Optimum Baking Level of Carbon Anodes for Aluminum Production

Khalil Khaji[1] **and Najeeba Al Jabri**[2]
1. Manager, Process Control and Improvements, Carbon & Port
Emirates Global Aluminium ("EGA"), Al Taweelah Operations, Abu Dhabi, UAE
2. Director, Reduction
Emirates Global Aluminium (EGA), UAE
Corresponding author: kkhaji@ega.ae

Abstract

Carbon anodes are consumed in electrolysis cells during primary aluminum production. Carbon consumption in pre-bake anode cells is at the rate of 400 kg C/t to 450 kg C/t Al and is affected by the carbon dioxide (CO_2) reactivity and air reactivity of anodes. The anode reactivities are affected by the properties of raw materials and by the parameters of the manufacturing processes. Carbon anode reactivities data over the last three years at Emirates Aluminum ("EMAL", also known as Al Taweelah Operations) were analyzed, with a particular focus on anode baking levels. This study indicates relationships between anode reactivities and the levels of anode baking, measured through the anode real density values. Low and high levels of baking result in higher anode reactivities, while optimum baking level gives the lowest anode reactivities. A real density value of 2.08 g/cm^3 is found to be optimum, as at this baking level both the CO_2 reactivity and air reactivity are lowest. Low chemical reactivities give low net carbon consumption during aluminum production. The understanding gained through this study helps to reduce anode reactivities by adjusting the anode baking level, thereby achieving low net carbon consumption.

Keywords: Carbon anode; CO_2 reactivity; air reactivity; anode baking; real density; net carbon consumption.

1. Introduction

Carbon anodes are consumed in Hall-Héroult electrolysis cells during primary aluminum production. The carbon anode consumption rate is expressed as "net carbon consumption" ("NCC") and is frequently used as a parameter for evaluating anode performance in reduction cells. The NCC in pre-bake anode cells is in the range of 400 kg C/t Al to 450 kg C/t Al. This includes consumption during the basic electro-chemical reaction as well as additional consumption due to current efficiency loss, secondary reactions with air, anode gases and other processes. In every smelter carbon plant, efforts are made to adjust anode manufacturing processes to sustain anode quality despite changing raw material quality. The quality of calcined petroleum coke, in particular, is changing. For example, sulphur content and metallic impurities are increasing. Use of different quality cokes impacts anode quality, which in turn affects anode performance and consumption in reduction cells.

Several papers have been published on how anode manufacturing processes influence anode reactivities and their impact on anode performance in the pots [1, 2]. In this paper, an analysis of three years' data is presented on baked anode reactivities at EMAL – an operating subsidiary of Emirates Global Aluminium ("EGA"). The analysis focuses on the baking process and on how the level of baking influences anode reactivities.

2. Plant Parameters

The EMAL smelter, located at Al Taweelah in Abu Dhabi, United Arab Emirates, has an installed capacity of 1.38 million tonnes of aluminium per year. The smelter has 1 200 electrolytic cells, of which 756 DX Technology cells operate at 405 kA and 444 DX+ Technology cells operate at 462.5 kA. The electrolytic cells use pre-bake carbon anodes, manufactured in two captive carbon plants. The paste plants, baking kilns and rodding plants operate the latest state-of-the-art technologies for green anode manufacturing, baking green anodes, rodding baked anodes and processing butts. The characteristics of the cokes used for manufacturing anodes are given in Table 1.

This paper presents correlations between anode baking level, as measured through real density parameter and baked anode chemical reactivities. Anode reactivities affect the carbon consumption in the pots during the electrolysis of alumina.

The study is based on the EMAL smelter data over a period of three years' operations (2014 to 2016). Process data from the baking kilns was used, along with laboratory analysis of raw materials and baked anode core samples.

Table 1. Typical characteristics of calcined petroleum cokes.

Analysis	Unit	Values
		Range
Vibrated bulk density ("VBD")	g/cm³	0.85-0.95
Real density	g/cm³	2.07-2.08
Lc	nm	2.9-3.1
Volatile matter ("VM")	%	0.40-0.45
Moisture	%	0.1-0.5
Ash	%	0.05-0.2
Sulphur	%	1.0-3.0
CO_2 reactivity	%	3-12
Air reactivity	%/min	0.1-0.3
Hard grove index ("HGI")	no	32 - 42
Electrical resistivity	µΩ.m	440-500

3. Finding

3.1. CO_2 Reactivity

As the baking level of anodes increases (indicated by the increase in real density), the study shows that:

- Baked anode CO_2 reactivity residue ("CRR") increases and then decreases after reaching a peak (Figure 1).
- Baked anode CO_2 reactivity loss ("CRL") decreases initially and then increases after reaching a minimum value with increasing real density (Figure 2).

- Baked anode CO_2 reactivity dust ("CRD") decreases initially and then increases after reaching a minimum value, with increasing real density (Figure 3).

In all cases, the reactivity changes direction at the real density value of 2.08 g/cm^3.

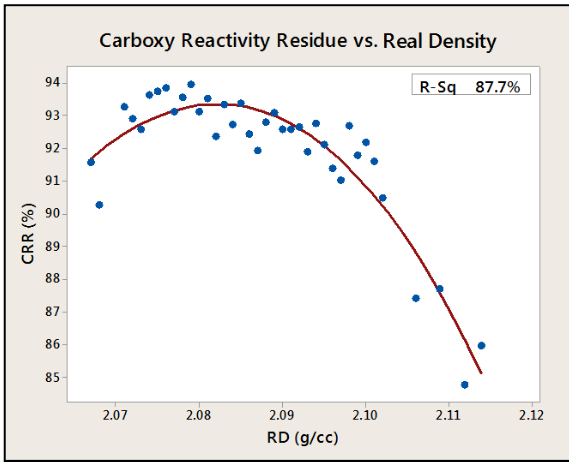

Figure 1. CO_2 reactivity residue vs. real density.

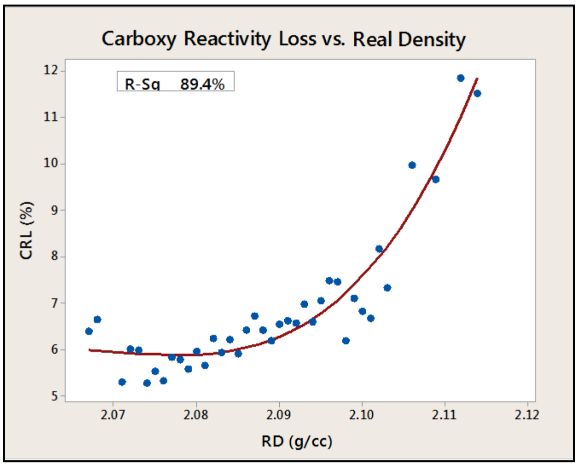

Figure 2. CO_2 reactivity loss vs. real density.

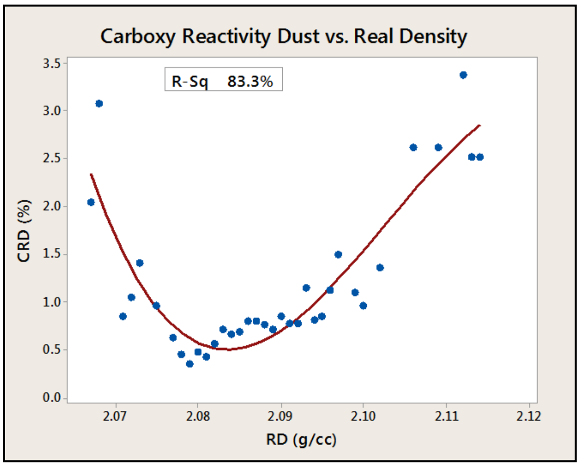

Figure 3. CO_2 reactivity dust vs. real density.

3.2 Air Reactivity

With increasing real density, the following changes in air reactivities are observed:

- Air reactivity residue ("ARR") increases initially, and then drops after attaining a maximum value (Figure 4).
- Air reactivity loss ("ARL") decreases initially, and then increases after attaining a minimum value (Figure 5).
- Air reactivity dust ("ARD") decreases initially, and then increases after attaining a minimum value (Figure 6).

In all cases, the air reactivities reverse direction when the real density of baked anodes reaches 2.08 g/cm^3.

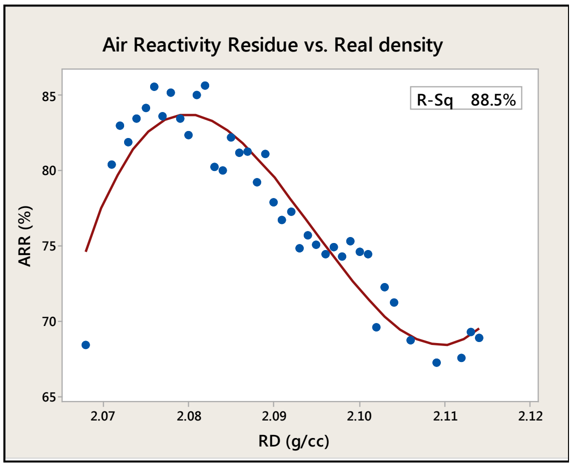

Figure 4. Air reactivity residue vs. real density

Figure 5. Air reactivity loss vs. real density.

Figure 6. Air reactivity dust vs. real density.

4.0 Discussion

The CO_2 reactivity of baked anodes is the result of reactivities of the base coke and binder pitch coke [3]. Pitch coke reactivity is a function of baking level and becomes a controlling factor in determining the CO_2 reactivity of baked anodes [4].

During anode baking, the pitch is converted into pitch coke. The real density of pitch coke, which is lower than the real density of base coke, increases with increased anode baking level; and the difference between the real densities of the base coke and pitch coke decreases. When the baking level is low, the difference in the reactivities of base coke and pitch coke is greater, favouring preferential oxidation of the pitch coke. Because of the preferential consumption of pitch coke, the bonds between the base coke particles are lost, and the base coke grains detach from the main anode body. This could explain higher CO_2 reactivity dust at low baking levels. As the baking level increases, the difference between the reactivities of pitch coke and base coke reduces; and preferential oxidation of the pitch coke does not take place. It is necessary to bake anodes sufficiently, such that the real density of the anode is equal to or higher than the real density of the base coke, so that preferential oxidation of the pitch coke does not occur in the pots.

The drop in CO_2 reactivity dust as the real density increases can be seen in Figure 3.

At a baking level corresponding to a real density value of 2.08 g/cm^3, CO_2 reactivity residue reaches a maximum (Figure 1), while reactivity loss and dust are at a minimum (Figures 2, 3).

During the baking of green anodes, some sulphur is released from the anodes [5, 6, 7]. This process – known as desulphurization of anodes – has been found to be dependent on the baking temperature and soaking time of anode baking. The sulphur is released mainly from the calcined petroleum coke. Many of the calcined petroleum cokes produced today are from sour crudes, which have higher sulphur content and higher levels of metallic impurities. During calcination of green coke, there is desulphurization as well as destabilization of the bonds between carbon and sulphur atoms [8]. The degree of desulphurization and destabilization of carbon-sulphur bonds depends on the coke calcination temperature and the residence time inside the calciner kiln. The sensitive, destabilized bonds between carbon and sulphur in calcined petroleum coke are prone to break further during the anode baking process, thus leading to further desulphurization of the anodes. The higher the sulphur content in the coke, the higher is the degree of coke desulphurization [9, 10]. The desulphurization increases the permeability as well as the chemically reactive surface area of anode [11].

Increased anode permeability encourages percolation of CO_2 into anodes due to the hydrostatic pressure of the CO_2 gas layer at the bottom surface of the anodes in the pots [12]. The percolated CO_2 reacts with carbon to produce carbon monoxide. This reaction – known as the Boudouard reaction – is favoured at pot operating temperatures of 960 °C. It is also well known that sulphur acts as an inhibitor to the Boudourd reaction [13]. However, in the absence of sulphur atoms due to desulphurization of the anodes, the Boudourd reaction is favoured.

The above could explain the drop in CO_2 reactivity residue of anodes as the baking level is increased beyond a certain level.

Air reactivity residue, loss and dust are also influenced by the difference in reactivities of base coke and pitch coke, and by the increase in reactive surface area available for reaction with atmospheric oxygen. The air reactive residue increases as the baking level increases because of the decrease in the difference between the real densities of base coke and pitch coke. However, after reaching a peak value, the residue begins to drop. This indicates that the adverse impact of the increase in reactive surface area due to desulphurization is greater than the positive impact of the reduced difference between the base coke and pitch coke real densities.

At a baking level corresponding to a real density value of 2.08 g/cm^3, air reactivity residue reaches a maximum (Figure 4) while reactivity loss and dust are at minimum values (Figures 5, 6).

It is seen that both CO_2 reactivity and air reactivity residues gradually increase as the baking level increases. After reaching peak values at a baking level corresponding to 2.08 g/cm^3, the reactivities decrease as the baking level is raised. It is interesting to note that both reactivities are at minimum values at the same baking level.

Reactivity residues are at maximum and reactivity losses are at minimum at the baking level corresponding to real density of 2.08 g/cm^3. Baking the anodes below or above this baking level is not desirable because of the higher levels of both CO_2 reactivity and air reactivity of anodes.

The NCC in pots is influenced by the reactivity residues (Figures 10, 11). The higher the reactivity residue, the lower is the NCC [7]. At optimum baking level, the anode reactivity residues are at maximum values, therefore NCC will be low.

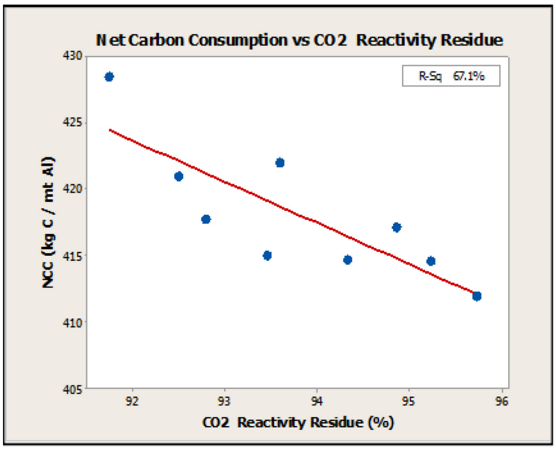

Figure 7. NCC vs. CRR.

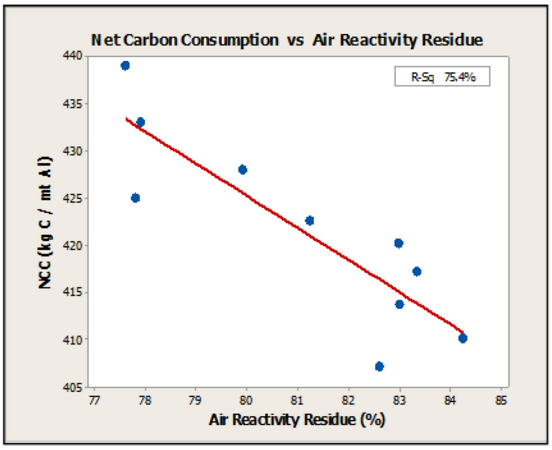

Figure 8. NCC vs. ARR.

Analysis of the data shows that baking the anodes till they reach a real density of 2.08 g/ cm^3 is beneficial. Baking levels higher than this are not value additive. Baking levels lower than these levels are detrimental in terms of anode reactivity.

Baking anodes made with cokes of real density above 2.08 g/cm^3 necessitates baking at high temperatures. High baking temperatures lead to increased desulphurization of anodes, in turn leading to degradation of the anode reactivities and higher NCC. The degradation of anode reactivities is significant after the real density value of 2.08 g/cm^3. To avoid baking the anodes beyond this level, it may be said that the green cokes should not be calcined beyond the level of 2.08 g/cm^3 real density.

Using low real density cokes as the base cokes could be a desirable option [14, 15] to ensure pitch coke reactivity is at the same level of main coke reactivity and to prevent preferential oxidation of pitch coke. Green cokes calcined at lower temperatures yield low real density calcined cokes with reduced desulphurization and low instability of carbon to sulphur bonds. Analysis of plant data of nearly three years indicates that anodes made with cokes of real density below 2.08 g/cm^3 must also be baked to a level that yields anode real density of 2.08 g/cm^3, to get maximum benefit in terms of reactivity. This ensures a sufficiently large window to equalize the reactivity of pitch coke with that of base coke. These anodes made with low real density cokes are also likely to desulphurize to a lesser extent during baking, because of reduced destabilization of bonds between carbon and sulphur during green coke calcination. Anodes that have not been desulphurized, and with reactivities of both pitch and base coke phases being nearly the same, are expected to have low chemical reactivities, reduced secondary carbon consumption in the pots, and therefore lower NCC.

By limiting the baking of the anodes to a level not higher than that which corresponds to real density of 2.08 g/cm^3, there can also be savings in fuel consumption and increased refractory flue wall life of baking furnaces.

5. Conclusions

- CO_2 reactivity and air reactivity residues of baked anodes increase as the baking level is increased to the level corresponding to anode real density of 2.08 g/cm^3. These parameters are at maximum values at this baking level.
- Above the level of baking corresponding to anode real density of 2.08 g/cm^3, there is deterioration in anode reactivities because of desulphurization and increased reactive surface area.
- A baking level corresponding to anode real density of 2.08 g/cm^3 may be considered as optimum for baking carbon anodes. Anodes baked to this level have maximum reactivity residues and minimum NCC.
- When cokes of real densities higher than 2.08 g/cm^3 are used, there is no gain in anode reactivity residues; therefore no drop in net carbon consumption is expected.
- There is gain in anode reactivities if cokes of real densities lower than 2.08 g/cm^3 are used. However, to obtain best reactivity residues, these anodes must be baked till the anode real densities reach 2.08 g/cm^3.

6. References

1. S.S. Jones and R.D. Hildebrandt, Anode Carbon Reactivity, Light Metals 1974, pp 901-932.
2. C. Dreyer, Anode Reactivity: Influence of the Baking Process, Light Metals 1989, pp 595-602
3. F. Chevarin, L.Lemieux, D. Ziegler, M. Fafard and H. Alamdari, Air and CO_2 Reactivity of Carbon Anode and Its Constituents: An Attempt to Understand Dusting Phenomenon, Light Metals 2015, pp 1147-1152.
4. B. Coste and J.P. Schneider. Influence of Coke Real Density on Anode Reactivity Consequence on anode Baking, Light Metals 1994, pp 583-591.
5. L. C. Edwards, K. J. Neyrey and L. Lossius, Coke and Anode Desulfurization, Light Metals 2007, pp 895-900.
6. H. Abbas, K. Khaji and D. Sulaiman, Desulphurization Control during Baking: Its Impact on Anode Performance and Operational Cost – ALBA’s Experience, Light Metals 2010, pp 1011-1014.
7. K. Khaji and M. Al Qassemi, Factors Influencing Baked Anode Properties, Light Metals 2015, pp 1135-1141.
8. C. Dreyer, B. Samanos and F. Vogt, Coke Calcination Levels and Aluminum Anode Quality, Light Metals 1996, pp 535-542.
9. S.S. Jones and R.D. Hildebrand and M.C. Hedlund, Influence of High-Sulphur Cokes on Anode Performance, Light Metals 1979, pp 553-574.
10. F. Vogt, K. Ries and M. Smith, Anode Desulfurization in Baking, Light Metals 1995, pp 691-700.
11. C. Dreyer, B. Samanos and F. Vogt, Coke Calcination Levels and Aluminum Anode Quality, Light Metals 1996, pp 535-542.
12. B.A.Sadler and S.H.Algie, A Porosimetric Study of Sub-Surface Carboxy Oxidation in Anodes, Light Metals 1991.
13. S.M.Hume, W.K.Fischer, R.C.Perruchoud, J.B.Metson and R.T.K.Baker et al, Influence of Petroleum Coke Sulphur Content on the Sodium Sensitivity of Carbon Anodes, Light Metals 1993
14. J. Lhuissier et al, Use of Under Calcined Coke for the Production of Low Reactivity Anodes, Light Metals 2009
15. D. Sulaiman and R. Garg, Use of Under Calcined Coke to Produce Baked Anodes for Aluminium Reduction Lines, Light Metals 2012, pp 1147-1151