On the role of hydrated calcium carboaluminate in the improvement of the production technology of alumina from nephelines

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Abstract. The coagulation properties of HCCA in the system “aluminate solution - nepheline sludge” were studied, which allowed to improve the processes of thickening and washing of nepheline sludge. Solutions were developed aimed at the improvement of the coarse alumina production technology on the basis of increasing the efficiency of the carboaluminate method for separating Al (III) and Si(IV) hydroxo complexes and using the combined crystal growing modifier CaCO3 – HCCA.

1. Introduction
Hydrated calcium carboaluminates (HCCA), derived from hydroaluminates of the type $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}_x$, are widely known in the field of cement chemistry [1-3].

The synthesis of HCCA in cement chemistry works, simulating the hardening of cement stone, is carried out in aqueous solutions of lime, calcium aluminates and soda at temperatures of 5-18°C during several months. The very low speed of the processes under consideration did not allow us to expect the creation of a technology for the separation of HCCA in the aquatic environment for technical purposes.

As a result of the study of the kinetics of forming hydrated calcium carboaluminates, it was found that in alkaline aluminate solutions the their crystallization rate increases by 4 compared with the release of these substances under neutral conditions and the synthesis time of HCCA amounts to only 40 minutes [4-6].

The industrial result of theoretical studies was the technology, first time ever created in the world practice, for the synthesis of HCCA for the complete separation of aluminum and silicon ions in the production of alumina from nephelines [4]. According to this method, the HCCA was synthesized by mixing an extremely pure circulating aluminate solution with a silicon module (w.rat. $\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$) equal to 4000-5000 units and calcium hydroxide in a volume ratio of 3:1.

2. The study area
From the literature [8, 9] it is known that as a result of studies carried out by the St. Petersburg Mining Institute and State Unitary Enterprise "Vodokanal", there have been new properties of HCCA revealed as a multifunctional coagulant (adsorbent, ion exchanger, weighting agent, densifier and activator). On the basis of these data, special studies were carried out on the use of HCCA in the system of thickening
and washing of nepheline sludge together with the highly polymerized import flocculant “Alclar-550; 600”.

The possibility of selective use of coagulants-flocculants is associated with differences in the electrochemistry of the surfaces of nepheline sludge and dispersion medium - aluminate solution under conditions of varying concentration. It was established that the surface charge of nepheline sludge particles is decisively affected by the concentration of Na$_2$O in the solution. The negative charge is due to selective adsorption of hydroxide ions at a concentration of 1-1.5 g/l of Na$_2$O. Increase in the alkali concentration in the solution leads to the fact that the diffuse part of the electric double layer is compressed and a larger number of Na$^+$ counterions enters the adsorption layer causing a decrease in the negative charge up to zero, and with a further increase in concentration - an increase in the positive charge, which is already determined by Na$^+$ ions. Therefore, the use of HCCA is especially effective in the most complex redistribution in the separation of the solid and liquid phases of the leaching process, namely, in the thickening redistribution, since the active part of hydrated calcium carboaluminate is represented by the seventh OH group in the solid solution system $\{[Ca_2Al(OH)_6](OH, aq) - CO_3^{2-}\}$, it neutralizes the Na$^+$ charges on the nepheline sludge surface, which activates the coagulation process.

It has been established that carboaluminate, as an active coagulant, is responsible for the sedimentation rate of large and medium sized sludge particles, while Alclar flocculates small and colloidal particles, and the effectiveness of Alclar in the presence of carboaluminate increases significantly, i.e. ceteris paribus, it is possible to reduce the consumption of expensive Alclar by about 2 times, the input of the HCCA is calculated at the rate of 1 g/l in terms of CaO. The coagulation of nepheline sludge should also be carried out in the washing system (except for the last stage, where the sludge particles are negatively charged).

Research of the coagulated slurries (figure 1) at temperatures of 85 °C and 70 °C shows that the pulp slurry, where the secondary losses are primarily in the form of HCCA, thickens with the addition of flocculant "Nalco-85010" is better than pulp, where secondary tumors after leaching are a mixture of Hydrated sodium aluminosilicate (HSAS) and hydrogarnets. Drain rate carboalumination pulp is 4.5 m/h, while the speed of draining the pulp, where the presence of HSAS and hydrogenate calcium equal of 3.48 m/h. Without flocculants, the rate of discharge of the slurry pulp tested is approximately the same (table 1).

![Figure 1](image.png)

**Figure 1.** Coagulation of slurry pulps 1, 2 – coagulation curves at temperatures 70°C и 85°C without flocculant Alclar 550 (practically coincide); 3 – coagulation curve at temperature 85°C; 4 – coagulation curve at temperature 65°C.
A significant role is played by hydrated carboaluminates in the super-deep desiliconization technology, in accordance with which high-grade alumina is obtained. As a result, metallurgical grade G-000 alumina is produced, which has no analogues in the world practice in terms of its chemical composition purity, the content of harmful impurities therein amounts to the following values: SiO₂ – 0.02%; Fe₂O₃ – 0.06%. The super-deep desiliconization technology of aluminate solutions is implemented with additives of the carboaluminate suspension at a rate of 7-8 g/l per CaOₐₓ, while the suspension is metered into the 2nd reactor, and recycled hydrogranate sludge is introduced into the 1st reactor after thickening at the rate of ~ 20 g/l of the solid one, the sludge here plays the role of a catalyst.

 Silicon module after completion of the process - 4000-5000 units. The main disadvantage of the technology is that the circulating sludge returns to the 1st reactor from time to time as it accumulates in the cone of the Dorr thickener (continuous unloading of the thickener due to the small amount of solid phase is impossible), which limits the separation efficiency of Al (III) and Si (IV) ions.

In order to increase the HCCA effectiveness, it is proposed to apply the fast thickening technology in a new type of apparatus - a thickener with a Larox filtering layer. This will increase the degree of sludge turnover by 2 times (up to 40 g/l of the solid one) and ensure its continuous unloading. Studies show that in this version of the technology, the consumption of HCCA is reduced by 1.5 times, to about 5 g/l of CaOₐₓ, and the silicon module reaches a value of 10,000 units.

The obtainment of qualitatively new aluminate solutions creates favorable conditions for the crystallization of coarse-grained aluminum hydroxide using the carbonization method, which follows from the cluster theory of the structure of aluminate solutions [7]. An additional contribution to the theory and technology of producing coarse-grained aluminum hydroxide and alumina is made by the method of using HCCA as a growth modifier and hardening agent for the above mentioned crystals. The modifier being the most suitable for these purposes is a mixture of CaCO₃ and HCCA obtained using an unburned method [10]. Entering a new modifier at the carbonization stage, ceteris paribus, at a dosage of 0.05-0.08% of Al₂O₃ contained in the solution, reduces the yield of small Al (OH)₃ crystals "-40 µm" from 15% to 8%, the strength of the crystals increases 1.5 times, the flow characteristics of alumina are significantly improved, the angle of repose decreases from 37° to 34°.

Based on the studies, there was proposed a mechanism of modifier (CaCO₃+4CaO-Al₂O₃·mCO₂·11H₂O) action.

Its essence is as follows. Carbonate is an unstable compound in an aluminate solution; it decomposes under the action of OH⁻ hydroxide ions:

$$\text{CaCO}_3 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3$$

The Ca²⁺ and CO₃²⁻ ions begin to actively interact with the aluminate solution by structuring a prototype of the future system therein:

$$[\text{Ca}_2\text{Al(OH)}_6][\text{mCO}_2\cdot(1-m)\text{OH}^⁻, \text{aq}] – \text{NaAl(OH)}_4$$

One of the elements of this system is the gibbsite residues Al(OH)₆³⁻, which, in the absence of silicon (Mₐₙ=10,000 units), are easily polymerized forming colloidal particles, which in turn strengthen the Al(OH)₃ nucleus, which occurs during the carbonization of aluminate solutions. The entire complex chain of interactions proceeds with the participation of active centers on the part of the modifier, which is represented by the HCCA. Leaving the sphere of influence of Ca²⁺ (product of the CaCO₃ decomposition), gibbsite residues release an area near the surface of the HCCA for the next structuring of the aluminate solution in relation to Al(OH)₆³⁻. Thus, a phase transition is performed through the combined modifier.

### Table 1. Characteristics of coagulation.

| №  | Deposition speed m/h | Compaction speed m/µ | Solid content g/l |
|----|---------------------|----------------------|-----------------|
| 1.2| 0.91                | 0.17                 | 717             | 904             |
| 3  | 3.48                | 0.13                 | 717             | 914             |
| 4  | 4.50                | 0.13                 | 680             | 873             |
\[ Td_{Al(OH)} \rightarrow Oh_{Al(OH)}^{1/2} / surface \left[ CaAl(OH)_6 \right]^{1+} \left[ m / 2CO_3^{2-} (1-m)OH^{-}, aq \right] \rightarrow Al(OH)_3 \]

where the HCCA surface, or rather its active centers, carry the elements of heterogeneous catalysis through the similarity model \( Al(OH)_3^{3-} \rightarrow Al(OH)_3 \).

Another advantage of super-deep desiliconization up to to \( M_{sl} = 10,000 \) units should be noted. Desiliconization almost up to Si (IV) traces significantly reduces the degree of overgrowth with aluminosilicates of evaporation tubes in the concentrated evaporation of soda-potassic production, which increases the heat transfer coefficient in evaporators and allows to install more economic 6-block evaporation batteries instead of 5-block ones, which reduces the steam consumption this stage of evaporation at 18%.

3. Conclusions
1. The coagulation properties of hydrated calcium carboaluminates were revealed. It has been established that the combination of HCCA with the Alclar-type flocculant increases the efficiency of thickening and washing of nepheline sludges.
2. The super-deep desiliconization technology on the basis of HCCA was improved with the increased recycling of hydrogarnet sludge and their continuous dosing into the process, which ensures the reduction of reagent consumption and the production of qualitatively new aluminate solutions with a silicon module of 10,000 units (instead of 4000-5000 units in case of using the already known technology).
3. It was demonstrated that the use of aluminate solutions with a silicon module of 10,000 units and the combined modifier “HCCA-CaCO_3” allows to obtain coarse-grained alumina using the carbonization method with a yield of limiting fraction “minus 40 microns” ~ 8%, while the strength of the crystals increases 1.5 times, the flow characteristics of alumina are significantly improved, the angle of repose decreases from 37° to 34°.

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