
Influence of Calcination Temperature and Sulfur Level on Coke Properties

Victor Buzunov, Victor Mann, Sergey Khramenko, and John Johnson

Abstract

The majority of RUSAL's Russian smelters have to deal with challenges that are created by blending and calcining green cokes with varying chemical and physical properties and, especially, the problem is associated with high-sulfur cokes. It has been widely reported in the literature that desulfurization, which occurs during petroleum coke calcination, negatively affects coke quality. To assess the risks of desulfurization and its influence on the coke physical structure, the RUSAL Krasnoyarsk Aluminum Smelter has run several experimental trials regarding the calcining of petroleum coke in an industrial rotary kiln at different temperatures. This paper discusses the physical changes in calcined coke with different sulfur contents in an industrial rotary kiln where the real density and carboxy reactivity of high-sulfur coke are shown to be extremely dependent on the temperature of calcination and non-predictable from 1200 to 1350 °C.

Keywords

Petroleum coke • Sulfur • Calcination

Introduction

The Krasnoyarsk Aluminum Smelter remains one of the largest in the world producing about one million tonnes of aluminum per annum. Due to the capacity, it uses several sources of green coke resulting in cokes with different properties. The range includes all types of coke of different sulfur content: low-sulfur—up to 1.5% of sulfur, medium-sulfur—up to 3.0% and higher-sulfur more than 3.0%. All the cokes come from the C.I.S counties (Table 1).

Four hundred thousand tons of green coke is calcined at the calcining facilities in the Krasnoyarsk Aluminum Smelter per year using four kilns (Fig. 1). The main characteristics of the four kilns are summarized in Table 2.

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In 2010–2011, the kilns were upgraded in order to increase the throughput up to 12.5 tons/h by:

- Adding secondary air supply and control to the burning zone,
- Installation of lifters in the volatile-producing area,
- A higher degree of kiln filling (a deeper coke bed).

The addition of the lifters reduced segregation, however the problem of segregation within the coke bed inside the kiln since during rotation, the coarse particles are concentrated in the outer upper layer, and fine particles go to the center, where they get isolated from the radiant heat source resulting in the finer fractions being under-calcined. In order to increase the degree of calcination of fine fractions, the target temperature was increased by 40°—from 1240 to 1280 °C since the calcination temperature is very critical for forming the desired structure and physical properties of calcined petroleum coke.

The process of calcining petroleum coke with different sulfur levels within the temperature range of 1200–1500 °C

Table 1 Cokes properties

Supplier	%/year	Volatile %	S %	Si %	Fe %	V %	Na %
A	35.5	7.9	3.62	0.006	0.013	0.084	0.004
B	19	9.4	3.04	0.009	0.02	0.05	0.024
C	17	10.4	1.72	0.005	0.021	0.03	0.016
D	2.0	8.2	1.64	0.012	0.018	0.02	0.005
E	0.5	9.9	0.61	0.062	0.024	0.002	0.059
G	26	9.6	0.57	0.009	0.029	0.003	0.012

Fig. 1 Rotary Kiln**Table 2** Rotary kiln design characteristics

Capacity, tonnes/h	10.0
Kiln design	
Diameter (mm)	3000
Length (mm)	45,000
Tilt angle (degrees)	3.5
Rotational revolutions/min	22
Power (kW)	75

has been studied in detail under laboratory conditions [1]. The results indicated that the properties of high-sulfur coke at temperatures above 1300 °C are determined by the following two competing processes: graphitization and desulfurization.

Moreover, the explosive-like release of sulfur during calcination at temperatures above 1300 °C rearranges the crystal structure of coke which negatively affects the coke structure in ways that alter the reactivity and porosity of the resultant calcined coke [2]. However, the literature does not provide enough data on the process of calcining coke with different sulfur levels

under industrial conditions. Coupled with the experience at the Krasnoyarsk Aluminum Smelter after modernization of the kilns led to a large number of temperature excursions above 1300 °C (Fig. 2) the decision was made to study desulfurization under industrial kiln operating conditions.

The rest of paper will discuss the results of calcining high-sulfur coke in the rotary kiln under industrial conditions to assess the risks of desulfurization. The RUSAL Krasnoyarsk Aluminum Smelter ran several trials regarding calcining petroleum coke in the rotary kiln at different temperatures.

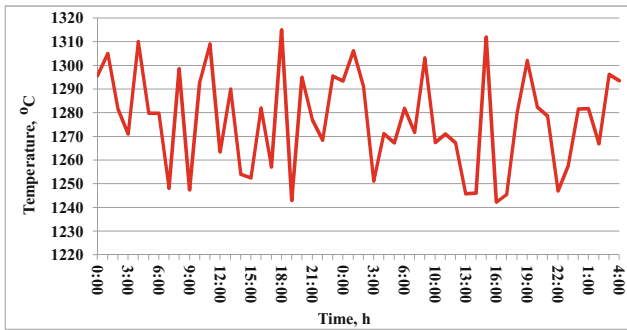


Fig. 2 Typical kiln daily temperature variations and a large number of excursions above 1300 °C

Calcination Results

Two cokes, “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 1200–1350 °C. The coke samples were subject to the following analysis: sulfur content, real density, CO₂ reactivity and attrition strength. The coke properties before and after calcination are given in Table 3.

Figures 3, 4, 5 and 6 show the coke properties as a function of temperature.

Figure 3 shows that the desulfurization of Coke A and Coke B begins at 1230 °C. The initial sulfur content in Coke A reduced from 3.6% down to 3.0% at a temperature of 1300 °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 1300 °C; Coke B lost 0.2% of sulfur. This is in accordance to the results obtained under laboratory conditions where the higher is the sulfur content, the greater is the loss [2].

Figure 4 shows the real density of calcined coke as a function of temperature. By comparing Fig. 2 with Fig. 3, one 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 1200–1350 °C.

Table 3 Coke properties before and after calcination

Parameters	Coke A		Coke B	
	Calcination		Calcination	
	Before	After	Before	After
Moisture (%)	8.1	–	8.8	–
Volatiles (%)	7.8	–	10.1	–
Sulfur (%)	3.6	3.1	3.1	2.8
Real density max (g/cm ³)	–	2.062	–	2.045
CO ₂ reactivity min (%)	–	4.6	–	9.5
VBD max (g/cm ³)	–	0.84	–	0.82
Resistance to attrition (%)	–	0.45	–	0.8

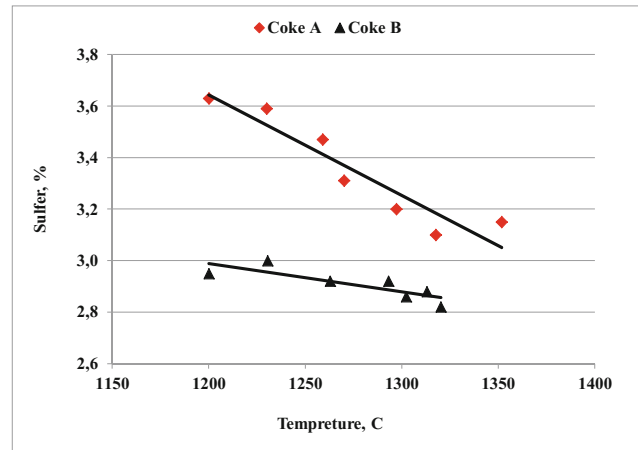


Fig. 3 Sulfur content in calcined coke at different temperatures

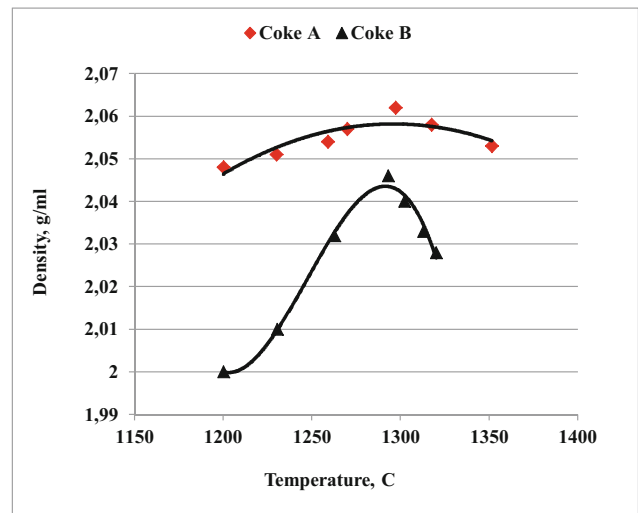


Fig. 4 Real density of calcined coke at different temperatures

Moreover, it has been observed that CO₂ reactivity and attrition strength are also extremely dependent on the calcination temperature (Figs. 5 and 6).

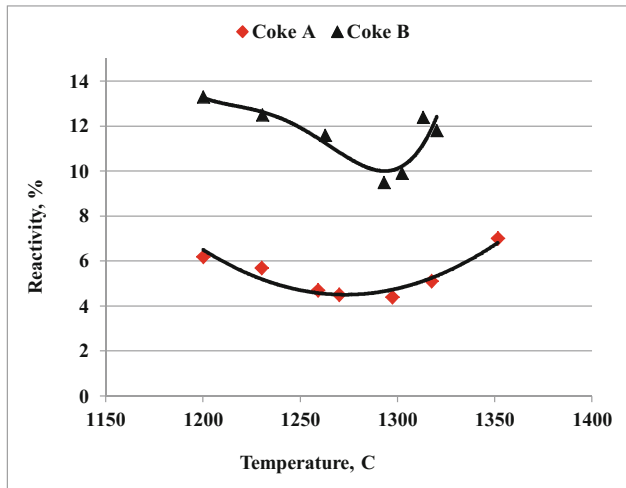


Fig. 5 CO₂ reactivity of calcined coke at different temperatures

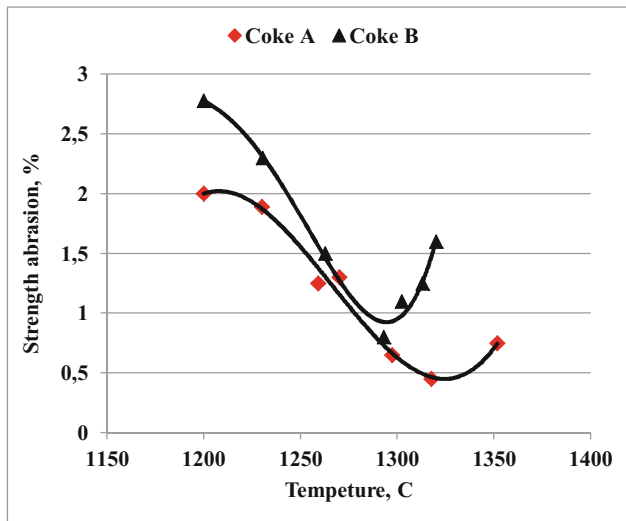


Fig. 6 Attrition strength of calcined coke at different temperatures

The results show that a temperature of 1300 °C is the limit for high-sulfur coke. It can be assumed that high-sulphur coke undergoes structural changes at this

temperature. The previous studies [2] on high-sulfur coke calcination—carried out under laboratory conditions show an increase in the pore volume in the size range of 0.014–0.1 μm.

In order to determine the characteristics of porous structure formation in high-sulphur coke, mercury porosimetry was used to study the samples of cokes A and B taken from an industrial kiln after calcined at 1300 °C, and the samples of said cokes calcined at 1300 °C under laboratory conditions.

Porous Structure Formation

Lab calcination was carried out in a closed graphite crucible under argon at a rate of 10 °C/min up to 1300 °C, with an isothermal retention time of 1 h. The results of both lab and industrial calcination are shown in Table 4 and in Figs. 7 and 8.

The results of mercury porosimetry were interpreted within the framework of the “Dusty—Gas Model” [3]. According to this model, the total volume of pores was divided in three structural zones, depending on the pore size.

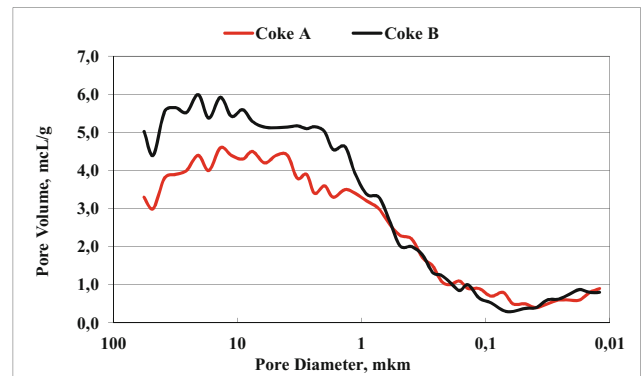


Fig. 7 Pore structure of coke A and coke B after kiln calcination

Table 4 Coke properties after laboratory and kiln calcination

Parameters	Laboratory calcination		Kiln calcination 1300 °C	
	Coke A	Coke B	Coke A	Coke B
Sulfur (%)	3.3	3.0	3.1	2.8
Real density (g/cm ³)	2.072	2.056	2.062	2.045
CO ₂ reactivity (%)	4.0	6.6	4.6	9.5
VBD max (g/cm ³)	0.88	0.85	0.84	0.82
Pore volume (mL/g)	—	—	—	—
Total volume	84.5	85.9	110.5	136.4
Viscous zone	57.5	55.8	82.1	108.7
Diffusion flow	15.5	16.9	21.5	21.3
Knudsen flow	11.5	13.2	6.9	6.4

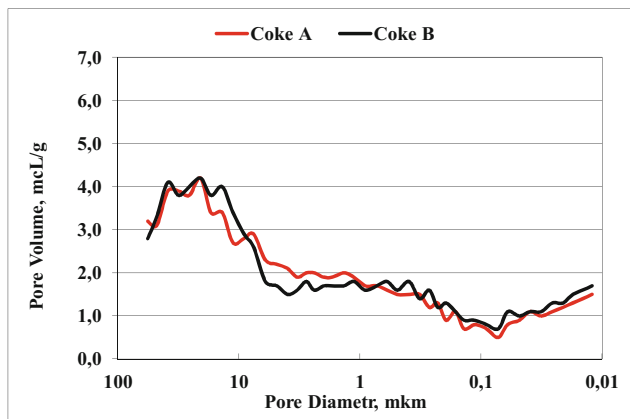


Fig. 8 Pore structure of coke A and coke B after laboratory calcination

Such zones differ from each other in terms of the nature of gas flow through porous media:

- In the pores with a diameter of 0.012–0.1 μm, there is a free molecular, or Knudsen, flow, in which the pore size is less than the free-path length, and, in this particular case, collisions between molecules can be neglected, as opposed to the frequency of collisions with the surface of the pores;
- In the pores with a diameter of 0.01–1.0 μm, there is molecular diffusion through a continuous medium; it is when the gases are moved under the influence of a concentration gradient (normal diffusion). In this case, intermolecular collisions occur more frequently than collisions with the surface of the pores.
- Viscous flow; it is when the gas flows as a continuous medium under a pressure gradient, and intermolecular collisions dominate over collisions with the surface of the pores. The pore diameter is 1.0–60 μm.

Table 4 shows the properties of cokes A and B calcined both under lab conditions and in a rotary kiln, and the pore volume distribution, by gas flow zone. The properties of the cokes show an increase in real density and a reduction in CO₂ reactivity under lab calcination. VBD (size 1.18–2.36 mm) cokes increase calcination in the laboratory condition and correlates to total pores volume.

Figure 7 shows the porous structure of cokes A and B calcined in a rotary kiln. The pore size distribution shows that coke B has a greater porosity than coke A under industrial calcination. Coke B contains more volatiles (Table 3), the release of which, under calcination, forms an additional pore volume in the viscous flow zone, with a pore diameter of more than 1.0 μm. The pore volume in the diffusion zone and the Knudsen flow zone in the porous structure of both cokes is the same.

Figure 8 shows the structure of cokes A and B calcined under lab conditions. Under lab calcination, there is a decrease in the total pore volume, compared to industrial calcination; the pore volume in all the zones for cokes A and B is almost equal. Comparing the results of laboratory and industrial calcination, one can see that porosity formation is effected not so much by the content of volatiles as by the rate of their release during calcination.

The comparison of porosity distribution under industrial and laboratory conditions, as in the case of Coke B (Fig. 9), shows that not only the total pore volume changes but also the pore volume distribution between the three porosity zones.

Figure 9 shows that, under industrial calcination, the volume of pores in the viscous flow zone and in the molecular diffusion zone is bigger, but the content of the Knudsen pores (0.1–0.012 microns) is less than under laboratory calcination. This suggests that the mechanism of nanoporosity formation during rotary kiln calcination might be different from what is described in [2].

It is likely that, under industrial calcination in a rotary kiln, there is not only an explosive release of volatiles, the result of which is an increase in the number of larger pores, but also an explosive release of sulfur at 1300 °C, which is accompanied by the formation of larger pores in the diffusion zone.

We can also assume that such extreme dependence of the properties of high-sulfur cokes calcined under industrial conditions (for example, CO₂ reactivity) can be explained by the characteristics of the porous structure.

In general, CO₂ reactivity is determined based on the presence of catalytic impurities, the rate of mass transfer and the reactive surface, the quantity of which is mainly determined by the amount of pores with a size of less than 0.01 μm.

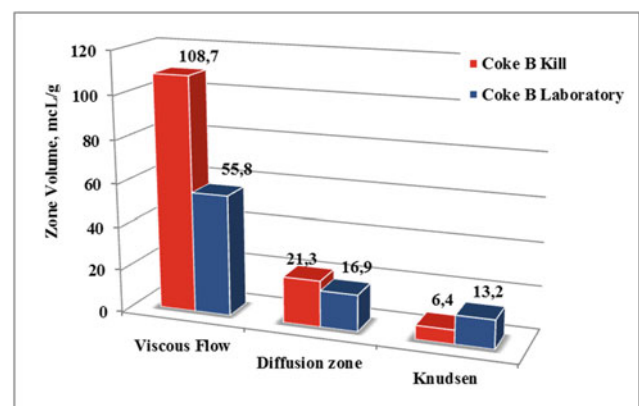


Fig. 9 Porous structure coke B after industrial and laboratory calcination

However, the reactivity of industrially calcined cokes is higher than those calcined in the laboratory (Table 4). This is because the rate of reactions in porous media is determined mainly by the intensity of the mass transfer of the reaction gas to the reaction zone, instead of the kinetic characteristics of the reaction itself. And there is a larger amount of big transport pores during industrial calcination.

Discussion

Sulfur compounds, which are present in coke, may be in the form of sulfides, thioesters, mercaptans, as well as heat-resistant thiophene rings [4]. The thermal stability of sulfur compounds determines the sequence of thermal transformations. First, in the course of desulfurization, the link between RC and S is broken, and free radicals (RS-, -S) are formed. Active -S may enter secondary reactions, forming heat-resistant compounds, such as thiophene, or transit into the vapor phase and escape [5]. The subsequent high-temperature destruction of thiophene rings breaks the crystal lattice and leads to the formation of pores of less than 0.1 μm .

The mercury porosimetry data show that the volume of these pores under industrial calcination is less than under lab calcination. Changes in the porous structure lead to an increase in the reactivity of industrially calcined coke, due to better conditions for the mass transfer of gas in larger pores.

It can be assumed that sulfur in coke is generally present in the form of thermally stable thiophenic compounds, which degrade at temperatures above 1300 °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 and their characteristics may vary significantly.

Overall, the sulfur content continues to increase as new sources of heavier crude oils are being processed in addition to the lighter sources which results in higher sulfur content in the petroleum cokes. 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.

Conclusions

The character of changes in the properties high sulfur cokes resulting by industrial calcination differs significantly from the calcination in a laboratory. In the range of calcination 1200–1350 °C the real density, reactivity and abrasability have an extreme character at 1300 °C. Under industrial calcination in a rotary kiln there is an explosive release of sulfur at 1300 °C, which is accompanied by the formation of larger pores in the diffusion zone. This increases the CO₂ reactivity that determined mainly by the intensity of the mass transfer of the reaction gas to the reaction zone.

To reduce the risk of desulfurization temperature 1300 °C should be considered as limiting the calcination. To stabilize the calcination temperature is necessary to improve the existing system of controlling the operation of the furnace.

References

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