



UDC 669.712.1

ABOUT THE ROLE OF HYDRATED CALCIUM CARBOALUMINATES IN IMPROVING THE TECHNOLOGY OF COMPLEX PROCESSING OF NEPHELINES

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The scientific justification and development of the method for industrial synthesis of complex aluminates of alkaline earth metals is an innovative solution that determined several directions in the development of technology for complex processing of nepheline raw materials. It ensures the production of high-quality metallurgical alumina, the effective utilization of nepheline sludge and production of new types of multipurpose by-products. The modern development of these technical solutions is associated with ensuring the energy efficiency of the synthesis of hydrated calcium carboaluminates (HCCA) and increasing the level of purification of aluminate solutions. The conditions for synthesizing HCCA with the use of calcareous materials of natural and technogenic origin have been experimentally determined, which makes it possible to isolate the average particle diameter as one of the determining factors of this process. The effect of the turnover of the hydrogarnet sludge on the removal of kinetic limitations in the process of deep desalination of aluminous solutions is theoretically justified. The conditions of a two-stage dosage of HCCA are experimentally determined. It is shown that the optimum ratio of the amount of the reagent supplied in the first and second stages is about 3:2. At the same time, the maximum degree of precipitation of silica provides the production of aluminate solutions with a silicon module at the level of 95,000, which is achieved by using a HCCA synthesized based on chemically precipitated calcium carbonate in the processing of wastes from the production of mineral fertilizers.

Key words: synthesis of reagents, complex aluminates, energy efficiency, directions of use, Portland cement, deep desilicination, regimes and indices, calcium carbonate, experimental study

How to cite this article: Sizyakov V.M., Brichkin V.N. About the Role of Hydrated Calcium Carboaluminates in Improving the Technology of Complex Processing of Nephelines. Journal of Mining Institute. 2018. Vol. 231, p. 292-298. DOI: 10.25515/PMI.2018.3.292

Introduction. The modern metallurgical complex of Russia produces about 1.35 million tons of alumina from nepheline raw materials and a significant number of by-products, including aluminum hydroxide of non-metallurgical grades, Portland cement and building materials based on it, silicate brick, sodium-potassium products, mineral fertilizers, metallic gallium and a number of other materials. The main characteristics of these products, including specific material flows, are well known, and its high technical and economic indicators are an incentive for designing and creating new production capacities. At the same time, the solution of the deficit of domestic alumina for the production of primary aluminum is invariably associated with the development of production on the basis of nepheline raw materials and its close analogs [9, 13]. The mandatory conditions for the effective implementation of such plans are: the solution of the number of tasks for the long-term provision of raw materials production, the reduction of energy costs, the provision of an economically justified correlation of basic and by-products, including products with high added value, and their quality.

Now the main trends and prospects for the development of a raw material base for the production of alumina from high-silica aluminum raw materials have been determined due to the identified resources of the urtite and rischorrite rocks of the Khibiny mountain range, involving the production of aged apatite tailings and low-quality bauxites, and the use of natural resources in Central and Eastern Siberia [1, 3, 16]. Significant reserves in maintaining the raw material base for aluminum production are associated with the use of aluminum-containing slags of ferroalloy and foundry, ashes of CHPP, waste water treatment and other raw materials of technogenic origin [2].

In the solution of the most critical issue for the technology of processing nepheline raw materials related to the high consumption of technological fuel and, consequently, the costs for it, some changes have also been observed. At the same time, economically feasible approaches have been identified and implemented, including the technology of dry preparation of limestone-nepheline charge and the use of low-grade process fuel based on regional deposits of brown and hard coal [15, 17].

A difficult problem is to ensure a balance of production of the main and by-products, which is associated with the disposal of nepheline (belite) sludge in the production of Portland cement.

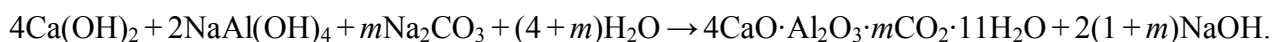


Theoretical study of this issue, carried out in the 80-90s years of the 20th century, has recently acquired the character of a systematic study that allows us to hope that it will find a solution of this problem [12].

Finally, the quality of the final product is invariably associated with the possibility of obtaining aluminum hydroxide and alumina, not only satisfying the requirements of GOST, but also exceeding the existing requirements in terms of its characteristics. This creates a significant reserve for processing of low-quality and high-siliceous raw materials, production of high-purity aluminum and innovative products in high-tech industries. The real revolution in this field is related to the development of the theory of the synthesis of metastable solid solutions in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{CO}_2-\text{H}_2\text{O}$ system and their use for fine cleaning of aluminate solutions from inorganic impurities and production of special binding materials [4, 6-10].

Statement of research and development problems. Hydrated calcium carboaluminates $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot m\text{CO}_2\cdot 11\text{H}_2\text{O}$ (HCCA), which are the derivatives of hydroaluminates of the type $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O}(\text{C}_4\text{AH}_x)$, they are widely known in the field of chemistry of cement. They are stable in aqueous solutions at temperatures below 20°C , which ensures their formation during slow hardening of cement stone [14]. When the temperature is raised, hexagonal hydroaluminates and hydrated calcium carboaluminates transform into a stable compound of cubic syngony – tricalcium hydroaluminate $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}\cdot(\text{C}_3\text{AH}_6)$.

For the first time, the possibility of synthesizing and using hydrated calcium carboaluminates in the field of special technologies appeared as resulting from studies establishing that HCCA crystallizes at a high rate in a medium of strong electrolytes under conditions of alumina production [4, 5]. The process of formation of hydrocarbon aluminates is described by the interaction of lime with an aluminate-alkaline solution:



This ensures the crystallization of hydrated calcium carboaluminates in a wide range of temperatures ($20-100^\circ\text{C}$), at a Na_2O_c concentration of up to 300 g/l , and the caustic modulus of the solution is $\alpha_c = 1.5-33.0$. Depending on the temperature, the lifetime of the HCCA is measured from 1 minute to 12-16 hours. With an increase in the temperature of the thermostating, the HCCA transits into the thermodynamically stable compound C_3AH_6 .

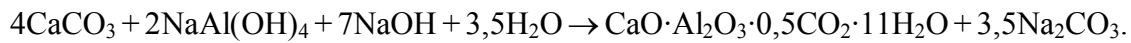
The successful use of hydrated calcium carboaluminates was facilitated by the development of an efficient method for their synthesis in an aluminate-alkaline medium [5], which is distinguished not only by the high rate of chemical transformations, but also by the uniformity of the chemical and dispersed composition of the products. Now, hydrated calcium carboaluminates of the type $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot m\text{CO}_2\cdot 11\text{H}_2\text{O}$ are widely used in alumina production technology for complete separation of aluminum and silicon ions, on which the well-known method of obtaining high-grade alumina is based on complex processing of low-quality aluminum raw materials [11].

As a result of the research, new properties of hydrated calcium carboaluminates are revealed, which contributes to their wide promotion into industry. The most promising directions of using HCCA in various branches of the national economy are the following:

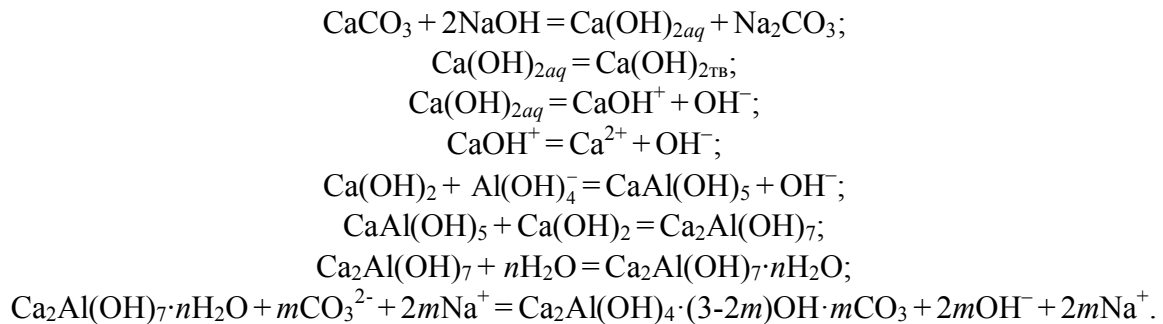
- 1) production of fast-hardening, packing and self-stressed cements;
- 2) production of high alumina cement;
- 3) production of waterproof mixtures and fillers;
- 4) production of dry cement mixtures;
- 5) synthesis of sulfur carboaluminate mineralizers for annealing of Portland cement raw mixtures;
- 6) streamlined synthesis of overactive ion-exchange units and coagulants for treatment of household and industrial effluents.

Experimental research and implementation of technological processes. Recently, scientific bases of synthesis and application of sulfo-carboaluminate compounds have been further developed, which contributes to the effective promotion of new technologies in this field. An alternative to the

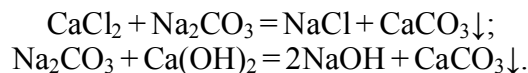
already existing method for the synthesis of hydrated calcium carboaluminates, introduced at the Pikalyovo Alumina Plant – SUAL, provides the possibility of obtaining metastable phases of the required composition under conditions of thermodynamic instability of alkaline earth metal carbonates. In this case, the approach to the metastable region should correspond to the following stoichiometry:



There is no doubt that these processes are complex and naturally have several stages. Judging from the existing understanding of the synthesis of HCCA based on calcium hydroxide, it can be assumed that at relatively low temperatures (50-70 °C), calcium carbonate reacts with the aluminate solution according to the following scheme:



Synthesis of HCCA was carried out on a laboratory scale using an artificial aluminate solution and calcium carbonate mixtures differing in the preparation method and physical-chemical properties. The research task was to determine the steady-state compositions of alkaline solutions in the synthesis of HCCA and the kinetic parameters of this process, depending on the nature and properties of the carbonate materials. During this research we used a sample of crushed natural limestone from the Pikalevsky deposit, a test sample of reactive calcium carbonate of the brand «ChDA», as well as samples of calcium carbonate synthesized in laboratory conditions on the basis of characteristic chemical interactions according to the following by reactions:



Of special interest are the results of laser microanalysis, since they allow to arrange all samples to by the average particle size. It decreases in the series from CaCO_3 of «ChDA» type (average particle diameter 89.7 μm) to CaCO_3 , obtained by the caustification of soda (average particle diameter 2.3 μm). In addition, all samples except for natural limestone have a limited fractional composition.

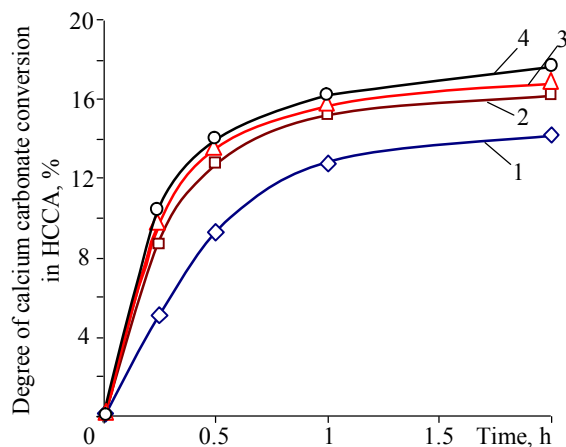


Fig. 1. Conversion of calcareous components during HCCA synthesis in low-modulus solutions with $\alpha_c = 1.45$

1 – CaCO_3 of ChDA type; 2 – natural lime stone; 3 – CaCO_3 precipitated from CaCl_2 solution; 4 – CaCO_3 precipitated in reaction of soda caustification

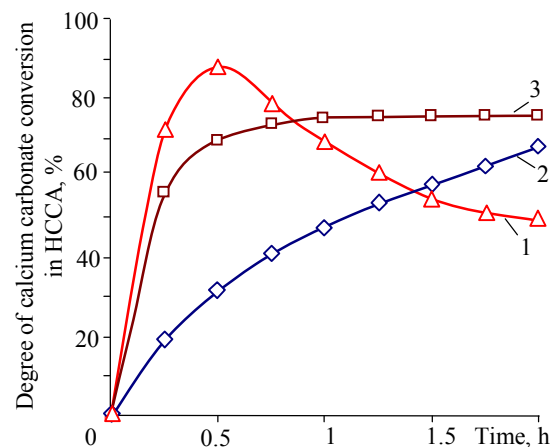


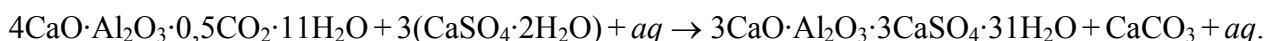
Fig. 2. Conversion of Pikalevsky deposit limestone during HCCA synthesis in high-modulus solutions with $\alpha_c = 3.0 - 3.3$ at different temperatures

1 – 90 °C; 2 – 50 °C; 3 – 70 °C



The parameters of the laboratory synthesis of HCCA are shown in Figures 1 and 2, which allows to justify the choice of the aluminate solution composition by the caustic module value, the preferred temperature regime, the duration of the process, and also to evaluate the nature and fractional composition of the calcareous material. These results indicate the need to use aluminate solutions with an increased content of free caustic alkali to shift the equilibrium of the system towards the formation of calcium hydroxide and its subsequent conversion to HCCA in accordance with the scheme considered. The use of lime materials of high dispersity creates the prerequisites for the use of lime slurries and chemically precipitated calcium carbonate, which are formed in various technological processes.

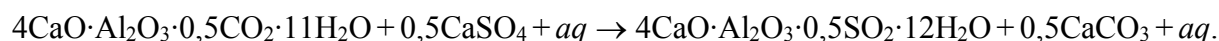
The high reactivity of HCCA is of considerable interest for the intensification of the processes of formation of cement stone and Portland cement clinker, taking into account the high rate of formation of products in this system. At the same time, the processes that are typical for the hydration of cements in the first case and the high-temperature annealing of raw mixtures in another are fundamentally different. With the participation of HCCA, the hydration process is accompanied by the formation of a thermodynamically stable ettringite (trihydrosulfoalumina calcium) and proceeds according to the reaction:



It has been experimentally established that up to 100 % of gypsum with HCCA binds to ettringite during the hydration period of 6 hours. With a duration of hydration about one day, the initial components in the reaction mixtures are not detected at all at the process temperature from 20 to 60 °C. The increase in temperature has a noticeable effect on the rate of gypsum binding only in the first hours of hydration and, regardless of the temperature over 6 hours of hardening, the interaction of the components in the system under consideration leads to a slight increase in the volume of the solid phase, which subsequently stabilizes. Thus, physical-chemical preconditions arise for the creation of highly active fast-hardening compositions using reagents synthesized in alumina production systems

On this basis, the technology for obtaining fast-hardening non-shrinking cement of Rapid-SFS type was developed [10]. With the use of ordinary clinker, dihydrate gypsum and factory sample HCCA in laboratory conditions, fast-hardening cement was obtained with 20-25 % improved characteristics in comparison with Rapid-SFS cement. In this case, the addition of HCCA in an amount of 2-2.5 % and the corresponding amount of gypsum leads to the formation of an additional amount of ettringite during the hydration process, which determines the ability of the hardening cement structures to expand. The study of cements with small additions of HCCA showed that it has no shrinkage deformations. It can be assumed that the small extensions that arise in the early stages of cement hardening allow us to fully compensate internal stresses and to ensure an increase in the strength of cement during this period. Comparative studies have shown that the decrease in the strength characteristics of fast-hardening cements at the stage of pilot-industrial tests is associated with a rougher grinding of the clinker due to the open cycle of the mills. The use of a closed cycle makes it possible to increase the specific surface area of ground clinker from 3500 to 5000-5500 cm²/g in production conditions and significantly improve the hydration conditions of its components. In this case, the strength of the product on the first day of hardening will increase to 32 MPa, which corresponds to the standard of VeryRapid cement.

With the use of HCCA, there is also a noticeable mineralization effect during annealing of Portland cement clinker, based on its interaction with phosphogypsum. During the development of this technology it was found that when phosphogypsum is introduced at the stage of the nepheline (belitic) slime, its interaction with HCCA ends with formation of a low-basic sulfur aluminate having a reduced reactivity due to alkali adsorbed on the surface of the HCCA:



When the sludge is re-milled, an appreciable fraction of alkali passes into the liquid phase and subsequently, when phosphogypsum is introduced into the final slurry-limestone charge, it does not limit the process of the ettringite crystallization. A method for the synthesis of a carbon sulfur aluminate mineralizer was introduced at the Pikalyovo cement plant, which contributed to the stable release of high-quality Portland cement [6]. The strength of clinker for compression in-

creased by 3-4 MPa. The lining stability in the clinker formation zone increased from 45 to 180 days, and fuel consumption decreased by 1 %. Excellent formation of clinker granules in combination with a reduced dust extract significantly simplified the process of automatic control of the technological mode of operation of cement kilns.

The second major direction of the HCCA use is well known due to the introduction at the enterprises for the production of alumina from nepheline raw materials, which resulted in the production of high quality products. The fundamental foundations of this technology were thoroughly worked out in the 70s-80s of the 20th century, which made it possible to establish the features of the mechanism of precipitation of calcium hydrogarnet in the interaction of aluminate solutions with HCCA [7-9, 14]. This allows to have stable production of aluminate solutions with a silicon module above 5000 units in production conditions and ensures the production of high-quality products but does not correspond to the achievement of true equilibrium in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$ system. At the same time, the approach to the equilibrium state can minimize the consumption of the lime component, and the need to produce products of even greater purity is associated with their use in high-tech sectors of the economy.

The solution to this problem largely lies in the removal of the kinetic constraints arising from heterogeneous chemical interactions by a topochemical mechanism. As it is known, all supersaturated solutions with respect to the thermodynamic ability to form a stable crystalline nucleus are divided into a labile and metastable region. In the first case, the crystallization centers arise spontaneously, which requires the system to go out of the metastable state, which has significant limitations for poorly soluble compounds and manifests itself as an induction period of indeterminate duration.

According to the theory of M. Volmer, the complete correspondence of the seed structure to the precipitated compound ensures its crystallization at any supersaturation within the metastable region. In case of structural mismatch, the work of formation of the crystalline nucleating seed reaches a maximum and the deposition process is possible only when leaving the metastable region. Thus, to remove kinetic limitations in the process of deep desiliconization of aluminate solutions, it is necessary to introduce a seed material structurally close to HCCA, which is the only stable product in this system. A clear and technically advantageous solution is the introduction of circulating HCCA sludge as a seed in combination with the optimal method of HCCA feeding. Figure 3 shows the performance of the 2nd stage of the desiliconization of aluminate solutions with fractional administration of HCCA at a dosage of 7 g/l in terms of the active calcium oxide content. In this case, the first portion of HCCA is varied in the range from 100 to 25 % of the total amount, and the remaining amount of the reagent is dosed after exposure to the set duration. The obtained results make it possible to determine the conditions for the in-

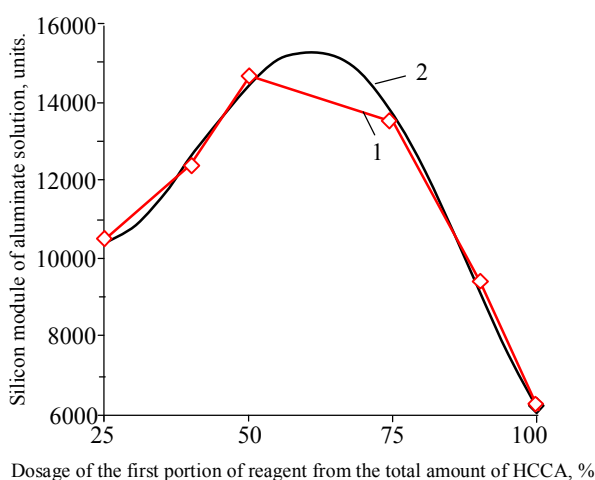


Fig. 3. Desiliconization of aluminate solution in the fractional introduction of the desiliconizing reagent as a function of the fraction of HCCA introduced by consecutive portions

1 – experimental data; 2 – results of statistical analysis;
 $y = 0.023x^4 - 0.6003x^3 + 49.987x^2 - 1506.9x + 25371$; $R^2 = 0.9966$

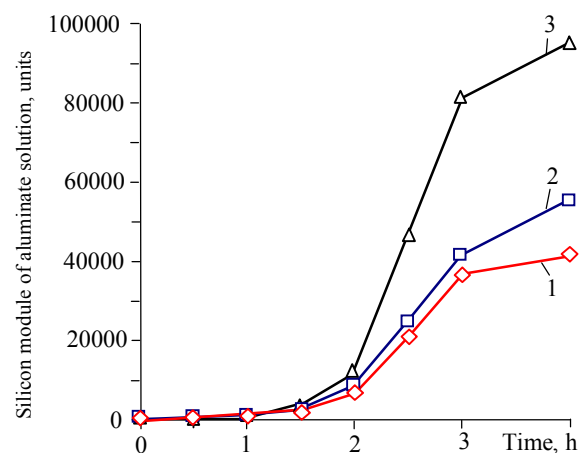


Fig. 4. Desiliconization of aluminate solution during fractional introduction of reagent as a function of nature of lime component used in HCCA synthesis

1 – lime milk; 2 – natural limestone;
3 – phosphate chalk

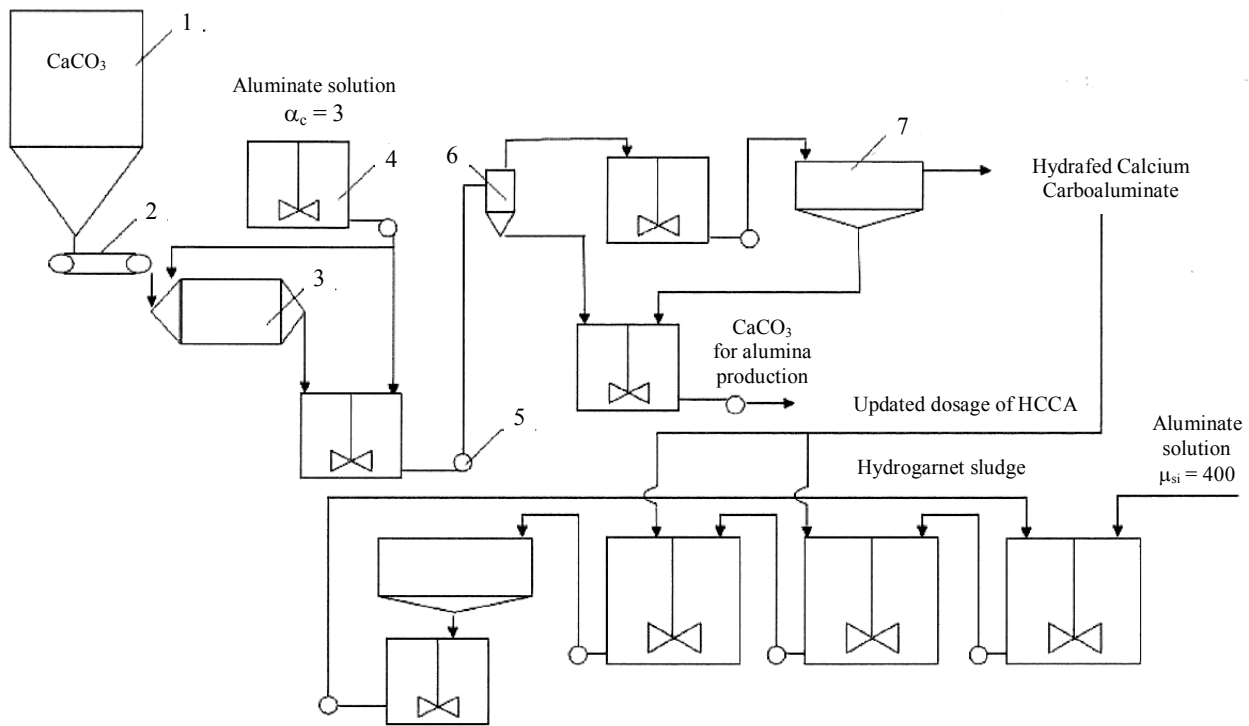


Fig.5. Instrumental-technological scheme of HCCA synthesis and deep desilicization of aluminate solutions
1 – lime materials tank; 2 – weight feeder; 3 – mill; 4 – mixer; 5 – centrifugal pump; 6 – hydroclassifier; 7 – thickener

roduction of HCCA, which ensure an optimal ratio of the rate of its decomposition and the interaction of the decomposition products with the aluminate solution with the participation of hydrogarnet sludge. An increase in the duration of the process to 4 h fully confirms the autocatalytic character of the process with the approach of the system to the state of technological equilibrium and corresponding to the kinetics obeying the Kolmogorov-Erofeev equation (Fig.4). At the same time, the nature of the calcareous component, associated with the particle size, and, consequently, the specific surface and activity of the material, has a significant influence on the process parameters [8].

The carried-out studies of HCCA synthesis technology and deep desalination of aluminate solutions determine the principal instrument-technological solutions adapted to the existing methods of processing low-quality aluminum-containing raw materials (Fig.5).

Conclusions

1. The wide range of compositions and the high activity of metastable phases in the $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O-CO}_2(\text{SO}_2)$ system provide the scientific basis for their effective synthesis and application in metallurgy, the production of binders and functional materials, which gives us hope for large-scale application of sulfur carbon aluminates of alkaline-earth metals not only in already well-known and proven technologies, but also in other areas of the national economy.

2. It is shown that the efficiency of the HCCA synthesis using unburnt calcium carbonate is determined by the use of aluminate solutions with an increased content of free caustic alkali in order to shift the equilibrium of the system towards the formation of calcium hydroxide and its subsequent conversion to HCCA. In this case, the use of calcareous materials of high dispersion contributes to the improvement of the synthesis parameters and creates the prerequisites for the use of calcareous slurries and chemically precipitated calcium carbonate formed in various technological processes.



3. The conditions for the HCCA dosage in desilication of aluminate solutions are established, which ensure an optimal ratio of the rate of its decomposition and the interaction of the decomposition products with the aluminate solution with the participation of hydrogarnet sludge. This confirms the autocatalytic nature of the process, which obeys the kinetics of topochemical interaction with the approach of the system to the state of technological equilibrium.

Acknowledgments. *The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation (project registration number 11.4098.2017/PCh of 01/01/2017).*

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The paper was received on 10 February, 2017

The paper was accepted for publication on 26 April, 2018.