Effect of coal-containing additives on the rheological properties of limestone-nepheline charge in the technology of 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. The process of extraction of humic compounds from brown coal is considered, the effect of humic additives on the rheological properties of pulp depending on the size and moisture content of carbon-containing additives is studied.

1. Introduction
Due to the sufficient contain of bauxite-containing ores, the actual production of alumina from nepheline-containing raw materials is a topical issue for the Russian aluminum industry [1].

One of the most important revamping of this technology is the process of nepheline sintering with limestone in a tubular rotating furnace [2-4]. This operation is associated with significant fuel and energy consumption, the reduction of which is one of the urgent tasks for the intensification of production. As a solution to this problem, it may be suggested to reduce the moisture content of the alumina-containing pulp entering sintering, while maintaining its mobility at the level necessary for transportation by pipelines, by adding lignite charcoal additives containing surfactants-humic acids.

From the literature data [5,6] it is known that humic compounds obtained from natural coal containing materials by alkaline treatment are effective liquefier of nepheline-lime pulps. Conducted studies proved that introduction of coal-alkaline reagent (CAR) into the nepheline-limestone pulp allows reducing moisture content of the pulp from 30% (current industrial value) to 24.5%, while retaining mobility allowing transportation by pipelines without increasing energy consumption[7-11].

For this purpose it is conceivable to use the additions of humic-containing lignite charcoal without preliminary alkaline treatment due to the interaction of humic acid with alkalis of the pulp liquid phase. To this end, it is necessary to determine conditions under which the humates extraction proceeds to the maximum extent, determine the optimal composition of the pulp salt phase, the effect of charcoal additives on rheological properties [12-14], depending on the content of humic acids in it, and also determine the amount of additives that have maximum diluting effect on the pulp and minimum critical humidity of the pulp with additives, at which its mobility for transportation is maintained.
2. The influence of particle size of coal on the rate of extraction of humic compounds

Limestone-nepheline pulps of industrial composition were used in studies. The research purpose was to study the effect of humic compounds on the rheological properties of limestone-nepheline pulps. It is known from the literature that humic compounds, being surface-active substances, have a liquefying effect based on their adsorption on the surface of dispersed phase particles, preventing the aggregation of these particles and reducing strength of the coagulation structures, adsorption blocking bonding sites of the particles.

To study the effect of surface-active additives on pulp rheology in laboratory conditions, the humates were used, previously obtained from charcoal by treating it with alkali. The action of NaOH is first manifested in decomposition of the complex formed from residual charcoals and humates, and then in ion exchange between insoluble cations of calcium and aluminum and sodium ions. As a result of the interaction of alkali with lignite charcoal, a coal-alkali reagent is formed, consisting of three parts: liquid; coarse-grained, easily precipitated; slowly precipitating gelatinous suspension. The amount of alkali necessary to saturate the exchange complex of humic acids with sodium cations is 0.12 g per 1 gram of humic substances. Dissolution of humic acids in alkaline solutions is preceded by peptization. At a certain ratio between humic acids and an alkaline solution, a polydisperse system is formed, containing the humate of the alkaline solution and salt of the humic acids. With acidification of alkaline solutions, as well as with introduction of calcium and magnesium ions, humic acids coagulate. At low pH values, humic acids are coupling into large micelles, so the viscosity of aqueous solutions of humates decreases with pH decreasing, and the surface tension is also decreases.

![Figure 1](image_url). Extraction rate of humic compounds from brown coal of various sizes:
1 - particles less than 50 µm
2 - particles less than 1 mm
3 - particles less than 5 mm

Figure 1 shows the dependence of charcoal solubility via the particle size. These data prove that the charcoal particles size significantly affect transition of humates to the solution. When the coal is crushed to a particle size of 50 µm, about 90% of the humates passes into solution within 2 hours. With a high content of humates in coal (60 - 90%), short time leaching of coal is sufficient to ensure the necessary mobility of low humidity pulps. This fact is confirmed by the experiments of the determination of the diameter of the circle spreading of coals of different sizes. In this case, an alkaline solution of humates was obtained by treating the lignite charcoal with a liquid pulp phase at
temperature of 60°C for 2 hours. For comparison, a solution of humates obtained by leaching charcoal of various concentrations separated from the solid charcoal phase were added to the dry charge, as well as solution after leaching, containing particles of residual charcoal (such as an coal-alkali reagent) of various sizes.

Coal solution containing solid phase significantly reduces the diluting effect of humates. This may be due to the pulp concentration increase caused by the increase of the solid phase content, the adsorption properties of solid charcoal particles, or increased viscosity of the colloidal component of the reaction product of charcoal with alkali. In the case of finer grinding of charcoal in a solution (to a particle size of less than 50 μm), its negative effect on the pulp mobility was reduced.

When pulp is stored for 1-3 days, its rheological characteristics improves significantly due to the ongoing process of humates isolating, further prolongation of the aging time does not significantly affect it. However, the complete release of humates is accomplished in 6 to 7 days, and the pulps stored during this time have a somewhat better fluidity than those stored for 3 to 5 days. This is especially evident for pulps that initially did not have the ability to flow, in which the structure is destroyed the next day by the process of humates releasing reducing its viscosity.

Dispersion composition of recommended size charcoal (not larger) after humic compounds leaching is as follows: less than 3 μm - 85% of the particles; of them - less than 1 μm - 30%, from 1 to 2 - 40%, from 2 to 3 μm - 15%. Density of such charcoal is 1.6 g/cm³.

**Figure 2.** Dependence of pulp flow time at 25% humidity via amount of humic lignite charcoal additive: 1 - nepheline ore; 2 - limestone; 3 - nepheline-limestone charge.
3. Study of the effect of brown coal additives of different moisture on the fluidity of limestone-nepheline pulps

In order to determine the rheological properties of the charge, into which the charcoal was introduced during grinding, a capillary viscometer with a hole of 3 mm in diameter was used. The obtained dependences of flow time via the coal additive amount at humidity of 25% are shown in Figure 2, the dependence on humidity for various coal additives is shown in Figure 3.

In order to establish on which component of a charge the charcoal exerts greater effect, the experiments were carried out separately with nepheline and limestone pulps, and then with nepheline-limestone pulp. According to the experimental data, it may be argued that the limestone slurry has a structure more prone to fracture and reorientation of the particles. For limestone, small amounts of charcoal (about 0.25% in terms of coal content) is sufficient, and further increase of coal content does not result in any changes of material consistency. The lamellar structure of limestone not only promotes formation of stable structures, but also their destruction. Probably, limestone particles move apart along the cleavage plane in the course of humic salts adsorption and reorient, causing the structure to rearrange.

![Figure 3](image-url)

**Figure 3.** Effect of the humic lignite charcoal on the fluidity of limestone-nepheline pulps at humidity of: 1 – 24.5%; 2 – 25%; 3 – 26%; 4 – 30%.

Nepheline has a hexagonal framework structure, so nepheline suspension, in order to achieve the maximum degree of dilution, requires a larger amount of surfactant — 1.5-2% (in terms of coal content) to reorient the particles of this form. With charcoal content increasing from 3% or higher, fluidity deteriorates again, the pulp loses mobility.

When considering the pulps mobility in presence of humic lignite charcoal addition, a range of moisture values below critical value is of interest to illustrate possibility of its reducing while maintaining liquid-flow properties.

Figure 4 shows dependence of lime-nepheline charge flow time when charcoal is added in the amount of 0.25% via moisture at size particle of less than 50 μm and on the particle size at 30% moisture.

Since the limestone component predominates in the charge (ratio of the limestone to nepheline amounts is approximately 2:1), the effect exerted by coal on its rheological properties is determining. Presumably, such an effective of small additive is explained by the fact that this amount of humates,
extracted from coal, forms a monomolecular layer on the surface of reoriented particles sufficient to destroy the structure of the suspension and change its properties.

Adsorbed on solid particles of the suspension, humic salts interact through hydrogen bonds and electrostatic forces with adsorbed cations and anions that are part of limestone and nepheline lattices. That is why, it is sufficient to form a monomolecular layer on the surface of the particles of the solid phase.

High content of alkalis in the liquid phase has a retarding effect on the humic compounds activity in limestone-nepheline pulp because presence of electrolytes in the solution promotes increasing of humic acids formation, and as with solution pH increasing, the viscosity of aqueous humates solutions increase. Dependence of pulp fluidity at constant value on the amount of coal additive up to the limit value, which has a diluting effect, can be described by equation:

$$\tau = A \cdot e^{Bx+Cx^2}$$

where $$\tau$$ – time of pulp flow, $$X$$ – content of coal additive, $$A$$, $$B$$, $$C$$ – empirical coefficients.

![Figure 4](image1)

**Figure 4.** Effect of humic lignite charcoal on the fluidity of limestone-nepheline pulp with 0.5% coal addition: a - depending on the particle size of charcoal at 30% humidity and b - depending on the moisture content of the pulp when particle size charcoal is less than 50 µm.

The essential factor for pulp liquefaction is the amount of humic acids contained in charcoal, because their number fluctuates depending on the formation. Therefore, for a guaranteed positive effect, the required amount of charcoal must be somewhat greater than the minimum.

The behavior of humates is determined by their content in the lignite charcoal. Charcoal with high humic acids content should be ground to sufficient finely, enough to increase the degree of humates extraction, which contributes to the higher effectiveness of surfactants on the rheological properties of the pulp. The extraction of sufficient amount of humates from the coals with reduced humic acids content in the solution is possible with the increase in the coal addition, but in this case the positive effect of additive is levelled due to the increase of the solid phase mass that does not contain humates and increase in the pulp water demand. Even fine grinding of charcoal does not improve the pulp fluidity, on the contrary, it contributes to its delamination during storage due to emergence of small coal particles due to their lower density compared to the pulp solid phase. In case of high humic acids content in the coal, fine grinding does not lead to the delamination of the pulp because most of the coal is dissolved in alkali and the solid residue consists mainly of mineral part of the coal, the graphitized residue being not more than 5% of the graphitized coal part.

From the foregoing, it can be concluded that the introduction of lignite charcoal into a limestone-nepheline pulp with a high alkali content in the liquid phase has a diluting effect associated with the
humates formation and is based on the fact that they are adsorbed on the surface of the particles of the dispersed phase and reduce the strength of the coagulation structures. The addition of lignite charcoal contributes to the increase in pulp flow, reduction of the flow time and decrease in shear stress. In this case, pronounced effect is achieved by the addition of charcoal with high content of humic acids (60-80%). The introduction of humates exerts greater effect on the limestone component of the pulp due to the specific features of the limestone particles structure. The range in which the charcoal addition is effective on rheology is from 0.5 to 2% in terms of coal content.

The production tests proved that also the energy consumption for transportation by pipeline is maintained, the addition of 1% of lignite charcoal in terms of coal content makes it possible to reduce moisture content of the pulp from 30 to 26%, which reduces the fuel consumption for moisture evaporation in the sintering furnaces.

4. Conclusions
1. The introduction of lignite charcoal into a limestone-nepheline pulp with a high alkali content in the liquid phase has a diluting effect associated with the humates formation and is based on the fact that they are adsorbed on the surface of the particles of the dispersed phase and reduce the strength of the coagulation structures.
2. The addition of lignite charcoal contributes to the increase in pulp flow, reduction of the flow time and decrease in shear stress. In this case, pronounced effect is achieved by the addition of charcoal with high content of humic acids (60-80%). The introduction of humates exerts greater effect on the limestone component of the pulp due to the specific features of the limestone particles structure.
3. The range in which the charcoal addition is effective on rheology is from 0.5 to 2% in terms of coal content.
4. The production tests proved that also the energy consumption for transportation by pipeline is maintained, addition of 1% of lignite charcoal in terms of coal content makes it possible to reduce moisture content of the pulp from 30 to 26%, which reduces the fuel consumption for moisture evaporation in the sintering furnaces.

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