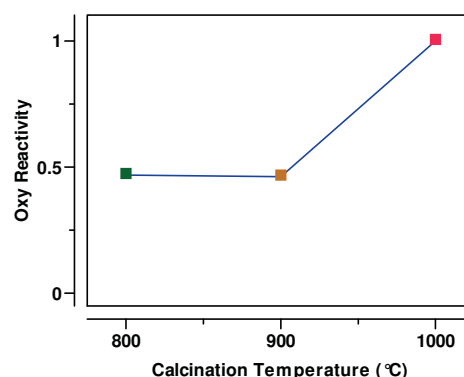


Figure 3: Oxy-reactivity of the three sets of samples produced with cokes calcined at different temperature.

The impact of the calcination level on the oxy-reactivity of the samples is significant. The total oxy-reactivity of anodes produced with coke calcined at temperatures below the baking temperature is about half that of anodes produced with coke calcined to the baking temperature. This would be an unexpected result if the anode reactivity was solely governed by the structure and reactivity of the coke.

Carboxyreactivity

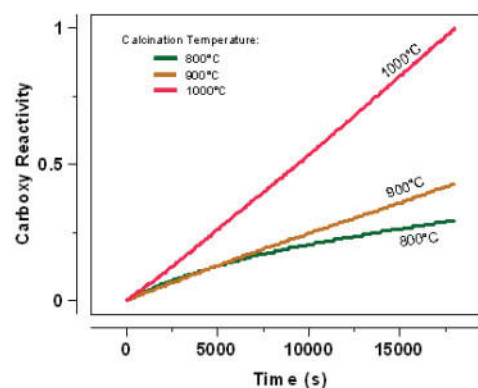


Figure 4: Weight loss curves (CO₂) of three laboratory anode samples produced with cokes calcined at different temperature.

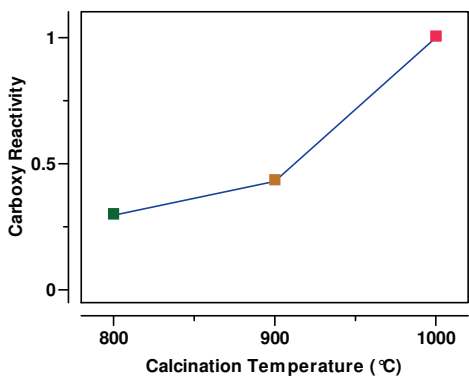


Figure 5: Carboxy-reactivity of the three sets of samples produced with cokes calcined at different temperature.

The trend of carboxy-reactivity with the calcination level of the coke used for the production of the samples is similar to that seen with the oxy-reactivity. The lower the calcination level of the coke, the lower the carboxy-reactivity of the sample. The lowest anode reactivity is observed when the difference between calcination level of the coke and baking temperature of the samples is high. This reflects the greater level of structural transformation of the skeleton and binder phases during baking when a low coke calcination temperature is used.

Densities

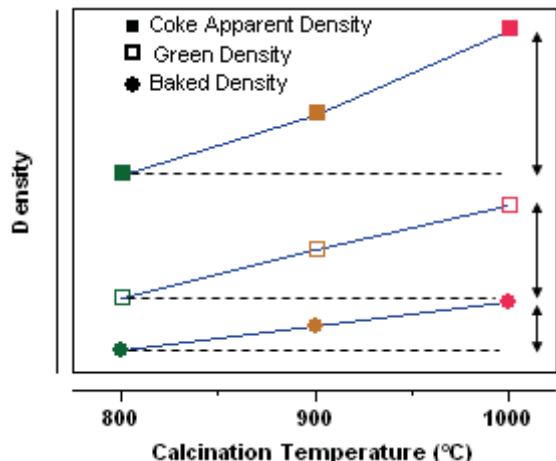


Figure 6: Densities of the three sets of samples at different stages of the laboratory scale production.

The laboratory anodes produced from cokes with a lower calcination level have a lower green and baked density (Figure 6). However, the lower density of the samples made from under-calcined coke is not related to the anode production process when using this grade of coke. It is due to the lower density of the coke itself. Furthermore, the difference in density between the extremes of samples tested (800 and 1000°C) is decreasing during the production of the laboratory scale anodes (the size of the arrows on the right side of the Figure 6 is reduced from coke to green and baked densities). This suggests that there is a partial compensation for the lower density of the coke during the green production and the baking of the samples.

The compensation occurring during the baking phase is related to the higher shrinkage of the samples produced with under-calcined coke (Figure 7).

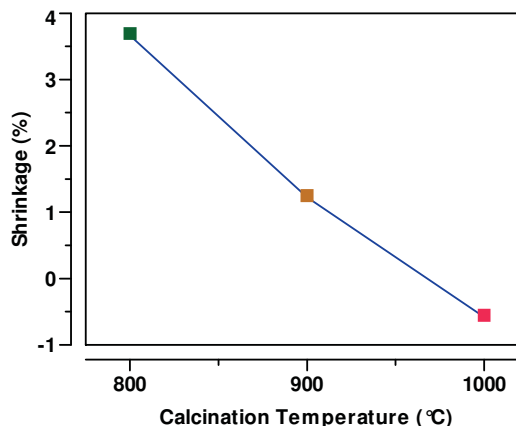


Figure 7: Shrinkage of the different samples during baking.

Thus, the lower density of the coke is partially compensated by a higher contraction during production.

The laboratory studies have shown a positive impact of under-calcined coke on oxy- and carboxy-reactivity of the anode. However, the anode density is lowered due to the lower apparent density of this grade of coke.

From Lab to Plant

Further studies were required to evaluate the lower reactivity and lower density of anodes produced using under-calcined coke and the effect on anode performance. A second study closer to industrial conditions (using industrial cokes and baking) was performed using:

- Under-calcined coke (UCC): RDf of 2.000 (L_c of 19.7 Å)
- Standard calcined coke (SCC): RDf of 2.059 (L_c of 26.7 Å).

In this case, the laboratory scale anodes were baked in an industrial closed furnace: one sample of each set was positioned in the stub holes of different anodes (Figure 8). The carboxy-reactivity of the samples was analysed.

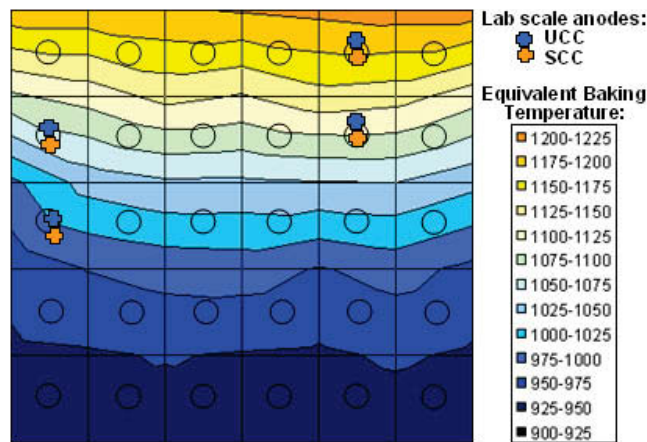


Figure 8: Temperature cartography of the pit and position of the samples.

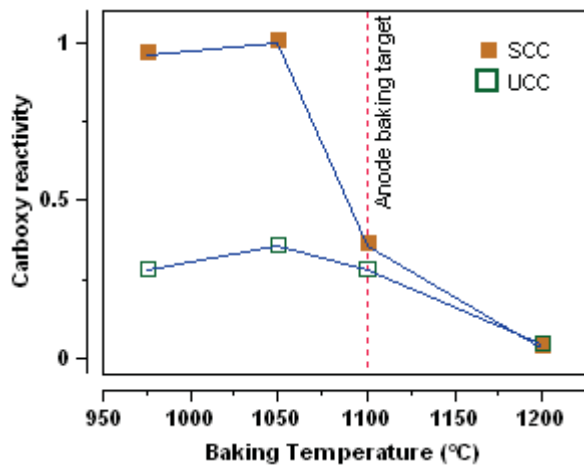


Figure 9: Carboxy-reactivity of the samples baked in the industrial closed furnace

The results show that the use of under-calcined coke has a small benefit on the carboxy-reactivity of anodes baked at or above the target temperature (given that there is no desulphurisation). However, when under-baked, the anodes produced with under-calcined coke are far less reactive than those made from standard calcined coke.

Thus, the use of under-calcined coke provides additional robustness to the baking process. If anodes are under-baked, the quality of the anodes will be less impacted if they are produced with under-calcined coke. This is of major interest in the case of highly heterogeneous baking furnaces or if a problem occurs during the baking process.

Industrial Experiments

Industrial trials have been conducted following the promising laboratory results and to understand the impact based on anode performance rather than laboratory tests.

Two examples of the use of under-calcined coke are provided:

- Results of a full, large scale industrial test
- An example of additional benefits of the use of this grade of coke.

Full industrial test

During 16 weeks of production a plant replaced standard coke (reference) with under-calcined coke (trial). Both cokes were produced by the same supplier, with a similar green coke blend. A summary of results are provided in Table 1.

Table 1: Results of the trial and reference batches

	Standard	Under-calcined
Number of weeks	18	16
Coke Real Density	2.058	2.037
Coke Apparent Density	1.74	1.72
Anode Green Density	1.636	1.628
Anode Baked Density	1.576	1.571
Carbon under pin (mm)	71.6	76.5

The results can be summarised as follows:

- The apparent density of under-calcined coke is lower than standard coke

- The green and baked densities of the trial anodes were lower than those of the reference batch
- The difference in density between both batches reduced from the coke to the baked anode (Figure 10)
- The carbon consumption of trial anodes was significantly lower than the reference batch, measured by carbon under the pin in the returned butts.

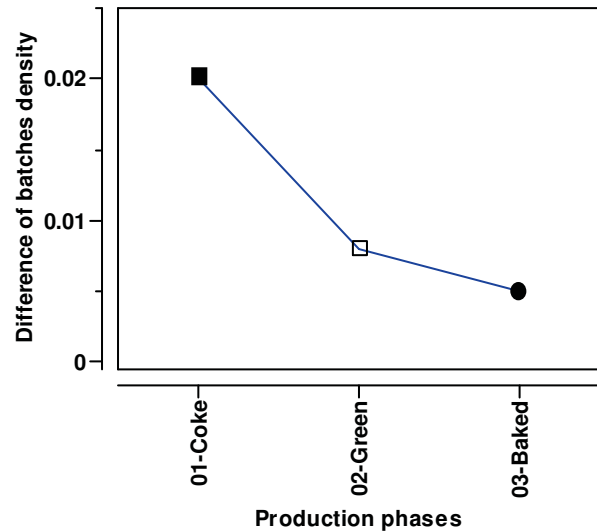


Figure 10: Density difference between trial and reference anodes during the production process

The observations made at the laboratory scale were confirmed in the industrial trial. In addition, despite the lower density of the trial anodes, more carbon is available for the electrolysis (thicker butts). This is explained by the lower reactivity of the anodes made from under-calcined coke.

Extra benefit

The benefit of using under-calcined coke was also illustrated during a period of an anode problem in a plant. In this case, the data presented includes all types of failures or abnormal behaviour of anodes in the pots (ahead of schedule, dust, spikes, cracks...). The historical evolution of the number of problems during 2002 and 2003 is shown in Figure 11. The anode problem can be seen from mid 2002 to beginning of 2003.

Statistical studies showed that the crisis was initiated by the introduction of a new supplier of standard calcined coke (dark area starting week 20). The return (week 28) to the usual standard coke supplier did not resolve the problem. On the contrary, the number of anode problems increased. This was due to the so called "snow-ball effect", where anode problems cause instability and a temperature increase in the pots. These changes then increase stress on the anode which results in the failure of what would normally be good anodes.

The significant decrease of the number of anode problems starting around week 50 is related to the introduction of under-calcined coke. This change in coke solved the crisis and the plant returned to a stable and typical number of anode problems. As a result, under-calcined coke has continued to be used in the plant, either alone, or as a blend with standard calcined coke. (For example, a blend was used around week 58).

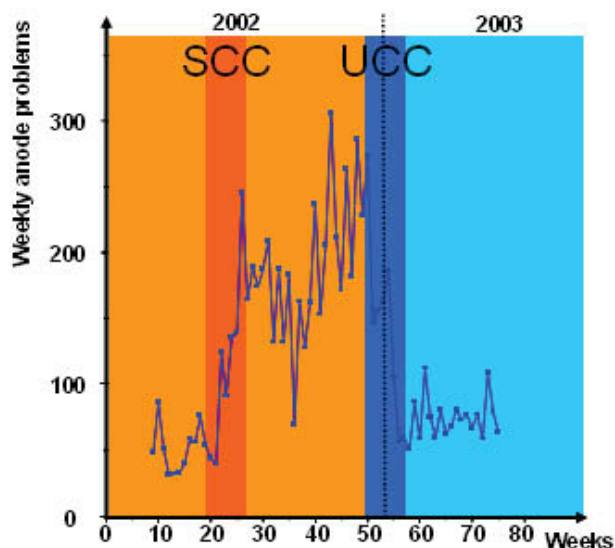


Figure 11: Historical evolution of anode problems and resolution using under-calcined coke

Global experience

Since the benefits of under-calcined coke were proven, the use of this grade has been extended to many RTA plants and its percentage has been increasing in the coke mix. Most of the plants in Europe and Africa are now running blends including a minimum of 50% of under-calcined coke, with some plants consuming 100% of the coke, (Figure 12). The low figures for 2007, and the lack of use in North America and the Pacific are related to a lack of availability of under-calcined coke on the market rather than the desire of the plants to reduce this grade in the blend.

The use of under-calcined coke is a robust way of reducing anode reactivity. The grade has been tested for many years, in different plants, using different technologies and at different percentages in the coke blend. During this period of time, no major anode crisis was experienced by any of the plants.

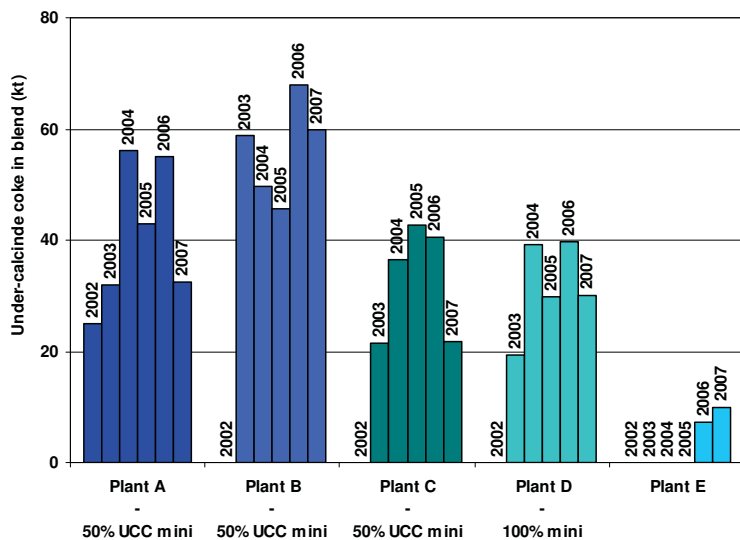


Figure 12: Historical trend of the consumption (kt/y) of under-calcined coke by RTA plants in Europe and Africa (includes minimum % used in the blend).

Conclusions and Recommendations

The use of under-calcined coke in the production of anodes provides a decrease in the overall reactivity of the anode, a reduction in carbon consumption and a lower risk of anode problems. These benefits are seen despite a slight decrease of anode density related to the lower apparent density of under-calcined coke and partly compensated for by a higher shrinkage rate during baking.

The reduction of anode reactivity and improvement in anode performance is observed with well baked anodes but is even more significant on under-baked anodes, thus improving the robustness of the baking process.

The benefits result in an increased quantity of carbon available to produce aluminium and a lower tendency to dusting in the pots, providing a more stable and productive electrolysis process.

The use of under-calcined coke for anode production (alone or in blend with standard calcined coke) is being extended to RTA plants in all regions as it becomes available from suppliers.

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The authors would also like to express their gratitude to the Rio Tinto Alcan laboratory teams at ARDC and LRF that have made the move from lab experimental tests to industrial use a reality.

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