COKE AND ANODE DESULFURIZATION STUDIES

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Abstract

The sulfur level of high sulfur cokes used by the calcining industry for blending is increasing. During calcination, petroleum coke desulfurizes and the rate of sulfur loss is dependent on both the sulfur level and final temperature. Desulfurization negatively affects coke properties such as real density and porosity and additional desulfurization during anode baking can negatively affect anode properties. This paper is a follow-up to a 2007 TMS paper on desulfurization and presents the results of additional studies on anode and coke desulfurization versus equivalent baking level and discusses the effect of the level of calcination of high sulfur cokes on anode reactivity. The results indicate that the coke calcination levels must be set with coke sulfur levels in mind. It also shows that blending with high sulfur cokes need not be detrimental to anode properties.

Symbols and Abbreviations

T_{eq} Equivalent temperature in [°E] as a measure of anode baking level according to ISO 17499
L_c Average carbon crystallite height in coke in [Å] according to ISO 20203 or ASTM D5187-02
S The sulfur concentration of the cokes in [wt%] determined by XRF according to ISO 12980 – 2000
HS High sulfur level petroleum coke, $S > 3$ wt%
NS Normal sulfur level petroleum coke, $2 < S < 3$ wt%
LS Low sulfur level petroleum coke, $S < 2$ wt%

Introduction

The loss of sulfur during calcination of petroleum coke was reviewed in detail in a paper published in 2007 [1]. At temperatures above 1250°C, thermal desulfurization of coke in rotary kilns and anode baking furnaces can significantly affect coke and anode properties. This is due to the creation of microporosity in the coke structure (typically <1µm) as carbon-sulfur bonds are broken and sulfur is driven out of the structure. Desulfurization has become an important issue for calciners and anode producers as the industry moves to blending higher sulfur cokes to achieve average coke sulfur levels.

The following paper presents the results of additional studies on coke and anode desulfurization and can be considered as Part 2 of the 2007 paper. The 2007 paper provides the necessary background for this work and should be referenced for additional context. This paper presents and discusses results in four areas:

- The variation in calcining level and desulfurization as a function of coke particle size from a typical rotary kiln.
- Sulfur-loss graphs and desulfurization rates for high and low sulfur cokes heated in an anode baking furnace.
- Desulfurization of anodes produced with high sulfur coke calcined at different levels.
- Modeling of sulfur emissions from a baking furnace section.

1. Variation in Calcining Level with Particle Size

Calcined petroleum coke contains a range of particle sizes from "fines" (<250µm) to larger particles up to 20mm in size. When green (raw) coke is calcined in a rotary kiln, the coke bed tumbles and coarser particles tend to "roll" on the surface of the coke bed. The coarse coke is subjected to higher radiant heat compared to the finer coke in the center of the bed. This is depicted in Figure 1.

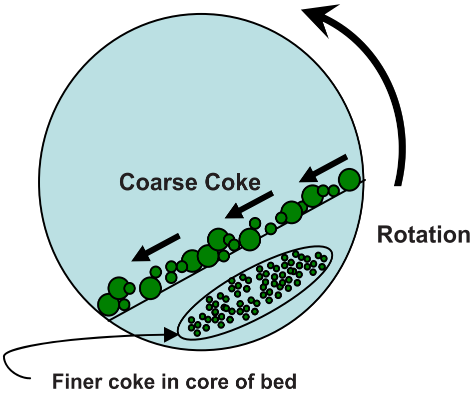

Figure 1: Coke Tumbling During Calcining

The ideal green coke feedstock for a rotary kiln is one with a good mix of coarse, medium and fine particle sizes. The coarse particles promote tumbling and mixing of the bed resulting in more uniform calcination. There will always be some variation in the degree of calcination between coarse and fine particles however, and this influences desulfurization. Coarser coke is always more highly calcined and therefore more susceptible to thermal desulfurization.

The data in Table I compares the properties of a typical calcined coke kiln product separated into three different size fractions: Coarse (+4.75mm), medium (1.70-4.75mm) and fine (<1.70mm). The properties are all measures of the degree of calcination or heat treatment where SER = specific electrical resistivity, L_c = L sub C by X-ray diffraction and RD = real density. As calcination level or temperature increases, SER decreases, L_c increases and RD decreases.

Table I. Coke Properties as a Function of Particle Size

	SER (Ω.in)	L_c (Å)	RD (g/cm^3)
Coarse	0.0360	34.3	2.070
Medium	0.0375	32.6	2.084
Fine	0.0400	30.1	2.078

Real density is the most common method used by calciners to control the degree of calcination and it is also the most common property specified by anode users. Calciners typically only measure average properties and the above shows clearly that the coarse coke is more highly calcined (as evidenced by lower SER and higher L_c) than the medium and finer size coke. The lower real density of the coarser fraction shows that some desulfurization has occurred due to the higher level of calcination.

Anode users need to be mindful of this sort of variability which occurs with all cokes produced in a rotary kiln. Cokes are typically delivered as a blend of high and low sulfur cokes with a range of particle sizes. The level of desulfurization of any given particle in a blend will therefore be a function of the starting sulfur level, the particle size and target level of calcination. Coarse, high sulfur particles are more susceptible to the negative effects of desulfurization described in Ref [1] at higher calcination levels, and during anode baking as described below.

2. Desulfurization of Cokes in a Baking Furnace

In the second part of this paper a series of calcined petroleum cokes with different sulfur levels were subjected to heat treatment in a commercially operating baking furnace. The series included single source, high sulfur (HS) coke, normal sulfur (NS) coke and low sulfur (LS) coke. Each coke is prefixed by a letter to distinguish the different coke sources with the full list shown in Table II. Most of the cokes were single source cokes. In addition a NS level blend containing a mixture of HS, NS and LS cokes was tested, along with a butts sample, also containing a mixture of cokes.

Test portions of 2.0-5.6 mm fractions of each coke were placed in crucibles under the packing coke of top layer anodes in Årdal Carbon Furnace #2, a Riedhammer type baking furnace. An equivalent temperature (T_{eq}) sample was sent through in parallel with each coke test portion to determine the baking level experienced by the coke.

Hydro Aluminium uses the equivalent temperature method to quantify the heat treatment anodes experience in the baking furnace. The method is described briefly in the next section of the paper with examples of use.

For each coke and each set of results, a linear curve was fitted to the data describing the desulfurization. Typical curves are shown in Figure 2. The horizontal line is the initial sulfur concentration before heat treatment. The thick line covers the measurement range. The dotted line is an extrapolation back to the initial sulfur concentration level, giving an estimate of the starting equivalent temperature of significant desulfurization.

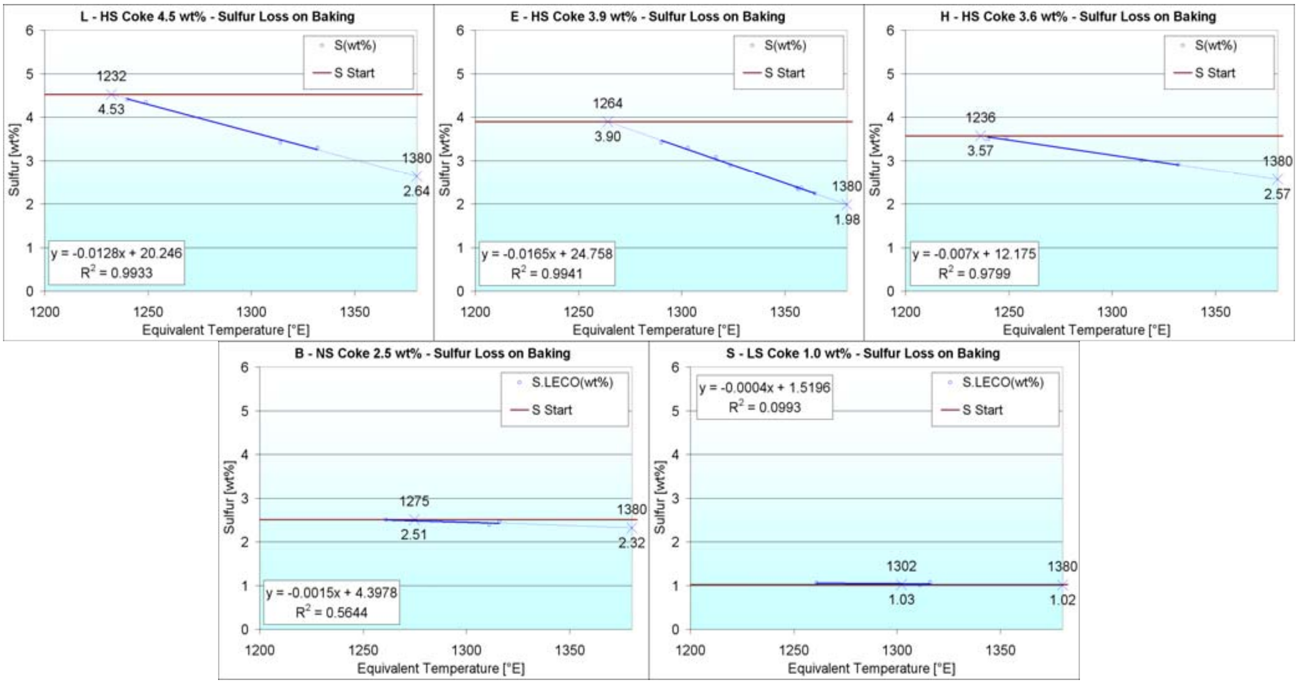

Figure 2. Desulfurization of HS, NS and LS cokes in an anode baking furnace plotted versus equivalent baking temperature.

The desulfurization rate varied significantly between the different sulfur level cokes where HS >>> NS >> LS ~ 0. It was observed that each single source HS coke and NS coke desulfurized linearly with equivalent baking temperature, and the linear curve fit was strong.

The important parameters of initial concentration, starting temperature for significant desulfurization and the rate of desulfurization are summarized in Table II. The single source cokes are sorted by decreasing sulfur level.

Table II: Petroleum coke and butts desulfurization. The starting temperature of significant desulfurization is measured by the equivalent baking level temperature.

	Initial Sulfur Concentration [wt%]	Starting Temperature [°E]	Rate of Desulfurization [wt% / °E]
L-HS	4.53	1232	0.0128
E-HS	3.90	1264	0.0165
M-HS	3.58	1233	0.0042
H-HS	3.57	1236	0.0070
B-NS	2.51	1275	0.0015
N-LS	1.37	[a]	0.0000
S-LS	1.03	1302[a]	0.0004
V-LS	1.01	[a]	0.0000
NS Blend	2.23	1219	0.0019
Butts	1.75	1304	0.0040

[a] Uncertain starting temperature and little or no change in concentration.

Among the HS cokes, the rate varied considerably. The E-HS and M-HS cokes had comparable starting sulfur concentration, but the desulfurization rates were as different as 0.0165 wt%/°E and 0.0042 wt%/°E respectively, a factor of four. Except for E-HS, the HS cokes had a starting temperature for significant desulfurization around 1230°E.

The single source B-NS coke desulfurized linearly and showed a moderate desulfurization rate of 0.0015 wt%/°E, much lower than the HS cokes. The start of significant desulfurization was high, 1275°E.

The single source LS cokes showed little or no desulfurization in the observed range.

For all cokes with measurable desulfurization parameters the desulfurization (ΔS) could be expressed by a linear relationship, e.g. for E-HS

$$\Delta S_E = 0.0165 \text{ wt\%/°E} * (T_{eq} - 1264\text{°E}) \quad \text{Eq. [1]}$$

For the NS blend and the butts, the linear curve fits are less well defined since they are based on only two data points. The NS blend was a blend of low sulfur (<1.5%) and higher sulfur coke (~3.2%). In general, desulfurization of blends will not be linear since blends are made up of several cokes which desulfurize at different rates, starting at different temperatures.

For the butts, the starting temperature for significant desulfurization was high, 1304 °E, since this material already had been baked at least once.

The Equivalent Baking Level

Before continuing with the discussion on anodes an example of use of the equivalent baking level will be given to illustrate what equivalent temperatures correspond to normal baking levels of anodes.

The equivalent baking level is a measure of baking level using a temperature scale (°E) and equivalent temperature, T_{eq}. To establish the scale, a green reference coke is given a series of 2-hour heat treatments at different hold temperatures, and the resulting L_c is measured. The series of (L_c, T_{eq}) pairs is used to establish a calibration curve, and from this, the equivalent temperature can be determined from the L_c value after any heat treatment of the reference coke.

When a green test portion of the reference coke is sent with an anode through the baking furnace, the resulting T_{eq}-value is termed the equivalent baking level of the anode. A more detailed description is provided in ISO 17499 and Lossius et al. [2].

An important difference between the method described above and thermocouple measurements is that it includes the effect of both temperature and time. Longer soak times at a given temperature will give higher equivalent baking levels. At any given temperature, the coke L_c will increase with increased soak time. Coke and anode desulfurization is also a function of time and temperature so the equivalent baking level method is very relevant.

The Hydro baking level target is 1230°E. Above 1320 °E, the anode is regarded as over-baked, and below 1150 °E, it is regarded as under-baked. The equivalent temperature is an important anode quality parameter and is part of Hydro Aluminium's routine analysis on anodes.

An example of equivalent temperature values observed in an anode baking furnace section from performance testing of a baking furnace are shown in Figure 3.

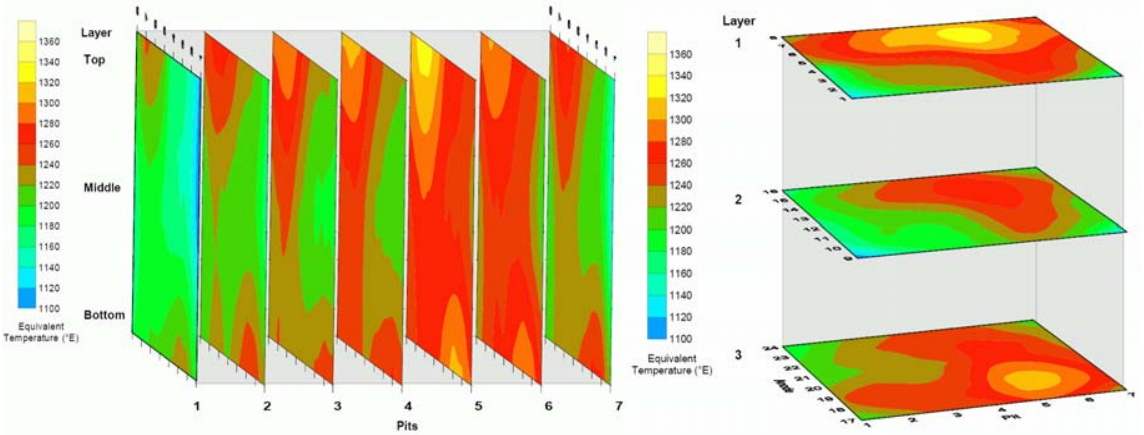

Figure 3. Equivalent baking level - Complete mapping by pit (upper plot) and by anode layer. Anodes are stacked vertically.

The distribution is obtained by determining the equivalent baking level of each anode in the section. The plots show one section of Årdal Carbon Furnace 3. Combined with Eq. [1] the sulfur emissions from an entire furnace section can be estimated.

3. Measuring Sulfur Loss from Anodes During Baking

A pilot scale anode testing program was run by Hydro to study effects of adding HS coke to anodes, especially how much HS coke can be added without negative effects. Measurement of the sulfur concentration and determining changes was part of the program.

Pilot scale anodes of this type can give valuable information if anode properties are realistic, and the pilot scale line in Årdal has been tuned to match the quality of production anodes at Årdal Carbon as shown in Table III. Most properties match well, although Young's Modulus is somewhat low and permeability somewhat high. The standard deviations were comparable.

The line consists of an Eirich batch mixer, a vacuum vibroformer (Wilkening design) and a laboratory furnace for controlled baking. Anodes are 3.9 kg with dimensions 130 mm diameter x 170 mm height.

Table III. Anode property comparison. Averages from 9 pilot anodes and 13 production anodes with the same coke fractions.

Anode Property with Abbreviation and Unit	Pilot Scale Anodes (Avg)	Production Anodes (Avg)
Reactivity, R.CO_2 [mg/cm^{2}h] [a]	14.9	15.3
Reactivity, Dust.CO_2, [%] [a]	3.2	2.0
Reactivity, R.Air, [mg/cm^{2}h] [a]	33.7	30.0
Density, [g/cm^3]	1.582	1.582
Resistivity, SER, [μΩm]	52.9	52.7
Young's Modulus, YM [MPa]	9394	10273
Strength, CCS, [MPa]	44.1	45.5
Permeability, [nPm] [b]	0.8	0.3
Expansion, CTE, [1/K*10^6]	4.5	4.7
Thermal Shock, TSR	19.6	18.1

[a] Reactivity by Hydro method (thermogravimetric method)

[b] Permeability by Hydro method (120 mm sample, 40% of RDC method)

3.1 Selection of a High Sulfur Coke for Use in Anode Tests

To determine which HS coke to use in the anode test program an investigation was made comparing several HS cokes to determine relative quality. The designations are the same as used in Table II. Rankings were (best first)

- Stability against loss of sulfur : M > H >> L > E
- Stability against shrinkage : H > M >> L

Based on this, coke L was judged to be a potentially difficult coke and was chosen for testing. The coke was calcined at two different levels (high and low) to compare the impact of coke calcination level. Specific electrical resistivity (SER) was used as the measure of degree of calcination. The high and low levels were selected to fall at the typical upper and lower levels of calcination in a commercial scale rotary kiln. It is not difficult to calcine coke to much higher and lower levels but this was not felt to be realistic, particularly for higher calcination levels. The SER targets selected were

- Low calcined (SER 0.040 Ω/inch)
- High calcined (0.036 Ω/inch)

3.2 Desulfurization of Anodes

The pilot anodes were made at the compositions shown in Table IV.

Table IV. Anode composition – Y_{HS} is the percentage of L-HS coke which was set at 0, 25 or 50 %.

Anode Data	S-level	Anode Composition
Butts	1.83 wt%	20 % of aggregate
NS blend coke	2.23 wt%	100 - Y_{HS} % of coke
HS low calcined	4.40 wt%	Y_{HS} % of coke
HS high calcined	4.10 wt%	Y_{HS} % of coke
Pitch	0.50 wt%	14 % of green anode
Coke yield		66 % of pitch

Part of the program consisted of small 2^3 factorial designs to quantify the effect of treatments. Examples of treatments were

- Adding 25 % low-calcined or high-calcined L-HS coke
- Adding 50 % low-calcined or high-calcined L-HS coke
- Increasing baking level from 1200 to 1320°E
- Halving mixing energy or vibroforming energy input

Table V gives an example of a 2^3 factorial. Only the effects relevant for desulfurization are described here.

Table V. Eight pilot scale anodes in 2^3 Factorial 1 with factor designation and sulfur concentration – HS coke was low calcined.

A L-HS low [%]	B Baking [°E]	C Mixing [min]	Sulfur [wt%]
0	1200	6	1.91
0	1320	6	1.94
0	1200	3	1.96
0	1320	3	1.90
50	1200	6	2.71
50	1320	6	2.51
50	1200	3	2.69
50	1320	3	2.36

Observations (percentages are averages from several factorials)

- At 1320 °E the desulfurization of the anode with 50% L-HS low calcined coke was -0.26 wt%, and the anode without HS coke 0.01 wt%. This meant the increase in desulfurization when adding 50% HS low calcined coke to the anode was 0.21 wt%.
- The corresponding increase in desulfurization for the 50% high calcined L-HS anode was 0.12 wt%.
- At 1260°E desulfurization of the low calcined L-HS anode was 0.02 wt%, and the high calcined L-HS anode was zero. The low calcined L-HS coke therefore started desulfurization at a lower baking level than the high calcined coke.

The change in sulfur concentration for the HS-coke added to the anode can be calculated using the information in Table IV. For the low calcined L-HS the change was 0.58 wt%, giving a sulfur concentration of 3.82 wt% at 1320 °E. For the high calcined, the change was 0.34 wt% giving a sulfur concentration of 3.76 wt% at 1320 °E.

This type of testing did not allow determination of a starting temperature for significant desulfurization, and therefore the rate of desulfurization cannot be determined accurately. Work is in progress to determine the starting temperature for significant desulfurization when a HS coke is used in anodes.

4. Estimating Sulfur Emissions in a Section

To model the sulfur emissions from a section in a baking furnace, one must know the desulfurization behavior of the components in the anodes, and the baking level of the anodes.

In Figure 4 the cumulative distribution is shown for two baking furnaces. Kiln 3 is a Hydro Aluminium vertical flue ring furnace with 105,000 ton annual capacity. Kiln 2 is an older Riedhammer vertical flue ring furnace with 25,000 ton capacity. The Kiln 3 data were used in the 3D representation of the baking level distribution in Figure 3.

Using the above furnace temperature distribution data, several cases were modeled to compare anode sulfur losses during baking.

Case 1: Anodes as in Table IV, but with a 50:50 NS:LS coke blend using the low sulfur S-LS coke in Table II. The sulfur content at the start was 13.4 kg/ton anode, and the desulfurization during baking was calculated to be:

Kiln 3 0.23 kg/ton anode
Kiln 2 0.60 kg/ton anode

Case 2: Exchanging the low sulfur S-LS coke with the high sulfur H-HS coke in Table II. This coke had an initial concentration of 3.57 wt%, starting temperature for significant desulfurization of 1236 °E and rate of desulfurization 0.0070 wt%/°E. The sulfur content at the start was 21.1 kg/ton anode, and the desulfurization during baking was estimated at:

Kiln 3 0.64 kg/ton anode
Kiln 2 1.71 kg/ton anode

Kiln 2, with the wider baking level distribution, would experience a higher increase in sulfur emissions when adding high sulfur coke to the aggregate.

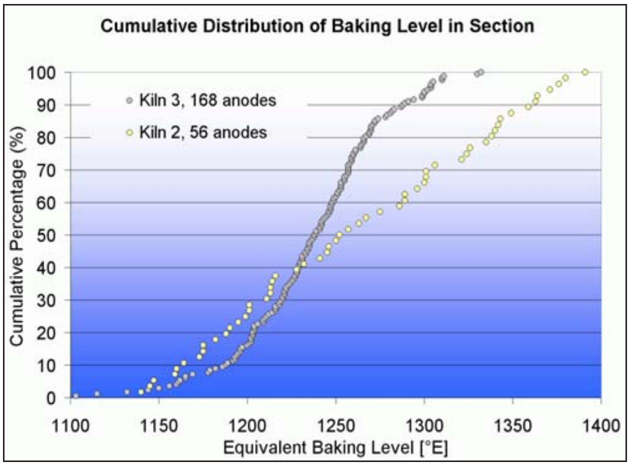

Figure 4. Equivalent baking level of anodes in two baking furnace sections, Årdal Carbon kiln 2 and 3.

Case 3: As in case 2 but with an average baking level 20 °E higher. The desulfurization during baking was estimated at:

Kiln 3 1.10 kg/ton anode
Kiln 2 2.19 kg/ton anode

For Kiln 3 the 20 °E increase in baking level would cause a significant number of anodes to reach the starting temperature for significant desulfurization, and to start desulfurizing, with a potential negative effect on anode properties.

To estimate the total sulfur emissions from a baking furnace, sulfur from fuel and from packing coke must also be included.

Discussion

The results presented in this paper provide additional information on desulfurization of coke during calcining and anode baking. During calcining, coke is not calcined uniformly and coarser particles are calcined to higher levels than finer particles. The coarse particles in the high sulfur components of coke blends are more susceptible to desulfurization as a result of this. Excessive desulfurization of coarse coke must be avoided to reduce the potential negative impact on anode density.

Desulfurization results from anode baking furnaces have been shown for cokes where the heat treatment was quantified using the equivalent temperature. For each HS and NS coke, desulfurization was linear with the equivalent temperature, and it was possible to assign a starting temperature for significant desulfurization and a rate of desulfurization. With these parameters known, sulfur emissions during baking could be modeled. In the examples, the modeling was somewhat simplified by assuming linear desulfurization also for the NS-blend coke and the butts used.

Modeling sulfur emissions showed that increased use of HS cokes will demand stricter control of baking level for anode producers who operate under sulfur emission limits.

The interrelationship of coke calcining and anode baking on coke integrity is complex. Heavy calcining and further desulfurization during baking damage HS cokes. This will negatively affect anode quality. Observations made during the pilot anode study referred to above indicate that carboxy reactivity, and especially carboxy dusting, is sensitive to desulfurization damage and can be used as a measure. Two examples are given.

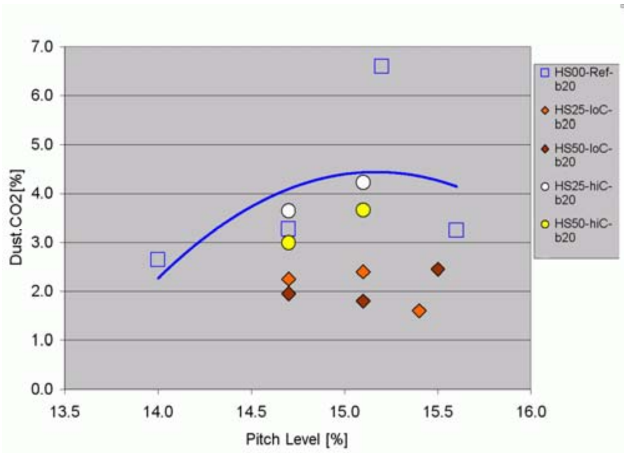

Figure 5. Carboxy dusting (Hydro dust index) for pilot scale anodes with 0, 25 and 50% addition of the high (hiC) and low calcined (loC) L-HS coke. b20=20% butts.

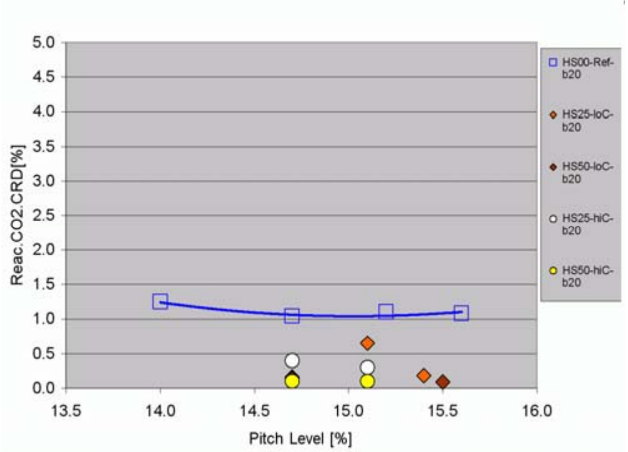

Figure 6. CRD Carboxy dusting (R&D Carbon method) for pilot scale anodes with 0, 25 and 50% addition of the high (hiC) and low calcined (loC) L-HS coke.

The carboxy dusting index by the Hydro Aluminium method is shown in Figure 5, and the carboxy dust percentage by the R&D Carbon method is shown in Figure 6. Generally, adding HS coke improves the carboxy reactivity properties due to the passivating effect of sulfur on sodium. This is seen in the plots, both for high calcined (circular legend) and low calcined coke results (diamond legend) relative to the blue line with no HS addition. However, the improvement is markedly better for anodes made with the low calcined HS coke (except outlier in Figure 6). Similar observations were made for the carboxy residue, R&D Carbon method, and the carboxy reactivity by the Hydro Aluminium method.

Conclusions

High sulfur cokes undergo desulfurization during both calcining and anode baking. The rate of desulfurization depends on both the sulfur content and the level of calcination or heat treatment in the baking furnace. Desulfurization during calcining is also dependent on particle size due to the tumbling effect in the kiln where coarser particles tend to be more well calcined than finer particles.

The equivalent baking level is useful for quantifying the heat treatment of anodes in the baking furnace. It can also be used to quantify the desulfurization behavior of petroleum cokes and butts during baking. It was observed that desulfurization was linear with equivalent temperature and could be defined by a starting temperature for significant desulfurization and a rate of desulfurization. Linear expressions could be combined with the baking furnace baking level distribution to model average sulfur emissions per ton of anode produced.

The sulfur level of high sulfur cokes used in blends is increasing and will likely continue to increase. This work has shown that high sulfur cokes can be used successfully in blends without negative consequences but care must be taken to avoid over-calcining these cokes and over-baking anodes made with these cokes. Both have the potential to negatively affect anode properties.

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