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DESUBFURIZATION AND ITS EFFECT ON CALCINED COKE PROPERTIES

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Abstract

As the petroleum industry processes crudes of increasing sulfur content, the sulfur content of anode grade cokes will continue to increase. As this occurs, it becomes necessary for petroleum coke calciners to better understand the effect of sulfur on production quality. This paper quantifies the desulfurization during calcination as a function of the green coke sulfur content and the degree of calcination. The effect on other coke physical properties is presented based on data from actual calciner runs. As desulfurization increases, physical properties can be more dramatically affected by changes in calcination. Therefore, calciner optimization of process variables has become more influential in selecting calcination level. This has resulted in calcined coke production with improved physical properties.

Introduction

Charts displaying trends in the sulfur content of green petroleum coke have been published. One is reproduced in Figure 1 (the then "non-communist countries"). The data indicates a progressively increasing world average sulfur content, projected to approach 4.0% early in the 21st century[1].

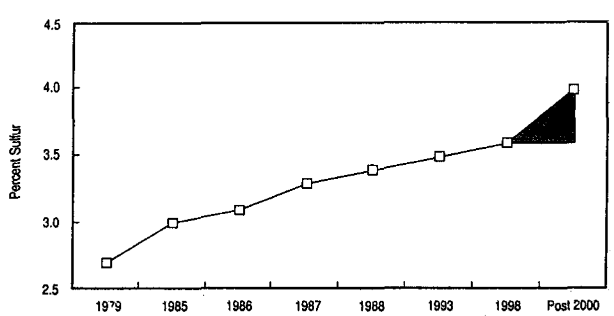

Figure 1: Sulfur content in green petroleum coke for the noncommunistic world. Shaded area indicate the range of future values.

Demand for calcined coke increases as aluminum production grows. The incremental green coke required to support this primary aluminum production increase will necessarily not be those currently utilized. Principally, the new cokes will be those with higher sulfur contents. For example, the second quarter 1992 U.S. demand was 1.35 million MT. The marginal sources of green petroleum cokes needed to meet such demand are those of higher sulfur content[2] as Figure 2 reproduced from Pace Consultants, Inc. would seem to indicate. If this trend continues and the use of higher sulfur cokes becomes more prevalent, it will be necessary for calciners to better understand how sulfur can affect the physical qualities of coke during calcination.

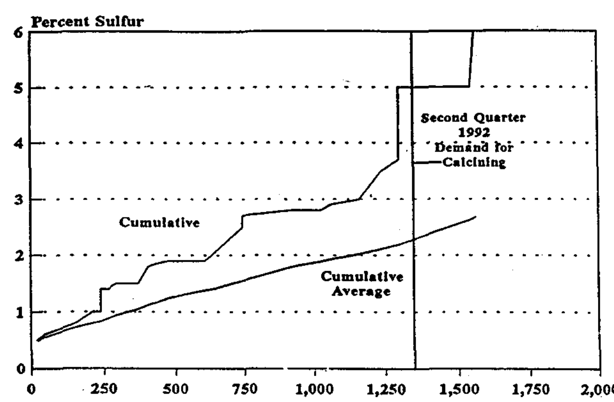

Figure 2: U.S. Calcinable green coke production in thousand metric tons.

In general, most of the sulfur component of green coke is retained in the coke product after calcination. The sulfur that is released during calcination is released in three ways:

1. Sulfur released with volatile matter (VM) during thermal devolatilization,

2. Sulfur lost or burned in association with coke entrainment or combustion in the kiln coke bed and in the kiln exhaust, and

3. Additional sulfur thermally dissociated from the coke during calcination.

One can make the assumption that a near proportionate weight of sulfur is lost with VM, and also with coke entrainment or combustion. This is equivalent to assuming that sulfur is evenly distributed in green coke. The difference between green coke sulfur concentration and the resulting calcined coke sulfur concentration would then represent only the additional sulfur loss attributable to thermal dissociation, or referred to from here on as "desulfurization".

Laboratory scale calcination studies have been published showing increases in porosity caused by desulfurization during calcination[3]. This study utilizes analyses of samples taken from full scale calciner production to show that the degree of desulfurization is a function of the green coke sulfur content and degree of calcination. The analyses provided quantifies the effect of each. The results will also confirm and quantify the porosity and structural effects of desulfurization. Based on these results, it is important for calciners to include changes in porosity and anticipated desulfurization in the selection of calcination level to maximize overall calcined coke product quality.

Results/Discussion

The data presented are from two sources; routine full scale calciner production and full scale calciner optimization tests. The calciner optimization tests involve known step changes in operating parameters, and subsequent measurement of the effects on product quality by sample analyses.

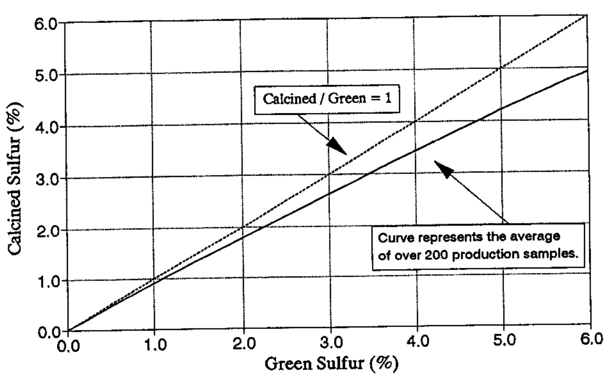

Figure 3: Weight percent sulfur relationship between green and calcined coke.

The weight percent sulfur content of calcined coke is generally observed to be less than the weight percent sulfur content of the green coke which is calcined (Figure 3). As shown in Figure 4 this relationship can be expressed as a ratio. A ratio less than 1 would indicate desulfurization. As can be seen in Figure 4, desulfurization appears to increase with the level of sulfur in the green coke at constant degree of calcination. As seen in figure 5, desulfurization also increases with degree of calcination (represented here by the coke Specific Resistivity) at constant green coke sulfur content.

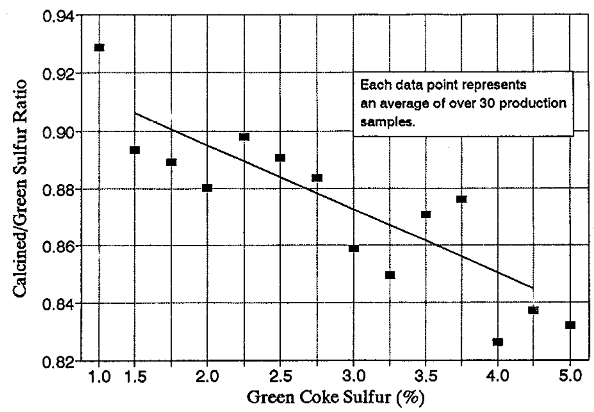

Figure 4: Desulfurization as a function of green coke sulfur content.

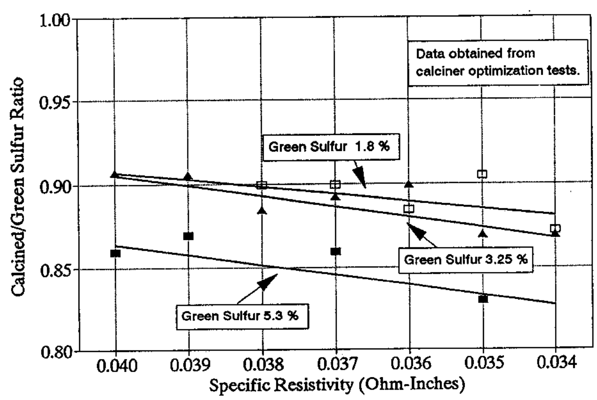

Figure 5: Desulfurization as a function of degree of calcination.

Porosity caused by sulfur removal during calcination has been documented by the work of Rhedey[4] and others[5,6]. Using data from calciner production run samples, porosity variation can be confirmed. For instance, in this study, analyses of calciner production samples at similar calcination levels show changes in both real density (Figure 6) and apparent density (Figure 7) with changing sulfur levels. Increases in porosity from desulfurization are observed by comparing real density (RD) measured by helium pycnometry (ASTM D-5004) on particles smaller than 200 Tyler mesh and apparent density (AD) measured by mercury displacement on the -10/+20 Tyler mesh coke fraction (Pechiney Method LRF-1618 BIS). Sulfur analysis is obtained by X-ray fluorescence. Specific Resistivity (SR) of the calcined coke is used in these studies as a representation of the degree of calcination.

By combining this data, a relative porosity value can be indirectly estimated by 1/AD - 1/RD. This is an estimate of microporosity greater in pore size than that unpenetrated by RD analysis and less than that displaced with Mercury in AD analysis. In general, this value appears to increase in green cokes with a higher sulfur content (Figure 8) even though porosity due to the release of hydrocarbon is believed to be similar between the different cokes.

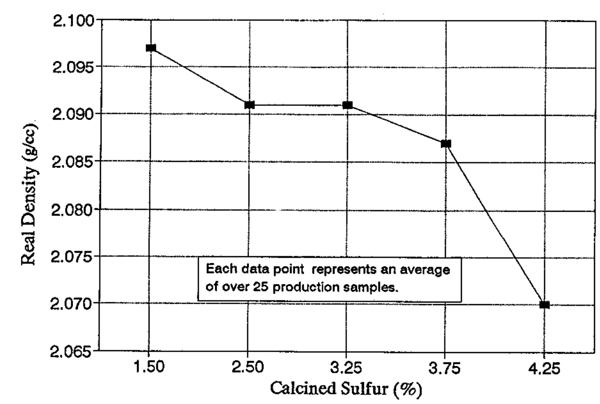

Figure 6: Real density as a function of sulfur content at equal degree of calcination represented by coke Specific Resistivity (SR).

A loss of real density implied by measurement with an air pycnometer is indicative of either a structural rearrangement or an increase in microporosity not penetrated by the technique. Therefore, the conclusion taken from figures 6,7 and 8 would be that the increased desulfurization creates not only porosity (comparison of AD and RD in Figure 8), but also microporosity not measurable and/or possible structural rearrangement (RD shown in Figure 6). All of these contribute to the lower apparent density at higher sulfur levels (Figure 7).

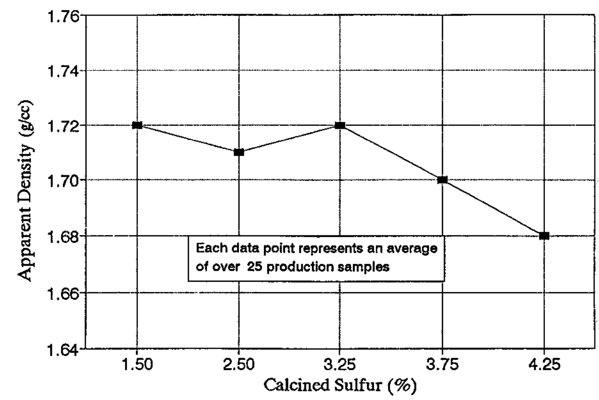

Figure 7: Apparent density as a function of sulfur content at equal degree of calcination.

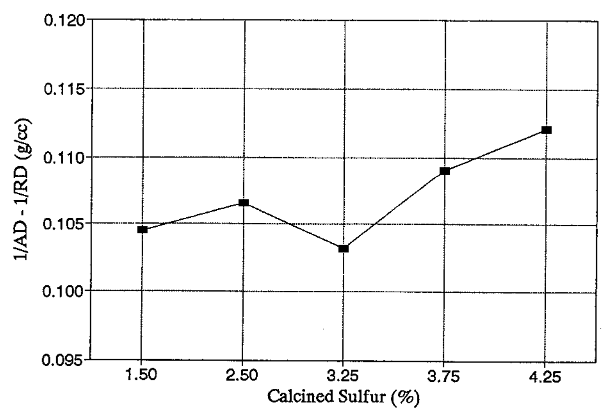

Figure 8: Porosity as a function of sulfur content at equal degree of calcination.

As already demonstrated, the desulfurization of coke during calcination is also a function of the level of calcination. Figure 9 presents porosity (as defined previously) as a function of calcination level for two different cokes. One is a high sulfur coke having a sulfur content equal to 4.5%. The other is a low sulfur coke with an average sulfur content of 1.6%. In the range of calcination show, the porosity increases for both cokes. However, it would appear that the high sulfur coke is more adversely affected. Figure 10 presents the apparent density as a function of calcination for the same cokes presented in Figure 9. Apparent density appears to decrease as the level of calcination increases for the high sulfur coke. One would conclude that very high sulfur cokes are especially sensitive to calcination level.

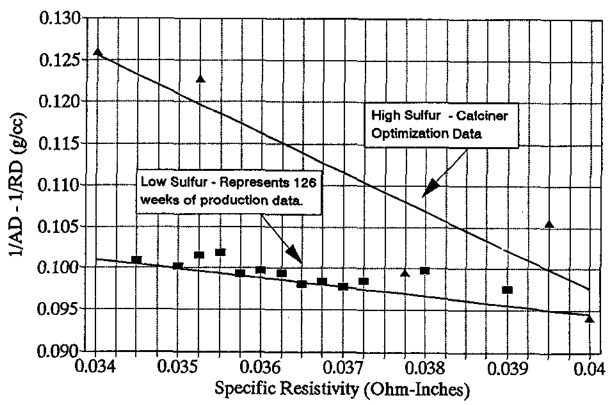

Figure 9: Porosity sensitivity to degree of calcination.

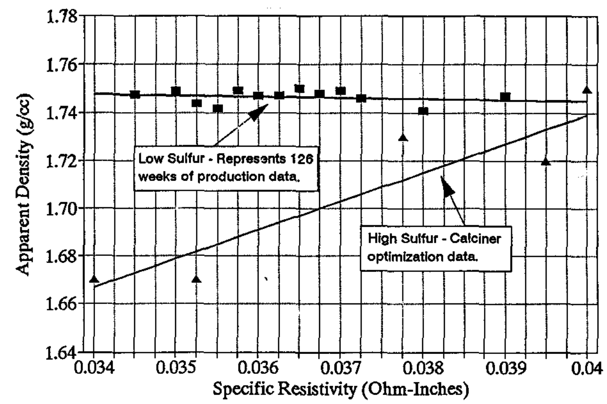

Figure 10: Apparent density sensitivity to degree of calcination for different sulfur level cokes.

The porosity of calcined coke is a direct factor in the resulting baked anode density.[6] Since calcined coke porosity directly affects the baked density of the carbon anode, it also impacts gross carbon usage. Improper selection of coke calcination level can, based on this study, result in a 3% decrease in apparent density. Because coke porosity and anode density are related, a change in coke density will translate to baked anode density. Let's assume in this scenario that there are no other quality impacts. Then, any increase in baked anode density will reduce gross carbon usage and reduce anode production and labor costs. A typical modern reduction plant will produce 200,000 MT aluminum per year. The same plant will manufacture and use 11,000 tons of anodes. Assuming a value of $120 cost per anode ton (not including coke or pitch), and a 3 percent change in gross carbon overall costs would vary by $400,000 per year. If the same smelter's aluminum production is limited by anode production, then variation in anode density would relate directly to aluminum production and have even more significant an economic impact.

Conclusions

Desulfurization during coke calcination is a function of both green coke sulfur content and the degree of calcination employed.

Porosity is increased as desulfurization occurs, resulting in a loss of apparent density. Some level of structural rearrangement or impenetrable microporosity also accompanies desulfurization as indicated by a change in real density.

As green cokes used by calciners continue to increase in sulfur content, physical properties such as apparent density and real density may therefore be negatively affected. Judicious selection of calcination level will therefore become more important to calcined coke quality as green coke sulfur contents are elevated as part of the calciner quality optimization process.

References

[1]M.F. Vogt, J. Waller and R.D. Zabreznik,"The Problem of Sulfur Content in Calcined in Calcined Petroleum Coke" JOM, July 1990.

[2]Pace Petroleum Coke Quarterly, Second Quarter 1992. Pace Consultants Inc.

[3,4]Paul Rhedey,"Structural Changes in Petroleum Coke During Calcination" Transactions Of The Metallurgical Society Of AIME, July 1967.

[5]R.E. Gehlbach,L.I. Grindstaff, and M.P. Whittaker,"Effect Of Calcination Temperature On Real Density Of High Sulfur Cokes"Publication unknown.

[6]M.E. Barrillon,"On the Texture of Cokes and Anodes Used in the Electrolytic Production of Aluminium"Proceedings of the Second International Symposium of ICSOBA, Vol 4 1971.