Influence of calcination temperature and sulfur level on coke properties

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Abstract

The Russian smelters have to deal with blending and calcining high-sulfur coke. It has been widely reported in the literature that desulfurization, which occurs during petroleum coke calcination, negatively affects coke quality. For assessing the risks of desulfurization, one of the RUSAL smelters has run several trials regarding calcining petroleum coke in the rotary kiln at different temperatures. This paper discusses the results of calcining coke of different sulfur content in an industrial rotary kiln where the real density and reactivity of high-sulfur coke are shown to be extreme in the temperature range of 1 200 to 1 350 ^{o}C.
Keywords: petroleum coke, sulfur, calcination.

1. Introduction

The calcination temperature is critical for forming the structure and properties of calcined petroleum coke. Typically, increasing the calcination temperature improves the performance properties of petroleum coke: real density increases, and resistivity and reactivity decrease. However, the process of calcining high-sulfur coke has its own characteristics. Sulfur is texture released rapidly at temperatures above 1 300 ^{o}C during calcination. Desulfurization destroys the of coke and negatively affects coke quality.
The process of calcining petroleum coke with different sulfur levels within the temperature range of 1 200-1 500 ^{o}C has been studied in detail under laboratory conditions. The results show that the properties of high-sulfur coke at temperatures above 1 300 °C are determined by the following two competing processes: graphitization and desulfurization [1]. However, the literature does not provide enough data on the process of calcining coke with different sulfur levels under industrial conditions.
This paper will discuss the results of calcining high-sulfur coke in the rotary kiln under industrial conditions.

2. Calcination results

Table 1. Coke properties.

Parameters	Coke A		Coke B	
	Calcination		Calcination	
	before	after	before	after
Moisture, %	8.1		8.8	
Volatiles, %	7.8		10.1	
Sulfur, %	3.6	2.9	3.0	2.9
Real density max, g/cm3		2.062		2.045
CO_2 reactivity min, %		4.4		9.5
VBD max, g/cm3		0.94		0.82
Resistance to attrition, %		0.45		0.8

Coke A (S = 3.6 %) and Coke B (S = 3.0 %) were calcined in the rotary kiln to assess the risk of desulfurization within the temperature range of 1 200 to 1 350 °C. Coke samples were subject to the following analysis: sulfur content, real density, and CO_2 reactivity and attrition strength. The coke properties before and after calcination are given in Table 1.

Figures 1-5 show the coke properties as a function of temperature.

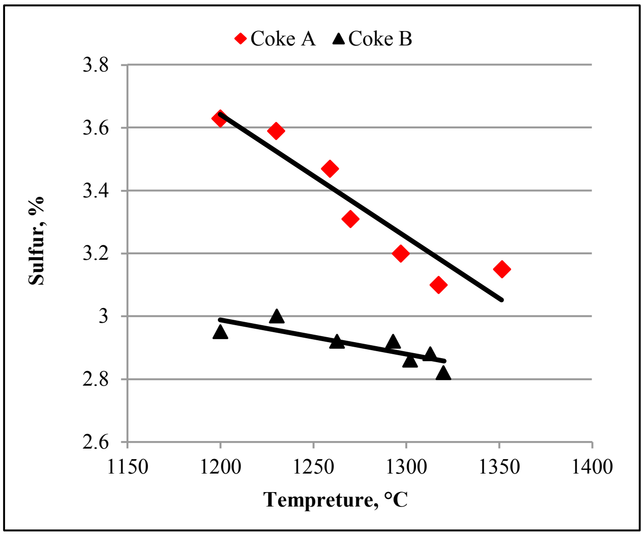

Figure 1. Sulfur content in calcined coke at different temperatures.

Figure 1 shows that the desulfurization of Coke A and Coke B begins at 1 230 °C. The initial sulfur content in Coke A reduced from 3.6 % down to 3.0 % at a temperature of 1 300 °C; Coke A lost 0.6 % of sulfur. The initial sulfur content in Coke B reduced from 3.0 % down to 2.8 % at a temperature of 1 300 °C; Coke B lost 0.2 % of sulfur. The above correlates with the results obtained under laboratory conditions: the higher is the sulfur content, the greater is the loss.

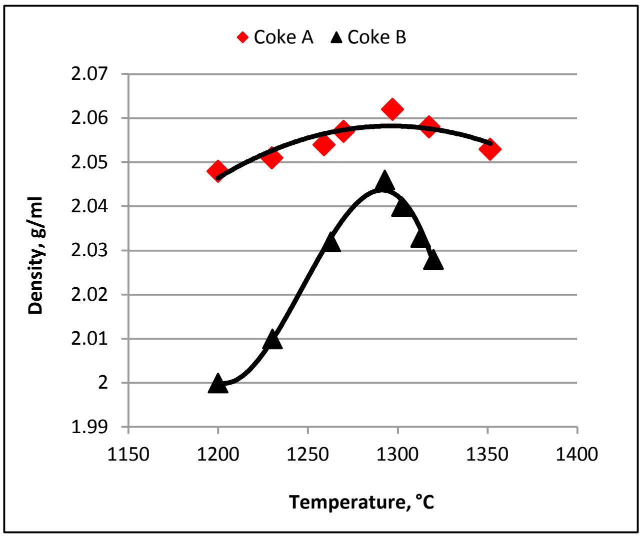

Figure 2. Real density of calcined coke at different temperatures.

Figure 2 shows the real density of calcined coke as a function of temperature. By comparing Figure 1 with Figure 2, we can see that a monotonic decrease in the sulfur content is not accompanied by a monotonic change in the real density: both cokes show that the real density extremely depends on the calcination temperature in the range of 1 200 to 1 350 °C. Moreover, it has been observed that CO_2 reactivity and attrition strength also extremely depend on the calcination temperature (Figures 3 and 4).

Mercury porosimetry data show that the volume of these pores increases four times in the course of calcining high-sulfur cokes [4].

It can be assumed that sulfur in coke is generally present in the form of thermally stable thiophenic compounds, which degrade at temperatures above 1 300 ^{0}C. In the meantime, a significant amount of sulfur in Coke A is present in the form of acyclic compounds, which degrade at lower temperatures. The results show that Coke A and Coke B, which have a similar sulfur level, behave differently during calcination. So, their characteristics may vary significantly.

The trends in the oil market lead to an increase in the sulfur content in petroleum coke. Aluminium producers are forced to blend coke of different sulfur content to meet the environmental requirements. Increasing the calcination temperature improves the characteristics of coke, but there is a risk of coke desulfurization.

Thus, high-sulfur coke calcination needs to be optimized, since the natural desire to improve the performance properties of coke by increasing the calcination temperature may lead to the opposite effect, i.e. desulfurization.

4. References

1. Hardin E.E., Beilharz C.L., Melvin L.L. A comprehensive review of the effect of coke structure and properties when calcined at various temperatures, Light Metals, 1993, p.501.
2. Akhmetov M.M. Production of low-sulfur coke from sulphurous oils, Acad. SUE INKhP RB, UFA in 2010, 180p.
3. Dyskin B.Sh., Yu.V.Kolupaeva, A.S.Korolev. Analysis of the desulfurization of petroleum coke, Science SUSU: Proceedings of the 66th Scientific Conference, Section of Natural Sciences, 2011. p.357-362.
4. Hardin E.E., Beilharz C.L., Ellis P.J., McCoy L. A comprehensive review of the effect of coke structure and properties when calcined at various temperatures, Part II/Light Metals, 1994, p.73.