Influence of Coke Calcining Level on Anode Real Density, L_C and Other Properties Using a Constant Baking Cycle

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Abstract

Real density (RD) and crystallite size (L_C) are common measures to control coke calcination levels. They are also measured routinely on anode core samples as a means of tracking anode baking levels. Many anode producers target anode RD levels which are at least 0.02 g/cm^3 higher than the calcined petroleum coke (CPC) RD to minimize differential reactivity between the CPC and binder derived carbon. Depending on the calcining process parameters and technology, coke RD and L_C can vary significantly. Shaft CPC often shows a higher RD and L_C than rotary kiln CPC due to the longer residence times. Coke blends with CPC having different RD and L_C values are now regularly used by aluminum smelters. This paper reports on the results of pilot anode studies to evaluate the impact of the starting CPC RD and L_C on final anode RD, L_C and other properties such as specific electrical resistivity and carboxy reactivity.

Keywords

Pilot anode testing • Anode baking • Coke L_C • Anode L_C

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Introduction

To control the calcination level of calcined petroleum coke (CPC) during production, real density (RD) and crystallite size (L_C) are key measures for coke calciners [1]. For rotary kiln calcined coke, calcination levels typically range from an RD of 2.04 to 2.07 g/cm^3 and L_C of 24 to 29 Å. Due to the different technology of a shaft calciner, the residence times are much longer, and it is not uncommon to see shaft calcined product with a higher RD (2.07–2.10 g/cm^3) and L_C (30–35 Å). As a result, blends of cokes having different RD and L_C are regularly used by aluminum smelters to produce carbon anodes.

In order to produce anodes with acceptable quality for aluminum production, the anode baking process is critical. It serves several important functions:

1. Converts the pitch material used as a glue to bind coke and butts particles into a solid, semi-graphitic form of carbon with good electrical conductivity.
2. Increases the mechanical strength of the anode block so it can be handled and rodded and does not suffer damage when undergoing the rapid heat-up that occurs in the electrolysis cell.
3. Reduces the reactivity of the binder derived carbon so that it is at least as low and preferably lower than the matrix carbon, i.e. CPC and butts.

The last point, in particular, is important for avoiding differential reactivity between the binder and the matrix carbon which is considered an important factor to reduce dusting problems in the electrolysis cell. To achieve this, the anode must be baked to a sufficiently high level so that it exceeds the initial calcining level of the CPC.

Smelters generally control anode baking levels by setting a target firing curve which includes a final target peak firing temperature as measured in the fluewalls. This is a real time, process control variable that should always be used to

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control heat-up rates during the critical period of pitch volatile emissions. Many smelters also record the final end-of-bake temperatures at several standard pit locations within the baking furnace section to ensure that anodes are baked above a minimum target temperature level. The equivalent temperature (T_{Eq}) method, as described in [2], is another method to determine the baking level which is successfully practiced by some smelters. It is helpful for monitoring the combined impact of the final baking temperature and duration of heat treatment (particularly soaking time) on baking levels but requires significantly more effort and is not a real-time measurement. Usually it is mainly used as a methodology to calibrate firing curves for a particular baked furnace design and pit loading configuration.

Another way to track or infer baking levels is through analysis of baked anode core samples. The industry normally uses similar measures to coke calciners by measuring the RD and L_C of anode core samples. Although measuring the L_C on anode cores can have some limitations as an indicator of baking levels, especially when trying to detect under-baked anodes [3], it is regularly used since it is a relatively simple method and the analysis techniques are usually readily available at smelters.

To ensure a reasonable match in reactivity between the pitch derived carbon and the matrix carbon, the industry has developed some experience and “rules of thumb” over the years. For example, it is common to target an RD in the anode that is at least 0.02 g/cm^3 higher than the original coke RD [4]. For the measurement of anode L_C, values above a crystallite size of around 29 Å are generally seen as a reasonable baking level, but most modern smelters are targeting anode baking levels in the range of 30–35 Å today.

During a carbon plant audit undertaken by Rain Carbon in 2017, a question was raised about the impact of the initial coke calcining level (L_C) on the final L_C of the baked anode. At this particular smelter, the anode L_C showed a general downwards trend that was attributed to a decrease in the coke L_C rather than being a result of a gradual decrease in anode baking levels. The question was raised whether the gradual decrease in anode L_C was raw material related or driven by maintenance or operational problems with the baking furnace. The smelter clearly wanted to avoid the risk of under-baking anodes which can ultimately lead to dusting problems.

This study aims to follow up on this question using well-controlled pilot anode testing. The goal was to understand how the starting coke RD and L_C affect the final anode RD and L_C. Baking levels were controlled by both final temperature measurements and via the T_{Eq} method. In addition, the study was also intended to provide clarity on the question of whether CPC specific electrical resistivities influence anode electrical resistivities. Previous studies have shown no correlation [5], but this question still gets asked frequently by anode producers.

Experimental

General Overview

A key part of the study was to select a single source coke and then industrially calcine to four different levels. The intention was to generate coke samples with a good spread across regular RD and L_C levels and with one sample exceeding the regular range. Cokes produced at the four calcining levels were then used for production of four individual sets of pilot anodes, with varying binder levels in the range of 14–15% with 0.5% increments. The resulting pilot anode sets were all baked to the same level, a T_{Eq} of 1250 °E, which can be considered a moderate minimum baking level.

In a second block of work, four additional anodes were produced at the optimum binder level of 14.5% and then baked to an elevated level of 1280 °E. The properties of these anodes were also evaluated. Special attention was given to the development of the anode RD and L_C with respect to the initial coke RD and L_C.

Raw Materials

CPC

A single source coke with ~2% sulfur (Coke S) was used for the majority of the work reported in this study. The coke was produced and sampled during an industrial scale plant trial. This straight-run low S coke was selected to avoid the complication that can occur when calcining a blend of cokes with different sulfur levels.

During the trial, Coke S was calcined to four different levels as shown by the RD and L_C results which are included together with the general coke properties in Table 1. The samples show an L_C spread from 25 to 32.5 Å and RDs ranging from 2.056 to 2.096 g/cm^3.

As a cross-check, some additional testing was then done on a regular CPC blend coke with an average S level of 2.8% (CPC Blend). Only selected results from these later trials will be reported. In this case, a range of different calcining levels were achieved by re-calcining industrially produced coke in a laboratory furnace at successively higher final calcination levels. An abbreviated set of results for the Blend Coke are shown in Table 2.

With reference to Table 1 for Coke S, as the coke calcining level increases, the specific electrical resistivity (SER) decreases due to the higher degree of orientation and crystallite growth during calcination, making the material more electrically conductive. Vibrated bulk densities (VBDs) were determined using an 8 × 14 Tyler mesh (1.2–2.4 mm); which is an internal VBD procedure commonly referred as the Kaiser VBD method (KVBD). VBDs were also measured via the ASTM D4292 VBD procedure (ASTM VBD). The VBDs

Table 1 Properties of CPC and butts used

Test	Standard	Unit	Coke S				Butts
			CL1	CL2	CL3	CL4	
L_C	ASTM D5187	(Å)	25.3	27.1	29.4	32.5	30.6
RD	ASTM D2638	(g/cm^3)	2.056	2.064	2.080	2.096	2.061
SER	GLC C-12A	(Ω in.)	0.041	0.04	0.037	0.036	
KVBD (8 × 14)	ASTM D4292	(g/cm^3)	0.794	0.769	0.800	0.813	0.877
ASTM VBD (28 × 48)	ASTM D4292	(g/cm^3)	0.901	0.885	0.893	0.901	0.935
XRF							
Ni	ASTM D6376	(ppm)	158	163	163	163	144
Fe	ASTM D6376	(ppm)	192	204	212	238	784
V	ASTM D6376	(ppm)	211	214	220	224	241
S	ASTM D6376	(%)	1.95	1.95	1.97	2	2.13
Si	ASTM D6376	(ppm)	155	140	145	173	272
Ca	ASTM D6376	(ppm)	57	57	51	74	211
Na	ASTM D6376	(ppm)	122	136	119	143	115

Table 2 Selected results from higher sulfur blend coke

Test		Unit	Blend coke				
			CL1	CL2	CL3	CL4	CL5
L_C	ASTM D5187	(Å)	26.0	28.1	30.0	32.8	36.5
RD	ASTM D2638	(g/cm^3)	2.052	2.071	2.083	2.093	2.096
SER	GLC C-12A	(Ω in.)	0.0426	0.0397	0.0374	0.0354	0.0337
XRF							
S	ASTM D6376	(%)	2.78	2.87	2.89	2.89	2.76
V	ASTM D6376	(ppm)	320	329	336	329	339
Ni	ASTM D6376	(ppm)	195	196	196	194	196

of the cokes vary somewhat and this is not unusual during industrial production. The coke labeled CL2 shows the lowest value. These differences are attributed to normal variation in the green coke volatile matter and particle size. The kiln was held at each calcination level for a relatively short time period (several hours), so the level of VBD variation is higher than typically seen in 24-h, daily production samples.

In terms of RD, CL1 and CL2 correspond to regularly used quality whereas CL3 would represent an elevated level and CL4 is a very high calcining level with a real density close to 2.10 g/cm^3.

Data is also included for the butts material used in all the pilot anode tests, which is actually baked anode scrap from an anode plant with a very low Na level. For the Blend Coke, an additional higher calcining level was added to give an L_C range of 26–36.5 Å and a real density range of 2.052–2.096 g/cm^3.

Pitch

For the binder pitch, a 112M Mettler straight run vacuum distilled pitch was used. Binder properties are shown in Table 3.

Table 3 Binder properties

			CTP 112M
Softening point Mettler	DIN 51920	(°C)	112.0
Coking value (Alcan)	DIN 51905	(%)	57.6
Toluene insoluble	DIN 51906	(%)	25.7
Quinoline insoluble	DIN 51921	(%)	5.1
Ash (800 °C)	DIN 51922	(%)	0.17

Pilot Anode Preparation

Dry Recipe

The dry aggregate recipe is shown in Fig. 1. This follows an industrial recipe but the top particle size was limited to 8 mm to minimize crushing in the Eirich intensive mixer. To ensure tight control on particle size variations, the recipe consists of 6 fractions and 2 different size butts fractions in the range of 1.7–8 mm. The CPC material prepared for each fraction was homogenized, using a rotary splitter to ensure a consistent granulometry throughout the trials.

The CPC fines were milled to 45% below 32 µm with control via laser particle size analysis. The Blaine Index of the ball mill fines used for the pilot anodes produced for the study was ∼4500.

Pilot Anode Production Procedure

5.5 kg of the dry aggregate was preheated to the mixing temperature, transferred to a preheated 10 L Eirich mixer (RV02/E) and homogenized for 1 min. The liquid binder was preheated to a temperature 100 °C above the SPM and added after 1 min of dry mixing. The anode paste was mixed for 10 min at 68 °C above the SPM of the binder. After mixing, the paste was cooled to 20 °C above the SPM, transferred into a preheated pilot anode press and subsequently pressed at 42 MPa for 1 min. Typical green anode sizes are: diameter 146 mm; height 190–200 mm; weight 5.2–5.5 kg.

The green anode was removed, cooled to ambient temperature and the green apparent density was calculated. Anode batches were baked to an equivalent temperature of 1250 °E/1280 °E. The equivalent temperature method (T_{Eq}), takes into account temperature as well as time and is described in more detail in [2]. After baking, the anode weight and physical dimensions were measured to calculate the shrinkage and baking loss. Three 50 mm Ø cores were drilled per anode.

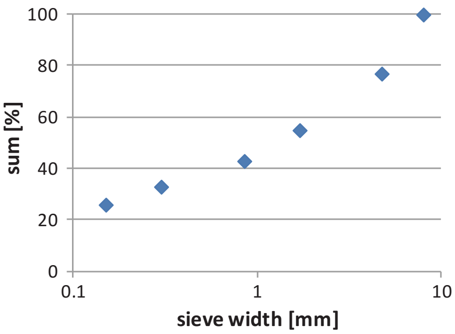

Fig. 1 Particle size distribution of aggregate recipe (cumulative for through fraction)

Core Analysis

The cores were analyzed according to R&D Carbon standard procedures [6]. Baked apparent density (BAD), specific electrical resistivity (SER), CO_2 reactivity, air permeability, flexural strength, compressive strength, and elasticity modulus of the resulting core samples were measured. For brevity, mechanical property results are not included but they all fell within typical industry ranges. In addition, anode L_C, RD, SER and chemical analysis results were measured on multiple samples in the Rain Carbon Lake Charles lab.

A more detailed overview of the equipment used for pilot anode preparation can be found in [7].

Results and Discussion

Pilot Anode Properties

In the following section, results of the evaluation of the pilot anode cores produced from Coke S at the different calcination levels are discussed with respect to key parameters like baked apparent density (BAD), SER as well as other baking related core parameters like L_C and RD.

Baked Apparent Densities

Baked apparent density curves of the anodes baked to 1250 °E are shown in Fig. 2a, with densities ranging between 1.598 and 1.612 g/cm^3. They are in good accordance with the VBD data especially KVBD of the base coke (Table 1). A similar trend can be seen for the set of pilot anodes with a 14.5% binder level baked to 1280 °E (Fig. 2b). Direct comparison of the BADs between the baking runs to 1250 and 1280 °E at 14.5% binder content suggest slightly higher densities for CL1–CL3 at the higher baking level but comparable densities for CL4 at both baking levels. Overall, it can be said that densities mainly vary according to initial CPC quality and binder level. Air permeabilities of the respective pilot anodes range between 0.3 and 0.5 nPm.

SER of Coke and Anodes

The higher the coke calcination level, the lower the coke SER was; which is shown very clearly in Table 1. Figure 3 shows the specific electrical resistivity curves of the pilot anodes produced from cokes CL1–CL4 calcined to different temperatures. They show no correlation between the initial SER of the coke and the SER measured on the anode sample. The pilot anodes produced from the lowest coke calcining level, coke CL1, showed the lowest anode SER results for 14.0 and 14.5% binder level. This is the opposite of what would be expected if there was any relationship between coke SER and anode SER. The SER range for the baking runs at 1280 °E was lower for all anodes (CL1–CL4)

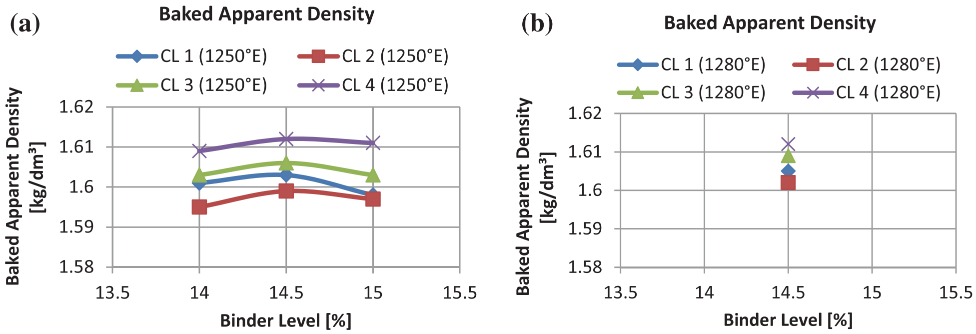

Fig. 2 Pilot anode baked apparent densities (coke S) **a** baking run to 1250 °E and **b** baking run to 1280 °E

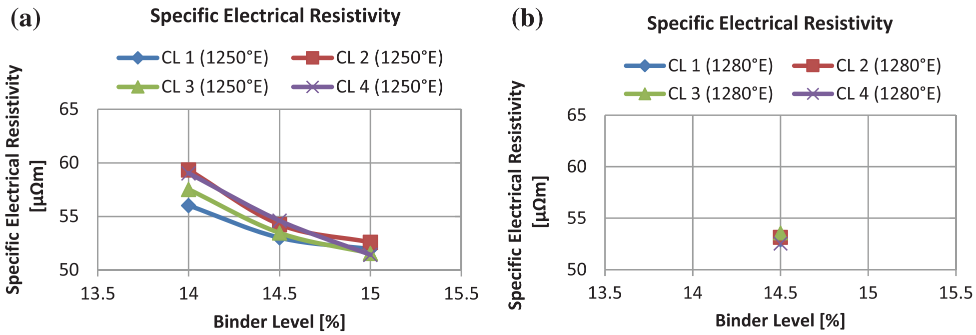

Fig. 3 Pilot anode SERs (coke S) **a** baking run to 1250 °E and **b** baking run to 1280 °E

and slightly lower than the 1250 °E results as expected due to the higher level of baking.

Anode L_C

As indicated in the introduction, the primary focus of this study was to look at the relationship between the anode L_C and RD and the starting CPC L_C and RD. The butts L_C is considered constant in the dry aggregate. Table 4 shows the theoretical average dry aggregate L_C, which is calculated as the weighted average of the L_C of the coke (80 wt%), and the butts (20 wt%). The same method is applied to calculate the aggregate RD in Table 4.

Figure 4 shows the development of the anode L_C as a function of the dry aggregate L_C for Coke S. The anode L_Cs in this case are the averages of the results for the pilot anodes made and baked to the respective temperature for each coke calcining level. The results show that a higher initial dry aggregate L_C yielded a higher anode L_C under constant baking conditions at the lower anode baking level of 1250 °E. For the higher baking trials level at 1280 °E, the anode L_Cs also increased but the difference between the CL1 and CL3 anodes was much lower compared to the range for the 1250 °E baking level. This suggests that a robust anode baking level decreased anode L_C differences between differently calcined cokes (CL1–CL3). The impact of the coke calcining level on the final anode L_C is therefore less significant when the anodes are baked to higher temperatures. At both baking levels however, the pilot anodes produced with coke at the highest calcination level (CL4), showed a significantly higher final anode L_C.

Another way to look at the data is to calculate the difference between the anode and dry aggregate L_C as shown in Fig. 5. This shows quite clearly that the anode L_C increase was lower when the starting coke was calcined to a higher level. During baking at 1250 °E, the L_C of the CL4 anodes showed almost no increase over the starting CPC L_C. At the

Table 4 Theoretical average of dry aggregate L_C and RD generic for coke S

	Coke S		Butt		Theoretical average dry aggregate	
	L_C (Å)	RD (g/cm^3)	L_C (Å)	RD (g/cm^3)	L_C (Å)	RD (g/cm^3)
Dry aggregate CL1	25.3	2.056	30.6	2.061	26.4	2.057
Dry aggregate CL2	27.1	2.064	30.6	2.061	27.8	2.063
Dry aggregate CL3	29.4	2.080	30.6	2.061	29.6	2.076
Dry aggregate CL4	32.5	2.096	30.6	2.061	32.1	2.089

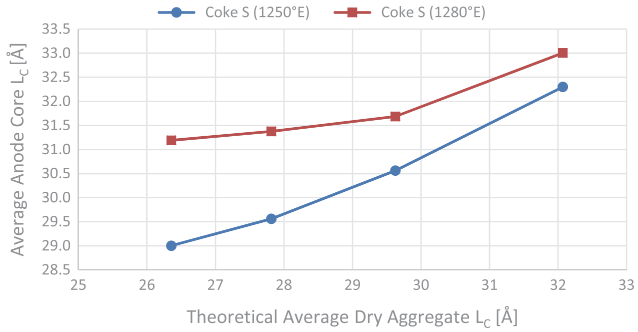

Fig. 4 Average anode core L_C versus theoretical average dry aggregate L_C for two baking levels

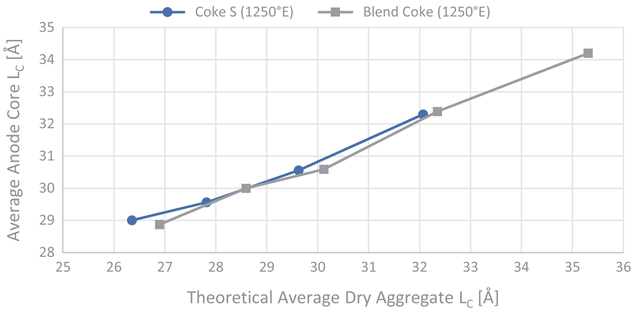

Fig. 6 Comparison of average anode core L_C versus theoretical average dry aggregate L_C for coke S and blend coke at 1250 °E baking level

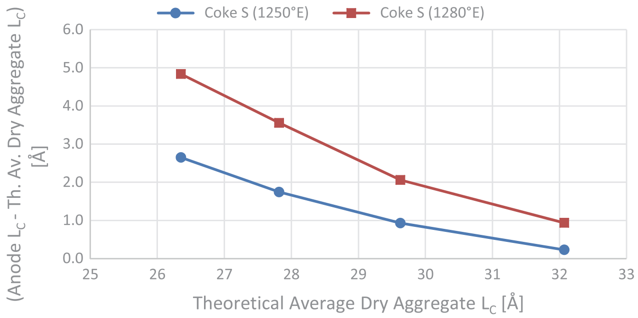

Fig. 5 Difference between anode L_C and theoretical average dry aggregate L_C versus theoretical average dry aggregate L_C for two baking levels

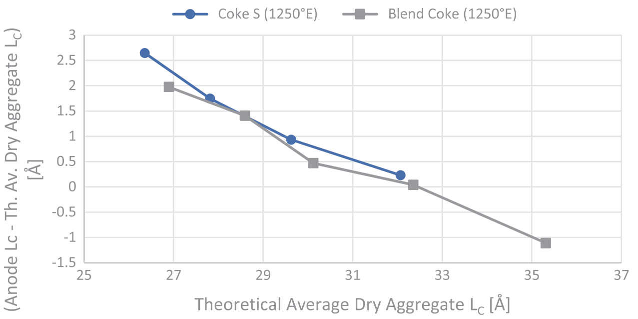

Fig. 7 Comparison of difference between anode L_C and theoretical average dry aggregate L_C versus theoretical average dry aggregate L_C for coke S and blend coke at 1250 °E baking level

higher baking level of 1280 °E, the L_C was also relatively small at 0.9 Å.

These results demonstrate quite clearly that the CPC and binder derived carbon in the anodes undergo a more significant increase in L_C at all baking levels when coke is calcined to lower levels. This is somewhat intuitive, but the data strongly supports this. In several previous papers on "under-calcined" coke [8, 9], data are presented to show that it is better to bake the CPC and the pitch derived carbon to a higher level than the starting CPC. The work in this study showed quite clearly that the rate of anode L_C increase was much greater for cokes calcined at a lower level, even at modest baking levels (1250 °E).

Figures 6 and 7 show similar data to Figs. 4 and 5 for a 1250 °E baking level but with the Blend Coke data added by way of comparison. The similarity in the curves for the anode L_C development with an entirely different CPC blend is quite remarkable. In this case however, an even higher final coke calcination level is included which further increases the anode L_C. The final data point for the Blend Coke shows that the anode L_C never reaches the coke L_C so it is quite clear the binder derived carbon does not achieve the same calcination level as the starting CPC.

Anode RD

Similar curves to Fig. 4 with coke RD versus anode RD for Coke S are shown in Fig. 8. In this case, the anode RD results do not appear to correlate as well as the L_C results and the trends are not as clear. The RD of the CL1 anodes is higher than the CL2 anodes at both baking levels which was unexpected. For the other calcining levels, it seems again a higher calcination level in the coke influences the final anode RD but the effect is less distinct at the higher baking level for CL1–CL3. All the RD results fall into a relatively narrow range of 0.017 g/cm^3 which needs to be compared to the published repeatability of the RD method at 0.018 g/cm^3. Some of the differences shown above are therefore likely to be due to the repeatability limits of the method. It is interesting to note, however, that the RD for both baking levels with the CL4 coke increases more significantly than the cokes calcined at lower levels. Given the better repeatability of the L_C test (0.5 Å), this study suggests that anode core L_Cs give more reliable measurement data for baking levels versus RDs notwithstanding the starting coke L_C impact.

Figure 9 shows the difference between the anode and dry aggregate RD. For the anodes baked to 1250 °E, only the RD difference between the CL1 RD and the anode RD is