

## APPLICATION OF CALCIUM HYDROCARBOALUMINATE FOR THE PRODUCTION OF COARSE-GRADED ALUMINA

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### ABSTRACT

The article is devoted to the improvement of the coarse-grained alumina production. The crystallization of aluminum hydroxide obtained by carbonization of deeply-desiccated aluminate solutions is considered. The effect of a new modifier based on calcium hydrocarboaluminate is studied. A mechanism of its behavior on the basis of CHCA participation in the process of formation of aluminum hydroxide precipitate is proposed. A technology of the new modifier synthesis is given. Results of industrial experiments testing the elements of sand-alumina production technology are presented.

*Keywords:* hydrocarboaluminate calcium, alumina, crystallization of aluminum hydroxide, modifier.

### INTRODUCTION

The method of complex processing of nephelines is much influenced by the work of Prof. V. M. Sizyakov and his collaborators [1 - 8] in the field of synthesis of calcium carboaluminate compounds in the medium of strong electrolytes – aluminate solutions. It is focused on issues connected with the possible use of calcium hydrocarboaluminate  $4\text{CaO}\times\text{Al}_2\text{O}_3\times\text{mCO}_2\times 11\text{H}_2\text{O}$ . In accordance with the Mining Institute method [9] based on calcium hydrocarboaluminate (CHCA), the aluminous plant in Pikalevo applies the technology of ultra deep desilicization of aluminate solutions (4000 units alumina to silica ratio) providing the highest grade alumina.

Significant experimental work [10,11] is carried out contributing to the study of the basic principle of activating the deep desilicization of hydrogarnet mud introduced in aluminate solution prior to the interaction of calcium hydrocarboaluminate with silica. This principle is tested using various aluminate and carboaluminates solutions. The tests show that it is possible to increase alumina to silica ratio up to 10000 units and above without increasing CHCA rate due to increase of solid

hydrogarnet mud turnover up to 50 g/dm<sup>3</sup>.

These solutions processing simplifies coarse-graded alumina production. A new modifier, a product of CHCA synthesis technology in  $\text{CaCO}_3\text{-NaOH-Al}_2\text{O}_3\text{-H}_2\text{O}$  system [12, 13], is offered for growth and hardening of aluminum hydroxide agglomerates.

### EXPERIMENTAL

The modifier synthesis was performed using an unburned method. Limestone of  $\text{SiO}_2$  content of ~1 % was used as a carbonate component. It was ground to coarseness of 80  $\mu\text{m}$ . The sieve residue (of 0,08 mm) was ~0,5 %. The limestone was treated with an aluminate solution (100 g/l  $\text{Na}_2\text{O}$   $k, \alpha_c - 3,3$ ) at a temperature of 70°C for 60 min. The liquid/solid ratio was 10:1. Based on the isotherms of the metastable equilibrium in the system  $\text{CaCO}_3 - \text{NaAl}(\text{OH})_4 - 4\text{CaO}\times\text{Al}_2\text{O}_3\times\text{mCO}_2\times 11\text{H}_2\text{O} - \text{NaOH} - \text{C}_3\text{AH}_6 - \text{H}_2\text{O}$ , the synthesis end product contained 50 % of  $\text{CaCO}_3$  and 50 % of CHCA.

The new modifier identification was performed using X-ray, a petrographic analysis and infrared spectroscopy.

The experiments referring to coarse-graded alumina production included:

- ultradeep desiliconization of the initial aluminate solutions aiming an alumina to silica ratio of 50 000 units;
- carbonization at an optimal mode with introduction of seed – 40  $\mu\text{m}$ , at a seeding ratio of 0,2 at 60°C; the seed was introduced to the non-carbonated solution with an exposure of 2 h; 1<sup>st</sup> carbonization – 4 h, Bayer decomposition – 4 h, 2<sup>nd</sup> carbonization – 4 h.

The modifier proportioning was performed during the induction period. Experiments were performed using a simplified method with Bayer decomposition exclusion for modifier comparative evaluation.

The aluminate solutions were prepared by leaching of an industrial sinter. The industrial hydrate “-40  $\mu\text{m}$ ” was used as a seed.

The initial aluminate solutions were desiliconized in an autoclaves reaching an alumina to silica ratio of 350 units - 400 units. Then the carboaluminate method was applied aiming to reach  $M_{cr}$  of 4000 units. The results of the comparative experiments are given in Table 1. It is evident that the best results were obtained using a combined synthesized modifier ( $\text{CaCO}_3 + \text{CHCA}$ ).

Further experiments with the combined modifier were performed in accordance with the complete program (Bayer decomposition in the course of 4 h carbonization process, the initial solutions contained traces of  $\text{SiO}_2$ ,  $M_{cr}$  of 50000 units).

The tests performed evidenced the high efficiency of the new combined modifier. The results of experiments are given in Figs. 1 and 2.

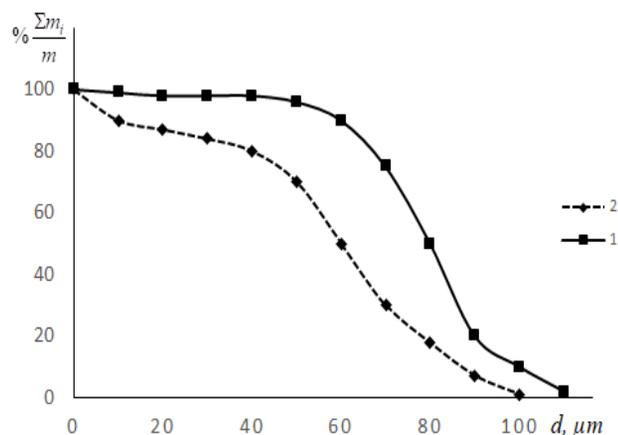


Fig. 1. The impact modifier  $\text{CaCO}_3 + \text{CHCA}$  on disperse composition of aluminum hydroxide: 1 - added modifier 0,06 %  $\text{CaO}_{act}$ ; 2 - without additives.

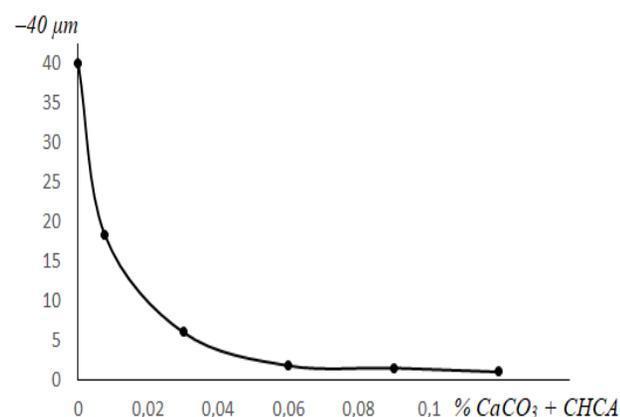


Fig. 2. The effect of amount of modifier  $\text{CaCO}_3 + \text{CHCA}$  on the particle size of the hydrate.

Table 1. The influence of different calcium-containing modifiers on the grain size composition of the hydrate (Dosage for  $\text{CaO}_{act}$  0,05 %. The source of aluminate solution, g/l:  $\text{Al}_2\text{O}_3 - 102,5$ ;  $\text{Na}_2\text{CO}_3 - 15,4$ ;  $\alpha_c - 1,52$ ).

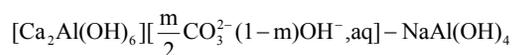
№	Modifier	Disperse composition of aluminum hydroxide, $\mu\text{m}$ , %			
		+100	-40	-10	-5
1	0	0,0	27,5	18,8	12,8
2	Limestone, 1% $\text{SiO}_2$	2,5	16,8	14,2	10,4
3	CHCA	0,8	15,6	12,6	9,7
4	$\text{CaCO}_3$ (slime caustification)	1,6	18,4	16,0	14,2
5	$\text{CHCA} + \text{CaCO}_3$ (synthesized)	6,4	8,2	6,6	4,1

## RESULTS AND DISCUSSION

The experimental data shows the effect of the combined modifier on the coarseness of the hydrate crystals obtained using carbonization of deeply desiliconized aluminate solutions.

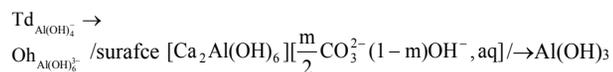
The limiting dust fraction (40  $\mu\text{m}$ ) is reduced to 2,5 % with the introduction of a modifier containing 0.05 % - 0.06 % of  $\text{CaO}_{\text{act}}$ , while the output fraction (5  $\mu\text{m}$ ) is 0,8 %. The crystals strength according to the methodology of the All-Russian Aluminium-Magnesium Institute (VAMI) – Alcoa (reduction of 40  $\mu\text{m}$  rubbing fraction in a closed loop circuit) increases 2 times.

It can be suggested that the complex limestone-carboaluminate modifier participates in the formation of an aluminium hydrate structure through decausticization and a subsequent interaction of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  with the aluminate solution. The result refers to the structuring (without nucleus fixation) of the aluminate solution



This system contains such components as gibbsite radicals  $\text{Al}(\text{OH})_6^{3-}$ , which polymerize easily in deeply desiliconized solutions [14] with formation of colloidal sized particles. The latter strengthen  $\text{Al}(\text{OH})_3$  nucleus appearing during aluminate solution hydrolysis. The entire interaction chain course involves active centers on the modifier side consisting of CHCA. The gibbsite radicals leave the area of  $\text{Ca}^{2+}$  effect, i.e. that close to CHCA surface, and proceed further to participate in the structuring of aluminate solution in relation to  $\text{Al}(\text{OH})_6^{3-}$ .

Thus, the phase transition



is performed through the combined modifier. CHCA surface, or in fact its active centers participate in the heterogeneous catalysis envisaged.

Based on the analysis performed it may be concluded that the structure of the aluminium hydrate deposit is formed under the impact of real crystal-forming factors, which change the mechanism of growth of the crystalline individuals and aggregates. This results in significant changes of the products properties. These processes understanding allow to optimize the deposition mode and to forecast the properties of the synthetic hydrargillite and alumina. This is demonstrated in the course of the experimental-industrial tests [14] referring to elements of the technology for production of sand type alumina.

The synthesized hydrates are calcinated in a laboratory silit furnace aiming alumina production. The technical parameters of the latter are as follows: an angle of repose of 33°; 6%  $\alpha\text{-Al}_2\text{O}_3$  content, a surface of 96  $\text{m}^2/\text{g}$ ; fluidity of 10 s (instead of 25 s for ordinary Pikalevo alumina); 2,5 % - 4,0 % content of -40  $\mu\text{m}$  fraction; 6 % - 7 %; content of + 100  $\mu\text{m}$  fraction; strength corresponding to that of Alcoa sandy alumina.

The strength diagram of the alumina produced using carbonization of aluminate solutions with various modifiers  $\text{Ca}(\text{OH})_2$ , CHCA,  $\text{CaCO}_3$ ,  $\text{CaCO}_3 + \text{CHCA}$  is given in Fig. 3. The strength of sandy alumina Alcoa (I) is also provided here. It is seen that the alumina produced with the addition of the new combined modifier

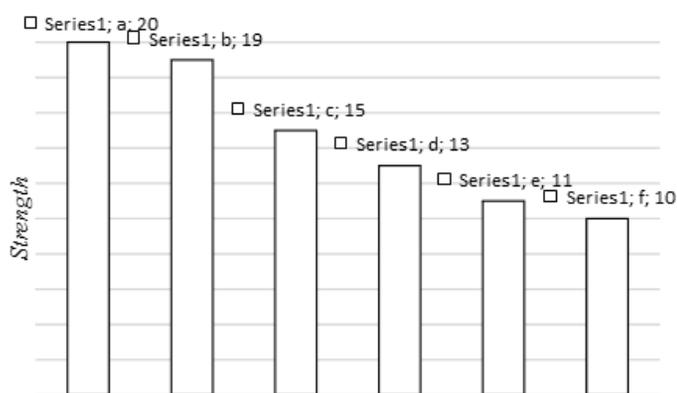


Fig. 3. The strength of the alumina by the method Alcoa with different modifiers: I – the standard of comparison, alumina Alcoa; II -  $\text{CaCO}_3 + \text{CHCA}$ ; III -  $\text{CaCO}_3$ ; IV – CHCA; V –  $\text{Ca}(\text{OH})_2$ ; VI – carbonizing alumina without modifier.

(CHCA+CaCO<sub>3</sub>) is approaching the level of Alcoa sand type alumina. The results of electron microscopy study show that it has the solid structure of agglomerative type crystals, i.e. it is close to Bayer sandy alumina.

## CONCLUSIONS

The results reported provide to conclude that the technology developed provides production of carbonized alumina in correspondence with the best world standards.

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