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.

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 cok 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 < 0.1µ) created by desulfurization.

The data indicate that real density increased with temperature up to a point, the critical temperature (Tc), 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 -75µm which is insufficient to open sub-micron pores. An important note is that Tc 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](image)

![Figure 4: Change in real density as a function of temperature and coke sulfur level](image)

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.