Influence of carbon-containing additives on sintering of limestone-nepheline furnace charge in alumina production

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Abstract. The article is devoted to the influence of brown coal additives on the sintering of the lime-nepheline charge in the technology of alumina production from nepheline. It is shown that carbon-containing materials added to the limestone-nepheline charge intensify sintering, and thus, contribute to a more uniform heat distribution along the furnace, improve the passage of the sintered material in the chain curtains, accelerate interaction of the charge components and increase recovery of alumina from the sintered mass. The mechanism of influence of coal during its combustion on the passage of solid-phase reactions in the charge is studied. Fossil brown coals with a high content of volatile substances and carbon graphite materials were used as coal additives.

1. Introduction
There has been plenty of evidence [1] – [7] that carbon-containing materials added to the limestone-nepheline charge intensify sintering, and thus, contribute to a more uniform heat distribution along the furnace, improve the passage of the sintered material in the chain curtains, accelerate interaction of the charge components and increase recovery of alumina from the sintered mass.

Almost any carbon-containing materials can be added into the charge. Various carbon-containing additives affect sintering in a different way, which depends on their origin and properties - calorific effect, content of volatile substances, etc. The target of our research was to identify the behavior pattern of carbon-containing materials during sintering, depending on their nature and properties, and to determine the influence mechanism of coal combustion on the solid-phase reactions in the furnace charge. Based on the data obtained, we can justify application of certain carbon-containing materials by their economic efficiency [8].

In order to study the effect of additives, we chose two types of materials, located at the extreme positions in the possible range of carbon-containing additives. These were: fossil brown coals with a high content of volatile substances and carbon-graphite materials. The effect of additives was studied in industrial furnace charges of alumina facilities.

Brown coals are the next metamorphism stage after peats, and are characterized by a low content of un-decomposed residues. Brown coals contain humic acids, bitumen, neutral products of molecular complication – humans and residual coal [9], [10], [11]. Mature coalification manifests itself in de-mineralization of the organic mass, increase in the carbon content, decrease in the content of hydrogen and oxygen, and release of volatiles; as a result, it leads to formation of coals and anthracites [12], [13], [14], [15]. In terms of the quality of carbon contained therein, anthracites are very close to carbon
graphite materials, the waste products of aluminum production, since the manufacture of carbon graphite materials gives less than 1% of volatiles [15], [16].

2. Research methods
We studied the influence of two types of coals on sintering in laboratory environment, in a silitic furnace under isothermal conditions. The furnace charge was placed in a furnace, pre-heated to a certain temperature, and kept for various periods of time. The sintered mass was, then, removed from the hot furnace and exposed to air hardening, taking into account worsening recovery of alumina from the sintered mass due to rapid cooling. The time of exposure was 5, 10, 20, 40 and 60 minutes at temperatures 600, 700, 800, 900, 1000, 1100, 1150, 1200, 1250, 1275, 1300ºС. The sintered masses were leached in a standard procedure, and then we determined recovery of alumina from the masses. We used raw materials of the Achinsk Alumina Facility (charge № 1) to study sintering of charge with the brown coal additive, and materials of Pikalevsky Alumina Facility (charge №2) to study sintering of charge with the carbon-graphite additive. The composition of the tested charges is given in Table 1. The amount of brown coal additive was 1% in terms of carbon, and of carbon graphite material - 3%. The partition size of the charge: 6-8% of particles are more than 80 microns.

Table 1. Composition of raw materials.

| Material   | Al₂O₃ | SiO₂ | CaO | Fe₂O₃ | MgO | Na₂O | K₂O | M_alk | M_lime |
|------------|-------|------|-----|-------|-----|------|-----|-------|--------|
| Charge 1   | 24.65 | 11.96| 17.88| 32.77 | 2.10| 0.70 | 7.01| 1.26  | 1.08   |
| Charge 2   | 26.31 | 11.60| 17.21| 31.71 | 1.42| 0.50 | 5.31| 2.79  | 1.01   |

3. Research results
Figures 1 and 2 show the dependence of the transformation degree on the temperature and time of exposure, in the course of interaction of nepheline ore and limestone, without additives and with the brown coal additive. At low sintering temperatures, coal volatile substances burn out without any effect on solid-phase interactions in the reaction mixture. As the limestone decomposes, interaction of the forming calcium oxide with nepheline intensifies dramatically, as evidenced by a sharp increase in the alumina recovered from the sintered mass at temperatures 800-900ºС. The difference in the recovery degree can reach up to 8%. A fairly high transformation degree in reactions is achieved even with a short-time exposure (up to 20 minutes), after which the process becomes stable and the difference in recovery maintains.

![Figure 1](image.png)
Adding brown coal to charge № 1 intensifies interactions in the charge, but does not affect the nature of the process in general. The dependence curve of recovery degree on temperature has three distinct sections that differ in the reactions rate. The brown coal additive does not affect the slowing rate at temperatures 900-1000°C, caused by a decrease in the diffusion of Ca ions through the layer of reaction products. The results obtained at the temperatures of sintered mass formation show that brown coal additives lead to a certain decrease in the sintering temperature and to expansion of sintering section. With 1% of coal additive, the recovery rate is equally high at temperatures of 1250, 1275 and 1300°C with exposure time of 10 - 30 minutes.

![Figure 2](image1.png)

**Figure 2.** Dependence of alumina recovery from charge № 1 on the sintering temperature and time of exposure: 1 - 11 - without additive; 1' - 11' - with the brown coal additive; at temperatures 1,1' - 600; 2,2' – 700; 3,3' - 800; 4,4' – 900; 5,5' - 1000; 6,6' – 1100; 7,7' - 1150; 8,8' - 1200; 9,9' – 1250; 10,10' - 1275; 11,11' - 1300 °C.

Adding carbon-graphite materials to charge № 2 somewhat changes the nature of the kinetic curve (figure 3). The charge without an additive has a "longer" sintering section at temperatures of 900-1100°C. The carbon-graphite additive materials lead to a remarkable displacement of that section towards lower temperatures and to its reduced range (800 - 900°C), which corresponds to the temperature of the most intense carbon burnout. Alkaline aluminates are formed much more intensively not only at the low-temperature stage during the limestone decomposition, but also at above 900 degrees, thanks to activated diffusion resulted from continuous supply of carbon combustion gases.

![Figure 3](image2.png)

**Figure 3.** Dependence of alumina recovery on sintering temperature in sintering of charge № 2. 1 - without additive; 2 - with the carbon-graphite material additive, sintering time = 1 hour.
The increased alumina recovery within the entire temperature range can be explained by more complete reactions of soluble aluminates formation. Based on the data we obtained, we further calculated the rate constants for reactions of alkaline aluminates formation in a charge without additives and with carbon-containing additives; we also calculated the apparent activation energy of the process (figure 4). The rate constants for alkaline aluminates formation given above show that the reaction rates increase with increasing temperature both for the charges without brown coal additives and with the additives (Table 2). The values of the constants with the additive are higher. We should also note that the influence of coal is more pronounced with a short heating time.

**Table 2.** Rate constants for reactions of alkaline aluminates formation in sintering of charge 1 without additive and with the brown coal additive.

| Temperature, °C | 20 | 60 |
|----------------|----|----|
| No additive, K | Coal additive, K<sub>С</sub> | K<sub>С</sub> /K | No additive, K | Coal additive, K<sub>С</sub> | K<sub>С</sub> /K |
| 800            | 1.026 | 2.677 | 2.61 | 0.602 | 1.021 | 1.70 |
| 850            | 2.295 | 3.466 | 1.51 | 1.050 | 1.326 | 1.26 |
| 900            | 3.326 | 4.067 | 1.22 | 1.268 | 1.547 | 1.22 |
| 950            | 3.675 | 4.338 | 1.18 | 1.338 | 1.613 | 1.21 |
| 1000           | 3.975 | 4.526 | 1.14 | 1.444 | 1.668 | 1.16 |
| 1050           | 4.545 | 4.961 | 1.09 | 1.730 | 1.854 | 1.07 |
| 1100           | 5.384 | 5.606 | 1.04 | 2.241 | 2.122 | 0.95 |
| 1150           | 6.517 | 7.464 | 1.15 | 3.334 | 3.316 | 0.99 |
| 1200           | 9.633 | 10.790 | 1.12 | 4.329 | 4.630 | 1.07 |
| 1250           | 13.303 | 14.761 | 1.11 | 4.879 | 4.921 | 1.01 |

The values of the apparent activation energy, calculated by Arrhenius equation (Table 3), show that sintering with brown coal is mostly intensified at low temperatures, on sections 1 and 2 of the curve. The activation energy is significantly reduced at the solid carbon combustion temperatures of 800 – 900°C, when the interaction of components is not inhibited by the layer of reaction products. Apart from that, the temperature range for achieving the same degree of Al₂O₃ transformation in case of the coal additive is shifted to a lower temperature area.

**Figure 4.** Dependence of the rate constants for reactions of alkaline aluminates formation in sintering of charge 1 without additive and with the brown coal additive (2), sintering time 20 (a) and 60 (b) minutes.
Table 3. Apparent activation energy of alkaline aluminates formation in sintering of charge №1 without additive and with the brown coal additive

| Temperature range, °C | Activation energy, kJ / mol | Time of exposure, minutes |
|-----------------------|-----------------------------|--------------------------|
|                       | Without additive | With coal | Without additive | With coal |
| 800 – 900             | 123.41           | 55.43       | 77.94           | 43.42       |
| 900 – 1100            | 36.15            | 12.97       | 14.13           | 7.48        |
| 1100 - 1200           | 122.26           | 101.39      | 112.35          | 112.35      |

Thus, brown coal added for sintering of nepheline with limestone promotes an increased completeness of interaction between the furnace charge components within the entire sintering temperature range.

4. Conclusions

When the additives to the charge are coals at a low stage of coalification, sintering is intensified, mainly, in a lower temperatures section (600-1000°C). In this case, the sintered mass with a coal additive is characterized by an increased content of soluble aluminates and a higher degree of alumina recovery at a constant temperature, or, in other words, reactions are shifted to a lower temperatures section, but the alumina recovery remains the same, as compared with the charge without additives. When additives to the charge are carbon graphite materials, where practically all carbon is in the form of graphite, sintering is intensified to a greater extent, which is manifested not only in the limestone de-carbonization section, but also over the whole sintering temperature range, which ensures a higher level of alumina recovery at finite sintering temperatures.

The range of carbon influence on sintering is related to the burning temperature of solid carbon in the additive: the higher it is, the greater the temperature affects the solid-phase reactions in the charge.

The addition of carbon-containing materials with a high content of solid carbon leads to a significant decrease in the apparent activation energy within the whole range of sintering temperatures, whereas the addition of brown coal decreases the apparent activation energy mainly in the low-temperature section (800-1000°C).

Thus, we can come to a conclusion that reactivity of carbon-containing material in the charge depends mainly on the amount of solid carbon residue formed at the beginning of the solid-phase reactions in the charge, which is determined by the nature of the fuel additive. The intensifying effect of the additives grows from peat and brown coals towards anthracite and carbon-graphite materials. The effect of the carbon-containing additive is more active at the combustion temperatures of solid carbon.

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