

A REVIEW OF COKE AND ANODE DESULFURIZATION

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Abstract

During calcination, petroleum coke desulfurizes depending on the sulfur content and final temperature. This has a negative effect on coke properties such as real density, porosity, and reactivity. Additional sulfur loss occurs during anode baking and this can further deteriorate anode properties such as density and reactivity. The sulfur level of high sulfur cokes used by the calcining industry has increased since 2003. Although the average sulfur content of cokes used by smelters has not increased significantly due to environmental limits, the difference in sulfur level of cokes used in blends has increased. Calciners must avoid “over-calcining” high sulfur cokes and smelters must be wary of additional desulfurization during baking. This paper presents a review of past and recent data on coke and anode desulfurization, and gives recommendations on how to best counter the problems that can arise from use of higher sulfur cokes in blends.

Introduction

The loss of sulfur during calcination of petroleum coke is a well established phenomenon and is typically referred to as thermal desulfurization or simply, desulfurization. Many papers have been published on this subject [1-7], and it is known that sulfur loss increases as the temperature of calcination increases and as the sulfur content of the coke increases. Desulfurization increases the coke micro-porosity and negatively effects properties such as apparent density and reactivity. When anodes are produced with calcined coke, further desulfurization occurs during anode baking as a result of the long soak times involved [8,9].

Since 2003, fundamental changes in the refining industry have resulted in a shortage of traditional quality anode grade green coke [10,11]. The difference in price between a barrel of low sulfur sweet crude and high sulfur sour crude, the “sweet-sour spread”, is causing more refineries to process cheaper, higher sulfur crudes. The graph in Figure 1 shows the significant change that has occurred in the sweet-sour spread since mid-2004.

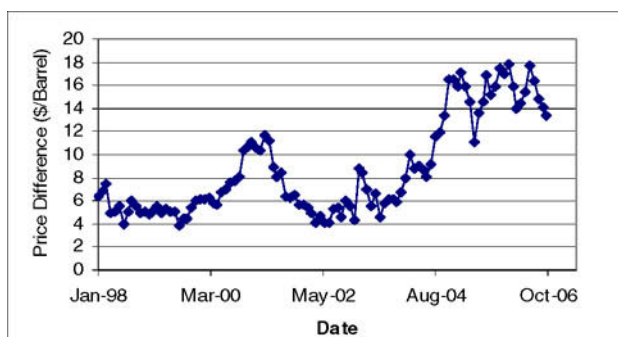


Figure 1: Sweet/Sour Spread – Average price difference between a barrel of low S sweet crude and high S sour crude.

These higher sulfur crudes produce cokes with higher sulfur and metal impurity levels (particularly vanadium and nickel). Calciners are using more of these cokes to satisfy the increasing demand from the aluminum industry. In addition, the sulfur level of many traditional “high sulfur” anode grade green cokes is increasing. Five years ago, a high sulfur anode grade green coke was regarded as one with a sulfur level of 3-4%. Today, a more typical level is 4-6%.

In the US, which produces 60% of the world’s anode grade green coke, some refineries have started supplementing their crude supply with heavy, sour crude from Canada. The US now imports more crude from Canada than any other country. The data in Figure 2 shows what has happened to the sulfur and vanadium level of one anode grade green coke in 2006 when the refinery replaced a portion of its crude supply with Canadian sour crude. Changes like this are driven by refining economics and anode coke quality is often not considered.

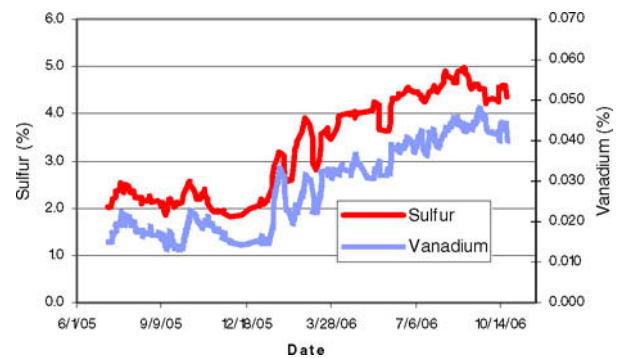


Figure 2: Impact of Canadian crude use on sulfur and vanadium level of a US anode grade green coke.

The trend in the US is expected to be mirrored elsewhere. China is expected to produce significantly more green coke over the next 10 years due to its rapidly growing refining industry and demand for energy and motor fuels [12]. China already imports over 3 million barrels/day of crude oil and this crude is typically heavier, and more sour than Chinese domestic crude. The trend toward higher sulfur green cokes is expected to follow the US as reported during the 2006 International Carbon Conference [12,13].

Aluminum smelters have not changed coke sulfur specifications significantly due to smelter environmental constraints. High coke sulfur levels must be offset by blending with lower sulfur cokes. As a result, the difference in sulfur level of cokes used in typical anode blends is increasing. Some people in the industry refer to these blends as “dumbbell blends” where cokes with a sulfur level

of 1-2% may be blended with cokes with sulfur levels up to 4-6% to achieve a smelter anode coke specification of 2.5-3.0%.

As a result, calciners and anode producers need to pay close attention to the negative effects of coke desulfurization. The objective of this paper is to review the literature on coke and anode desulfurization and present the results of past and recent studies on this problem. Desulfurization is a manageable problem but some changes may be required by both calciners and smelters to respond to the higher sulfur cokes being used today.

Mechanism of Thermal Desulfurization

Morsi and Al-Haj-Ibrahim [4] present an excellent review of thermal desulfurization. Most of the sulfur in petroleum coke occurs as organic sulfur bound to the carbon matrix [1]. The exact structure of the organic sulfur compounds is not well known but thiophenes are the most prevalent form in crude oil and coke.

At temperatures up to 850°C, any sulfur residing in the pores of the coke is lost through the simple process of desorption. Cracking of side chains containing sulfur can also occur at these temperatures resulting in sulfur loss. For cokes made with more aromatic feed-stocks, very little sulfur loss occurs after 850°C until temperatures approach 1300°C.

At temperatures above 1300°C, desulfurization can increase dramatically. These temperatures are high enough for the decomposition of sulfur-hydrocarbon compounds like thiophene. A further increase in temperature above 1500°C is not certain to lead to more desulfurization but this depends on the nature of the coke.

Desulfurization Results and Effect on Coke Properties

The previously published work reviewed in this section focuses on four key papers, two related to coke desulfurization and two related to anode desulfurization.

Coke Calcining Study I

Gelbach et al. [2] studied laboratory calcination of four green cokes at essentially two different sulfur levels, three high (3.8-4.5%) and one relatively low (1.9%). Samples were calcined at temperatures between 1100°C and 1600°C in 100°C increments.

The desulfurization of the four cokes was shown in terms of the decrease in sulfur content, Figure 3; the effect on real density, Figure 4; and the effect on mercury apparent density. It was also noted that bulk density was reduced during desulfurization and that the absolute density, as measured by x-ray diffraction, increased with increasing temperatures because the measurement was not affected by microporosity (diameters < 0.1 μ) created by desulfurization.

The data indicate that real density increased with temperature up to a point, the critical temperature (T_c), after which the real density decreased due to thermal desulfurization. The decrease is due to microporosity created when sulfur leaves the coke. The porosity remains inaccessible in the real density test because samples are ground to -75 μ m which is insufficient to open sub-micron pores. An important note is that T_c varies with individual cokes, and is not necessarily related to the sulfur content. Some cokes desulfurize more readily than others presumably due to differences in structure and sulfur-carbon bonding. The apparent

density showed similar trends, albeit not necessarily at the same temperatures.

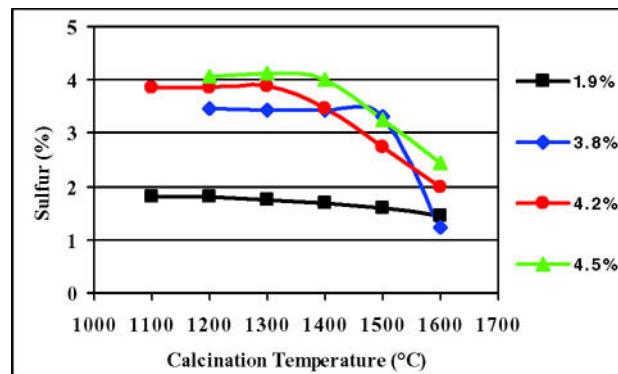


Figure 3: Sulfur loss at different calcining temperatures for cokes of different S level

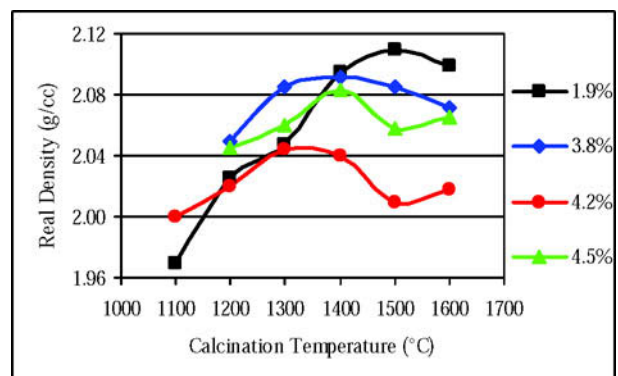


Figure 4: Change in real density as a function of temperature and coke sulfur level.

Coke Calcining Study II

Garbarino and Tonti [5] examined the effect of desulfurization on numerous production samples taken from a commercially operating rotary kiln calciner. The recap here will focus on data related to the ratio of sulfur in the calcined coke to sulfur in the green coke, hereafter referred to as the desulfurization ratio. A lower desulfurization ratio indicates a higher sulfur loss during calcination. Data were compared for the numerous cokes at the same level of calcination and at different levels of calcination.

Figure 5 shows the desulfurization ratio as a function of green coke sulfur content of different production samples at the same calcination level. In this case, calcination levels were controlled by measuring the specific electrical resistivity of the coke. The four data points shown as circles are additional, more recent data points. The data indicate that, in general, the rate of desulfurization increases with increasing green coke sulfur content at the same level of calcination. What is surprising about this data, is how linear and predictable the sulfur loss is based on the coke sulfur level.

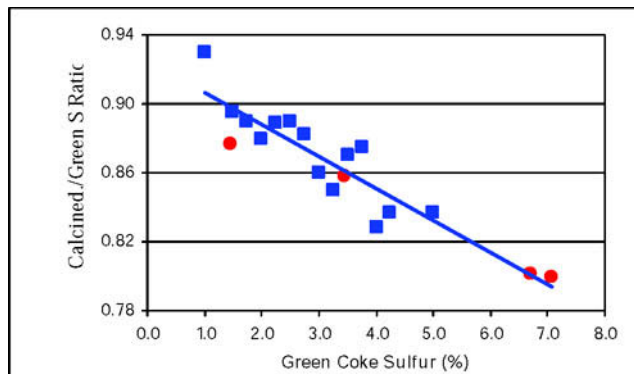


Figure 5: Desulfurization ratio of cokes calcined in a commercially operating rotary kiln

Additional data presented by Garbarino and Tonti [5] show that the level of desulfurization increases with the degree of calcination at constant green coke sulfur content, results like those found in Coke Calcining Study I.

Anode Baking Study I

Vogt et al. designed an experiment where cores from a green anode having a sulfur content of 2.3% were baked in a laboratory furnace at varying temperatures and soak times. Physical and chemical properties of the anode cores were correlated to temperature and soak time.

Figure 6 shows the sulfur level for different temperatures, with each line representing a different soak time at maximum temperature. Temperatures represent anode temperatures rather than flue temperatures. The data illustrate that, unlike thermal desulfurization of green coke, anodes desulfurize at a constant rate and are not triggered at a certain critical temperature. Furthermore, the level of desulfurization increased with increasing soak time for all temperatures.

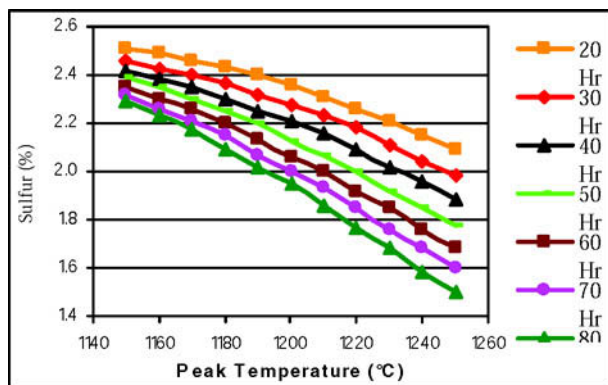


Figure 6: Sulfur level in laboratory anodes after baking at different temperatures and soak times.

Figure 7 shows the baked anode density for different temperatures, with each line representing a different soak time at maximum temperature. The data illustrate that, for a given soak time, there is an optimum peak temperature at which the baked

anode density is maximized. The study showed similar trends for other anode properties.

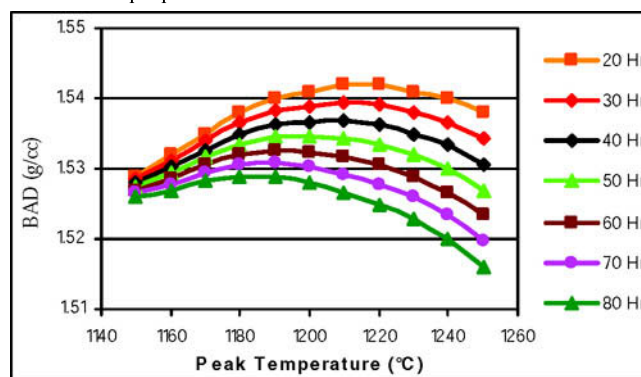


Figure 7: Baked anode density variation as a function of peak temperature and soak time.

Mercury porosimetry was used to characterize porosity development. Anodes baked at 1150°C for 80 hours lost the same amount of sulfur (0.25%) as anodes baked at 1250°C for 20 hours. There was a significant difference in porosity development however. The anodes baked at the lower temperature and longer time showed a significantly higher porosity (161 mm³/g versus 155 mm³/g). This indicates that the way in which the sulfur is lost, not just the total amount lost, will affect the porosity of the anode.

Anode Baking Study II

Dreyer et al. [9] measured the effect of different coke calcination levels on anodes produced from cokes of two different sulfur levels, one high (HS) and one low (LS). The L_c measurement was used to characterize the degree of calcination; a higher L_c indicates a higher level of calcination. Bench-scale anodes were produced and baked in the laboratory at temperatures from 920-1260°C, and physical and chemical properties were measured.

Figure 8 shows the sulfur released from the anodes produced with the low and high sulfur cokes calcined at different levels (↓L_c = low L_c and ↑L_c = high L_c). For the LS coke, the sulfur loss was moderate at temperatures greater than 1100°C, and was limited to the coke calcined to the higher temperature.

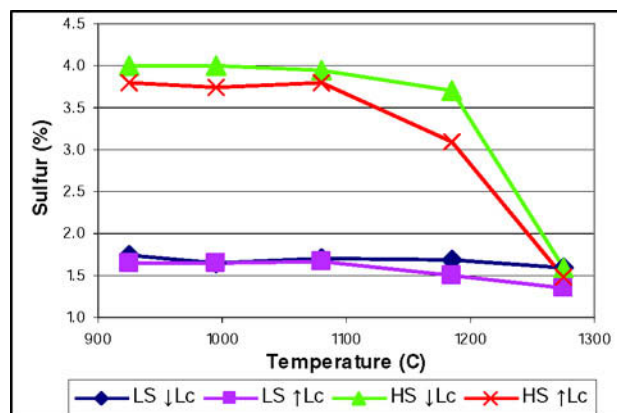


Figure 8: Desulfurization of anodes produced with low sulfur coke calcined to low and high levels.

The sulfur released from anodes produced with the HS coke was very high at temperatures greater than 1100°C. Desulfurization also started at a lower temperature in anodes made from the coke calcined to a higher temperature.

Sulfur loss during anode baking affects almost every anode property and the study showed results for anode density, CTE, CRR, ARR, resistivity, Young’s modulus and air permeability. Figure 9 shows baked apparent densities (BAD) of anodes produced from the HS coke. The density of anodes produced with more highly calcined coke was lower than those produced with coke calcined to a lower level.

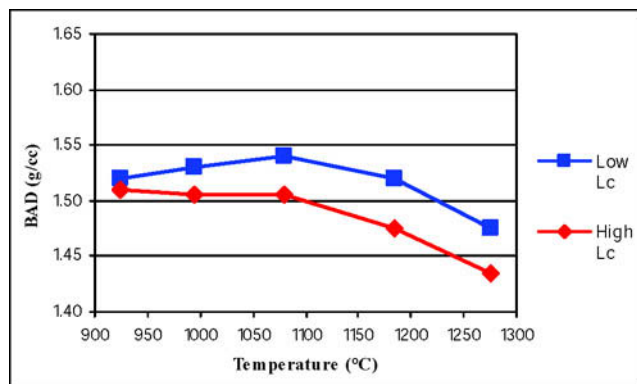


Figure 9: Baked apparent density of anodes produced with coke calcined to a low and high level.

This last point was an important finding showing that desulfurization during baking increases when a given coke is calcined to a higher level. This seems counter-intuitive at first, but a possible reason is given in the discussion section.

Desulfurization of Coke in an Anode Baking Furnace

In this next set of experiments, calcined coke samples were placed in the stubholes of anodes baked in an anode baking furnace. A high sulfur calcined petroleum coke with 3.9 wt% S (referred to as HS-A) was selected to examine the effect of the heat treatment experienced by anodes. This coke is used today as a blend coke.

The furnace was Årdal Furnace 2, a Riedhammer furnace with 56 anodes per section. The hold temperature was 1280°C. The length (along the fire direction) of the anode area is 3200 mm and width is 3800 mm. Eight HS coke samples were placed with the eight top layer anodes, Figure 10.

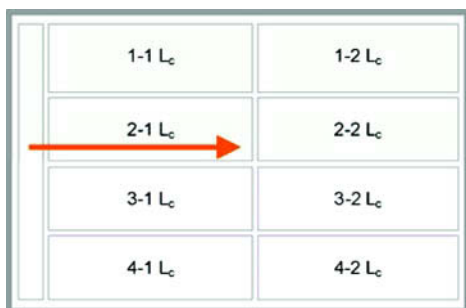


Figure 10: Eight top layer anodes in the section with positions of the eight test samples. Arrow shows direction of the fire.

The baking level was monitored by placing equivalent temperature coke samples with each HS coke sample. The equivalent temperature, T_{eq} , is a measure of baking level using a temperature scale (°E). To establish the scale, a green reference coke is given 2-hour heat treatments at several temperatures, and L_c measured [14, 15]. The series of (L_c , T_{eq}) pairs give the equivalent temperature scale.

When a test portion of the green reference coke is sent with an anode through the baking furnace the resulting L_c -value of the coke is input to the (L_c , T_{eq}) calibration and yields the equivalent temperature. See ISO 17499 [16] and the TMS paper by Lossius et al. [17] for a description of the method.

Results for Sulfur and Baking Level

Figure 11 shows the baking level (T_{eq}) and the resulting sulfur level from XRF analysis in the eight positions.

1290°E 3.4 wt%	1316.5°E 3.1 wt%
1356°E 2.4 wt%	1364.5°E 2.2 wt%
1358°E 2.4 wt%	1356.5°E 2.3 wt%
1303°E 3.3 wt%	1323.5°E 2.9 wt%

Figure 11: Baking level and sulfur after baking. The initial sulfur level was 3.9 wt%.

The variation across the fire direction is seen in Figure 12a and 12b. The baking level followed a shallow bell-shaped curve across the section. The sulfur level changed considerably and varied in an inverse manner compared to the baking level.

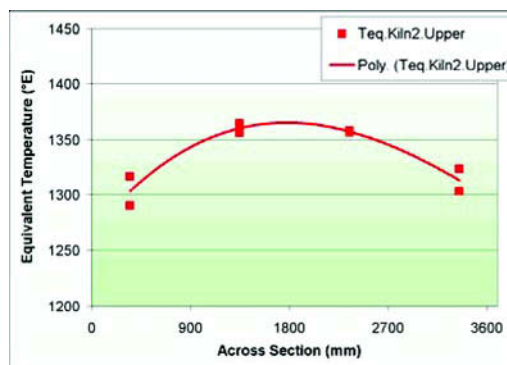


Figure 12a: Baking level across the section.

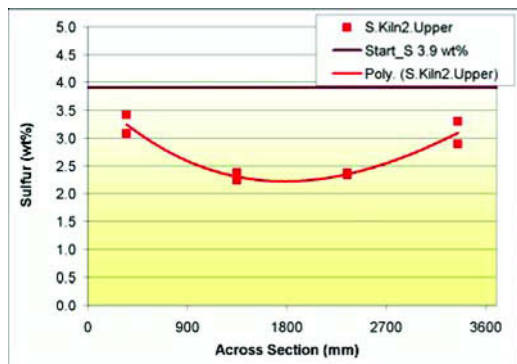


Figure 12b: Sulfur level across the section.

Plotting the sulfur level vs. the baking level showed a linear relationship, Figure 13 and Eq. (1) with sulfur in weight percent.

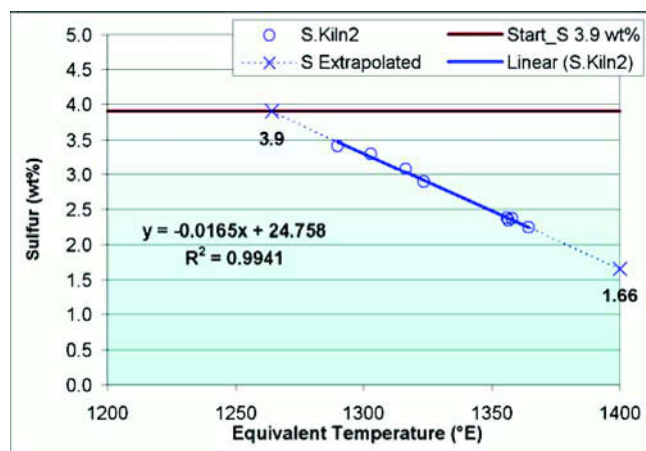


Figure 13: Sulfur vs. Equivalent Temperature extrapolated

Extrapolating to the initial sulfur concentration of 3.9 wt%, indicated that significant sulfur loss started at 1264 °E. Above 1264 °E, sulfur loss was linear at least to 1370 °E with a rate of loss of 0.165 wt% per 10 °E so that 15% of the initial sulfur would be lost at 1300 °E, and 36% at 1350 °E.

$$\text{Sulfur.HS-A} = -0.0165 T_{eq} + 24.76 \quad \text{Eq. (1)}$$

Eq. (1) can be converted to give desulfurization above 1264 °E.

$$\text{Desulf.HS-A} = 0.0165 \text{ wt}\%/\text{°E} * (T_{eq} - 1264 \text{ °E}) \quad \text{Eq. (2)}$$

Compared to other cokes tested, coke HS-A showed high desulfurization in the baking furnace. For a normal sulfur coke NS-B the expression was

$$\text{Desulf.NS-B} = 0.0035 \text{ wt}\%/\text{°E} * (T_{eq} - 1255 \text{ °E}) \quad \text{Eq. (3)}$$

Estimating Desulfurization

The equivalent temperature method has been used to map the baking level distribution of Hydro Aluminium baking furnaces. Figure 14 shows the cumulative distribution for Årdal Furnace 2 and Årdal Furnace 3. Furnace 2 was described previously and Furnace 3 is a 168-anode/section Hydro designed furnace with modern process control.

Combined with Eqs. (2-3) the baking level distribution was used to estimate the expected sulfur emissions. With 100% coke NS-B in the anodes, the desulfurization in Furnace 2 was 0.90 kg/ton anode, and in Furnace 3, 0.09 kg/ton anode. These differences are significant and illustrate the impact of baking level variation.

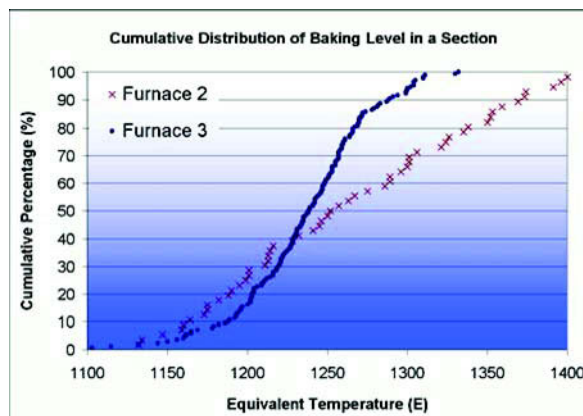


Figure 14: Mapping of baking level in a section.

If 20% of coke NS-B is replaced with HS-A the desulfurization in Furnace 2 would be 1.47 kg/ton anode, and in Furnace 3, 0.28 kg/ton anode.

This example illustrates both the significant increase in sulfur emissions when normal sulfur cokes are replaced by high sulfur cokes, and the importance of controlling baking level variation.

Generally the study has shown that the onset temperature for anode desulfurization in the baking furnace is comparable for low-, normal- and high-sulfur cokes, but the rates of desulfurization differ significantly, with higher sulfur cokes showing higher rates of desulfurization.

How the rate of desulfurization in the baking furnace differs for cokes calcined to different levels is now being investigated.

Discussion

Most aluminum smelters today use a blend of calcined coke to meet anode sulfur specifications. The blending is done by the calciner, the smelter, or a combination of both. Blending involves mixing low and high sulfur cokes to achieve a target sulfur level. Changes in the refining industry are driving an increase in the sulfur level of high sulfur cokes and this magnifies the desulfurization problem. The data presented in the last section of this paper shows just how significant the sulfur loss can be during anode baking from a high sulfur coke.

All anode baking furnaces have temperature variation, so the level of desulfurization will vary as a function of furnace location. This will contribute to anode property variation. Anode producers must be mindful of this variation. A furnace maintained and operated the same way today as it was ten years ago, could give a greater level of anode property variation if the temperature variation is significant and if the sulfur level of cokes used in the blend has increased.

To minimize the negative effects of desulfurization, coke calciners must avoid very high coke calcination levels. Coke calcining levels are typically set by smelter coke specifications such as real density, specific electrical resistivity and L_c .

One of the most damaging consequences of desulfurization during calcining is the increase it promotes in desulfurization during anode baking. Although the mechanism for this is not well understood, it is believed to be related to activation of the carbon structure during calcination. Partial breaking or disruption of carbon-sulfur bonds during calcining may result in a destabilized structure which desulfurizes more readily during anode baking. The long soaking times involved in anode baking may be sufficient to promote additional desulfurization from a structure already disrupted during coke calcining.

It is recommended that smelters review coke specifications to avoid the tendency for over-calcining. This would typically mean lower average specifications for real density and L_c and higher levels for specific electrical resistivity. Some smelters in Europe have adopted lower coke real density specifications (2.00-2.05 g/cm³) as a result of work completed and published by Dreyer and Samanos [18].

The analysis of sulfur levels in baked anodes will provide smelters with a useful indicator of desulfurization problems in baking. Increases in the sulfur level of blend cokes can significantly increase the sulfur loss from anodes made with these cokes. The extent of desulfurization will be dependent on the anode position in the furnace with an almost linear increase in sulfur loss as the temperature increases. Baking furnaces will release more sulfur and anode densities and reactivity will be negatively affected for those anodes located in hotter positions in the furnace. Data provided in the paper highlights the importance for smelters in controlling and reducing baking level variation.

The work started in the last section of this paper is being continued and the next step will be to produce and bake anodes with different sulfur level cokes to quantify the effect of coke calcination level and baking level on sulfur losses and anode properties. It is hoped to report on the results of this new work at the 2008 TMS meeting.

Conclusions and Recommendations

Changes in the refining industry are having a significant effect on the sulfur level of high sulfur cokes used in coke blends for the aluminum industry. Although the average sulfur level of blends used by smelters has not increased significantly, the difference in sulfur level of cokes has increased, a trend expected to continue. With the growth rates projected in primary aluminum production, the industry will have no choice in using these higher sulfur blend cokes.

To minimize the negative effects of desulfurization, calciners must understand the desulfurization behavior of individual cokes to avoid "over-calcination." Calcining cokes to higher temperatures to meet current smelter coke specifications results in greater desulfurization, both during calcining and anode baking. Smelters must be mindful of this problem when setting coke specifications.

Smelters must monitor anode baking furnace temperature variation and look for evidence of desulfurization during baking. Changes in anode sulfur levels will give a clear indication of changes in desulfurization. Desulfurization negatively impacts anode properties, particularly density and reactivity.

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