Light Metals 2012 *Edited by: Carlos E. Suarez*
TMS (The Minerals, Metals & Materials Society), 2012

USE OF UNDER CALCINED COKE TO PRODUCE BAKED ANODES FOR ALUMINIUM REDUCTION LINES

Daniel Sulaiman, Rajesh Garg

Aluminium Bahrain, P.O.Box 570, Manama, Kingdom of Bahrain

Keywords: Low Real Density Coke, Under Calcined coke, Anode Performance, Anode Reactivity

Abstract

Anodes produced using under calcined coke (or Low Real Density Coke) are reported to have less and homogeneous reactivity of all anode components following baking, which results in lower carbon consumption and less carbon dust in pots. Increased butt thickness due to lower carbon consumption provides opportunity for amperage creep in Reduction lines. Aluminium Bahrain (Alba) has unique arrangement of an in-house coke calcining operation with carbon plants for anode manufacturing. This gives Alba an added advantage of lower fuel consumption in calciner on use of under calcined coke for anode production. Alba used this opportunity and a trial batch of under calcined coke was produced at calciner with lower Real Density of 2.04 g/cm^3. Anodes manufactured using this under calcined coke was tested in a trial group of pots for 3-anode cycles. This paper discusses the quality of anodes produced using under calcined coke and their performance in pot rooms.

Introduction

Alba is an 870,000 MT/year aluminium smelter operating at Bahrain, Middle East. Its line 4 and line 5 pots presently operate at 340 and 350 kA current. The pot lines 4 and 5 are based on AP-30 smelter technology and use prebake anodes. The green anodes are made using vibro-compactors, baked in open top horizontal flue kilns, sealed with 6-stub yokes in rodding plants and delivered to pot rooms.

For a given dry aggregate composition of green anodes, pitch content in green anodes is determined by using the well known "dry density test" method. The green anodes are baked according to a baking curve using state-of-the-art heat regulation system. The peak flue wall temperature during anode baking is determined to achieve anode baking level with real density of baked anodes equal to or higher than coke real density by 0.02 g/cm^3.

Excess consumption of anodes used for aluminium production mainly occurs through attack by O_2 and CO_2 in the cells. Earlier papers presented at TMS provided some preliminary studies and results on the use of under calcined coke to reduce the reactivity of carbon anodes. This paper provides an update on the use of under-calcined coke in Alba smelter by comparing under calcined coke performance with standard calcined coke performance at following 3 stages:

- Green anode production
- Baked anode production
- Anode performance in pot room, evaluated through Net carbon consumption test and pot performance

Coke properties of low RD coke (under calcined coke) are also compared with normal RD coke (Standard calcined coke).

Definitions

The range of calcination level of cokes, measured by the real density (RD) and the Crystal Height (L_c), commonly used in the aluminium industry can be divided into 3 categories (Density expressed in g/cm^3 (Figure 1):

- Under-calcined coke : RD<2.05 (L_c <25.3 Å)
- Standard-calcined coke : 2.05<RD<2.09 (25.3 Å < L_c <32.7 Å)
- Highly-calcined coke : RD>2.09 gm/cc (L_c >32.7 Å)

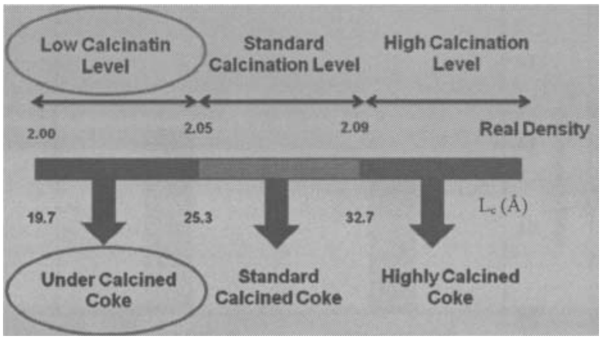

Figure 1: Explaining under calcined, standard calcined and highly calcined coke

Industrial Trial

Industrial tests were undertaken in plant. About 1000 MT of under calcined coke was produced with in-house green coke calciner facility. Properties of under calcined coke are compared with standard calcined coke in Table 1.

Table 1 : Comparison of under calcined and standard calcined coke produced at ALBA

S.N.	Particulars	Under-Calcined Coke	Standard Calcined Coke
1	Real Density (g/cm^3)	2.043	2.08
2	Apparent Density (g/cm^3)	1.735	1.739
3	L_c (Å)	25.9	28.4
4	Air Reactivity (%)	0.26	0.15
5	CO_2 Reactivity (%)	13.4	11.2
6	Sulphur (%)	2.79	2.97

- As expected, Real Density & L_c of under calcined coke was significantly lower than standard calcined coke
- CO_2 and Air reactivity of under calcined coke was higher than standard calcined coke
- Sulphur content in under calcined coke (2.79%) was slightly lower than sulphur content in standard calcined coke (2.97%)

Calciner fuel consumption: Calciner fuel consumption for under calcined coke was about 29% lower than fuel required for standard calcined coke. Calciner fuel consumption for under calcined coke reduced to 0.8 GJ/MT from 1.1 GJ/MT for standard calcined coke (Figure 2).

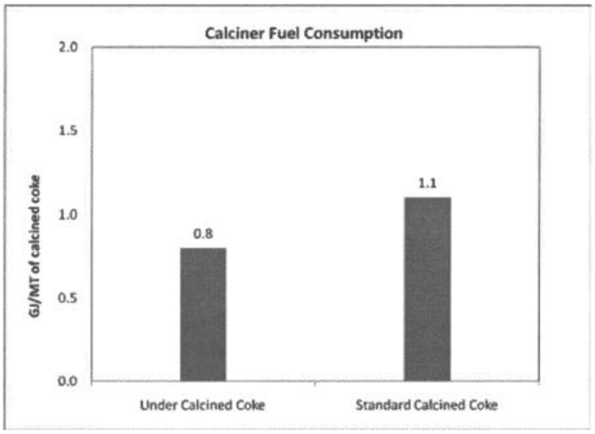

Figure 2: Calciner fuel consumption for producing under calcined coke and standard calcined coke

About 1500 anodes have been produced using under calcined coke to conduct trials in 9 pots of Alba Reduction Line-5 for 3 anode cycles. Quality of green anodes produced using under-calcined coke is compared with quality of green anodes produced using standard calcined coke under similar conditions in Table 2.

Green anode density & Dry Density for under calcined coke was slightly lower than standard calcined coke.

Table 2 : Comparison of green anodes properties produced using under calcined and standard calcined coke

S.N.	Particulars	Under-Calcined Coke	Standard Calcined Coke
1	Green Anode Density (g/cm^3)	1.621	1.627
2	Dry Density (g/cm^3)	1.405	1.408
3	Pitch Content (%)	13.3	13.5

Green anodes produced using under-calcined coke and standard calcined coke were baked in kilns under similar conditions. Table 3 shows comparison of baking conditions and core sample analysis for under calcined and standard calcined coke anodes

Table 3 : Comparison of baked anodes properties produced using under calcined and standard calcined coke

S.N.	Particulars	Under-Calcined Coke	Standard Calcined Coke
	No of core samples	**100**	**100**
1	Peak Flue Temperature for Anode Baking (°C)	1155	1155
2	Soaking time (h)	36	36
3	Fire Cycle (h)	26	26
4	Baked Anode Density (g/cm^3)	1.584	1.592
5	Real Density (g/cm^3)	2.104	2.094
6	Crystal Height, L_c (Å)	31.5	31.6
7	CO_2 Reactivity Residue (%)	89.2	90.4
8	CO_2 Reactivity Dust (%)	2.2	1.8
9	Air Reactivity (%)	67.5	64.9

The results can be summarized as follows:

- Anodes produced using under calcined and standard calcined coke were baked at same peak temperature of 1155 °C and same soaking time of 36 h at fire cycle of 26 h
- Same L_c for anodes produced with under calcined and standard calcined coke indicates similar baking level for both types of anodes.
- While CO_2 reactivity of anodes was almost similar, Air reactivity of anodes produced with under calcined coke was slightly better than standard calcined coke (Figure 3).

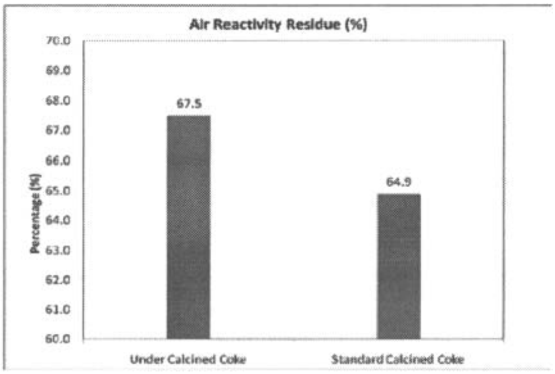

Figure 3 : Air Reactivity Residue for anodes produced with under calcined coke and standard calcined coke

Discussions

Alba's objective behind use of under calcined coke was three fold:

- Reduce calciner fuel consumption
- Improve anode reactivity to reduce carbon consumption
- Minimize negative effects of desulphurization

Reduction in calciner fuel consumption

Reduction in calcination temperature resulted in reduced fuel consumption in the calciner. Fuel consumption for under calcined coke was about 29% less than standard calcined coke. This would give Alba annualized saving of USD 0.22 million on full implementation.

Improve anode reactivity to reduce carbon consumption

Anode reactivity determines the larger part of the excess carbon consumption. For more than 50 years it has been known that excess consumption occurs mainly from either direct oxidation of the anode by oxygen (1):

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

This reaction mainly concerns the top of the anode, which may be in contact with the ambient air. Or oxidation of the anode by carbon dioxide gas, according to Boudouard's reaction (2):

$$C + CO_2 = 2\,CO \qquad (2)$$

This reaction occurs in the pores of the anodes or on the grains of carbon dust floating in the bath. These grains of are themselves the results of preferential oxidation of binder matrix (pitch coke +dust) according to same reaction as binder matrix is more reactive than the anode coke grains [1]. During baking of an anode, the carbon constituents undergo a re-organization of structure resulting in a decrease in anode reactivity. The traditional approach has been to provide sufficient heat treatment during anode baking to achieve Real Density of the anode just above the Real density of the calcined coke. 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 low RD coke (Under calcined coke) and traditional baking temperature level, there is common transformation of coke and binder phases during the baking process. This results in a lower difference of reactivity between two phases. A more homogeneous product, with no components preferential consumed and with a lower dusting tendency is produced [2].

In order to minimize difference in reactivity of coke and binder matrix under calcined coke is being tried by several plants. The more under calcined coke is the better the coke pitch contact, results in improvement in anode reactivity. But comparison of core sample analysis of under calcined coke and standard calcined coke shows that while air reactivity of under calcined coke (67.5%) was better than air reactivity of standard calcined coke (64.9%), CO_2 reactivity of both type of coke was similar.

Minimize negative effects of desulphurization

During calcination, petroleum coke desulphurises depending upon the sulfur content and final temperature. This has a negative effect on coke properties such as reactivity, porosity and real density. Additional sulphur loss occurs during anode baking and this can further deteriorate anode properties such as baked density and reactivity. Globally there is increase in sulphur content of cokes used by smelters. High sulphur cokes are more prone to desulphurization during anode baking compared to low sulphur coke.

Under calcined coke also minimizes negative effects of desulphurization in anodes baking. At high coke calcination level desulphurization gets started and one of the consequences of desulphurization during calcining is increased anode desulphurization during baking process.

Peak flue wall temperatures and high soaking time in kilns are sufficient to promote desulphurization from a structure already disrupted during coke calcining[3].

Sulphur content in Alba calcined coke is in the range of 2.5-3.0%. Alba also used coke with sulphur content more than 3.0% several times in past. Use of high sulphur calcined coke for anode production resulted in anode desulphurization during anode baking causing environmental and anode quality issues. So desulphurization is also one of the issues that could be tackled by increasing use of under calcined coke.

Under Calcined Coke's Anode Performance in Pot room

1500 baked anodes produced using under calcined coke were set on 9 trial pots in Alba Line-5 for 3 anode cycles and net carbon consumption was determined. Pot performance parameters were also recorded for 9 trial and 9 control pots for comparison. Table-4 shows comparative performance of anodes produced using under calcined coke and standard calcined coke

The results can be summarized as follows:

- Net carbon consumption for anodes using under calcined coke was 2.5-3.0 kg/MT Al lower than, net carbon consumption for anodes produced using standard calcined coke (Figure 4).

Table 4 : Comparison of performance of pots using under calcined and standard calcined coke

S.N.	Particulars	Under-Calcined Coke	Standard Calcined Coke
	No of butts samples measured	**360**	**180**
1	Net Carbon Consumption (kg/MT of Al):		
	Anode Cycle 1	411.8	414.6
	Anode Cycle 2	411.5	414.6
2	Avg. Volts/Pot	4.115	4.117
3	Instability	0.052	0.051
4	AE's/Pot day	0.14	0.13

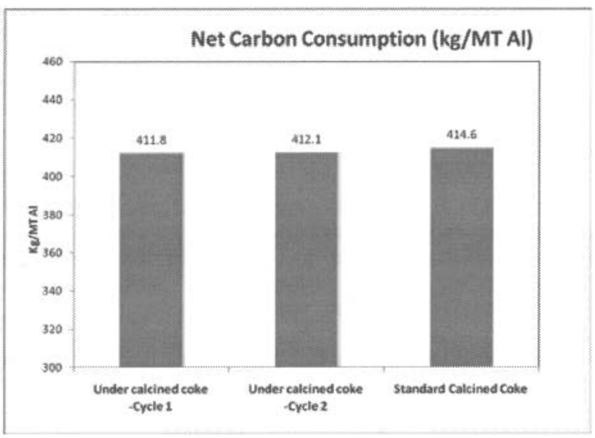

Figure 4: Net Carbon Consumption for anodes produced with under calcined coke and standard calcined coke

- Pots performance parameters Avg Volts/pot, Instability and anode effects for trial pots using under calcined coke anodes and control pots using standard calcined coke anodes were almost similar (Figures 5,6&7)

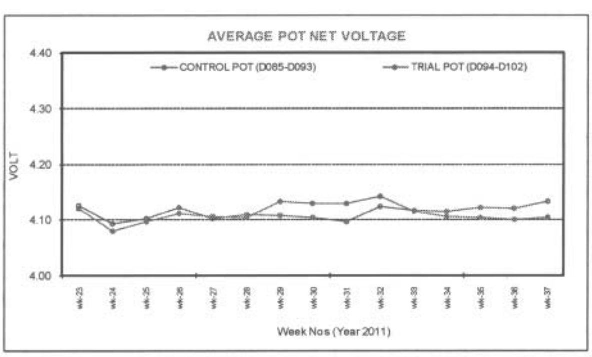

Figure 5: Average pot voltage for trial pots using under calcined coke anodes and control pots using standard calcined coke anodes

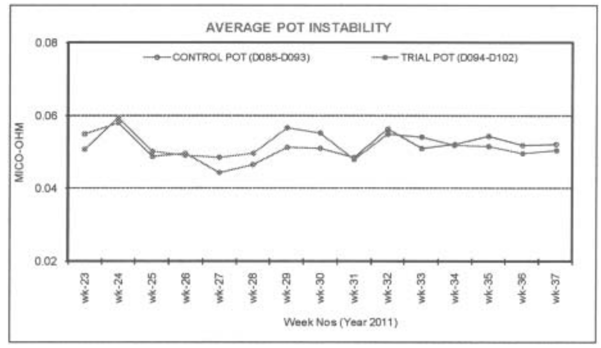

Figure 6: Pot instability for trial pots using under calcined coke anodes and control pots using standard calcined coke anodes

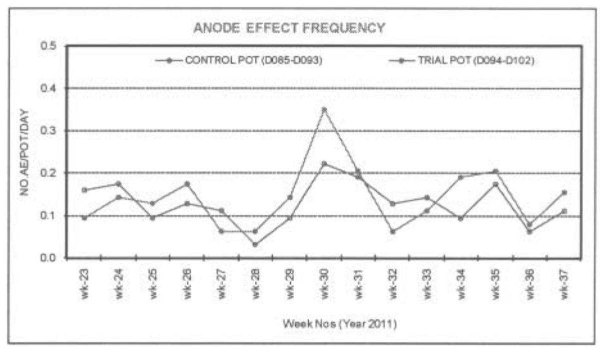

Figure 7: AE Frequency for trial pots using under calcined coke anodes and control pots using standard calcined coke anodes

Conclusions

Comparison of anode properties as indicated by core results for trial batch of anodes produced using under calcined coke and standard calcined coke shows that anode reactivity with under calcined coke is better than for anodes made with standard calcined coke. Net carbon consumption for under calcined coke anodes was also slightly lower compared to standard calcined coke. A reduction in coke calcination temperature is favorable to anode reactivity. The results obtained up to now through the small scale industrial trial are encouraging and appear to confirm the laboratory results.

Combining all above results and considering significant reduction in calciner fuel consumption by producing under calcined coke, it is proven now that with use of under calcined coke Alba can reduce calciner fuel consumption by 29% without any adverse effect on baked anode quality and anode performance in pot rooms.

It is necessary to continue trial for longer time and with greater decrease in coke calcinations level in order to determine the optimum coke calcination level. This will also help to study the impact of low RD coke on anode desulphurization during anode baking

References

1. Bernard Samanos and Christian Dreyer, *"Impact of Coke Calcination Level and Anode Baking Temperature on Anode Properties"*, Light Metals 2001,

2. Jeremie, Lailah, Magali, Marie-Josee, *"Use of Under Calcined Coke For the Production of Low Reactivity anodes"*, Light Metals 2009

3. Les Charles Edwards, Keith J Neyrey, Lorentz Petter Lossius, *A review of coke and anode desulfurization*, Light Metal 2007